Quality Assurance Project Plan

Hydrogeology and Potential for Groundwater Recharge and Storage on Alluvial Fans in the Yakima Basin

June 2024

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Each study funded by the Washington State Department of Ecology (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, the final report will be publicly available through the Department of Ecology and a YBIP Groundwater Subcommittee data sharing website, scheduled to be built in summer of 2024. This QAPP describes a project selected by the Washington State Department of Ecology in support of the Yakima Basin Integrated Plan.

This Quality Assurance Project Plan is available via Ecology's website at https://apps.ecology.wa.gov/publications/SummaryPages/2412005.html.

Data for this project are available in Ecology's Environmental Information Management (EIM) database under Study ID: CWUFAN-001. This QAPP is valid through May 31, 2029 (five years from the date of approval).

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COVER PHOTO: Manastash Creek alluvial fan. PHOTO BY CAREY GAZIS.

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Hydrogeology and Potential for Groundwater Recharge and Storage on Alluvial Fans in the Yakima Basin

IAA C2400168

By Lisa Ely and Carey Gazis

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2.0 Abstract

Securing the future water supply for agriculture, domestic use, instream flow and habitat in the Yakima Basin is the focus of coordinated efforts under the Yakima Basin Integrated Plan (YBIP). Managed aquifer recharge (MAR) is one sustainable and cost-effective approach to store water underground for recovery during seasonal dry periods or drought. This proposal presents a plan to study two large alluvial fan aquifers to provide a detailed hydrogeologic characterization and assess their potential as groundwater storage reservoirs.

Broad questions that will be addressed in this study include: 1) How much storage capacity is available at different points on the alluvial fans and what is the proximity to sources and outflow locations? 2) What are the general patterns of surface water infiltration, mixing and flow directions? 3) How do the physical properties of the alluvial fan and the human-built water infrastructure affect groundwater recharge and storage? and 4) Which locations show promise as recharge sites?

The selected study sites are Ahtanum Creek alluvial fan in the Yakima Valley and Manastash Creek alluvial fan in the Kittitas Valley. The proposed project will assess the physical characteristics and hydrology of these sites to provide a necessary foundation for an informed decision about the implementation of MAR projects. We will combine existing data from wells logs, maps and reports with field observations of sediment characteristics, water levels and geochemistry. The results will be used to identify areas with suitable permeability rates, head space and surface water penetration into the unconfined aquifer. These are the sites where additional recharge is most likely to infiltrate and the maximum amount of water can be added during months of surplus. We will estimate directions of groundwater flow and quantify the additional aquifer storage capacity at identified locations within these two alluvial fans.

3.0 Background

3.1 Introduction and problem statement

Securing the future water supply for agriculture, domestic use, instream flow and habitat in the Yakima Basin is the focus of coordinated efforts under the Yakima Basin Integrated Plan (YBIP). Managed aquifer recharge (MAR) is one sustainable and cost-effective approach to store water underground (Dillon et al., 2019). Previous projects for the YBIP Groundwater Storage Subcommittee have used groundwater modeling and field investigations to identify sites within the Yakima basin or sub-basins with promising potential for shallow aquifer recharge (SAR) (Anderson et al., 2009; Gibson and Campana, 2018; Kittitas Reclamation District, 2020). The stored groundwater would naturally discharge and could be available for use during drier summer periods. This proposal presents a plan to conduct a field study of two large alluvial fan aquifers to provide a detailed hydrogeologic characterization and assess their potential for infiltration through MAR and use as groundwater storage reservoirs.

Broad questions that will be addressed in this study include:

- How much storage capacity is available at different points on the alluvial fans and how long will it take stored water to reach nearby streams?
- What are the general patterns of surface water infiltration, mixing and flow directions?
- How do the physical properties of the alluvial fan and the human-built water infrastructure affect groundwater recharge and storage?
- Which locations show promise as recharge sites?

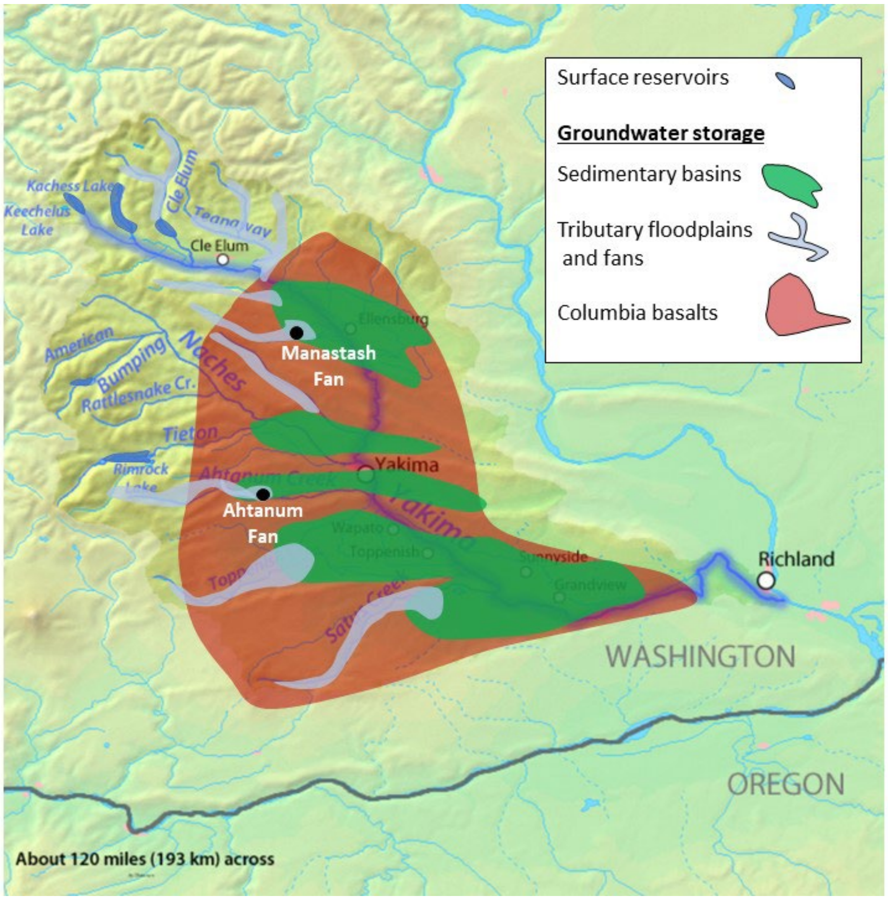

Figure 1. Map of larger study area. Schematic map of surface water and groundwater storage reservoirs with location of proposed study sites on Ahtanum and Manastash Creek alluvial fans in the Yakima River Basin.

The selected study sites are Ahtanum Creek alluvial fan in the Yakima Valley and Manastash Creek alluvial fan in the Kittitas Valley (Figure 1). We will compile existing data from wells logs, maps and reports, which will be combined with new field observations of sediment characteristics, water levels and geochemistry data. The results will be used to identify areas with suitable permeabilities, head space, and hydraulic gradient, such that water can infiltrate into the sedimentary aquifer and be stored.

The geochemical analysis of surface water and groundwater will indicate how deep the surface water penetrates the unconfined aquifer and mixes with groundwater and also help to identify where there are barriers to flow. Areas where there is sufficient head space and where the geochemical signature indicates mixing of surface water and groundwater at depth are sites where additional recharge is most likely to infiltrate and the maximum amount of water can be stored during months of surplus. We will estimate directions of groundwater flow and quantify the additional aquifer storage capacity at identified locations within these two alluvial fans at different times of the year. Based on our improved understanding of these aquifers and their characteristics, we will use simple equations to estimate the travel time of recharged water from potential recharge sites to nearby streams. The proposed project will produce a detailed assessment of the physical characteristics and hydrology of these sites to provide a necessary foundation for an informed decision about the implementation of MAR projects.

3.2 Study area and surroundings

Alluvial fans develop where rivers exit confined mountain canyons into wide basins. The sediment that is transported in the steeper, narrower mountain streams is deposited as the streams widen or diverge upon entering the basin. Alluvial fans incorporate features that are favorable to the implementation of effective MAR projects. The tributary water supply is initially confined to a single source at the head of the fan, which can be diverted or contained in an infiltration basin for MAR. Alluvial fans tend to be composed of relatively permeable sand and gravel near the upstream head, transitioning to finer sediment at the distal end (Bull, 1977). The fan sediments are therefore conducive to infiltration and transmission of water in the shallow subsurface. The fining distal sediments provide a means of slowing groundwater flow and loss from the storage volume. The stratigraphy of the alluvial fans and underlying sedimentary aquifer of the upper Ellensburg Formation can be heterogeneous, however, due to shifting channel positions, debris flows, volcanic layers and other factors. Investigations of the site-specific hydrogeology before implementation of a MAR project can help determine which locations on a fan would better function under MAR operations.

Ahtanum Creek has a drainage area of approximately 450 km^2 and flows into the western end of the Yakima subbasin. The creek divides into multiple channels, some of which are used as irrigation canals, shortly after it exits the confined canyon at the upstream end of a large, long alluvial fan that joins the Yakima River near Union Gap (Figure 2). As one of the major tributaries and alluvial fans within the Yakima River Basin, Ahtanum Creek is a logical site to investigate the potential for aquifer recharge and storage. Several portions of the fan have been identified as promising hydrogeological areas for MAR (Anderson et al., 2009; Gibson and Campana, 2018).

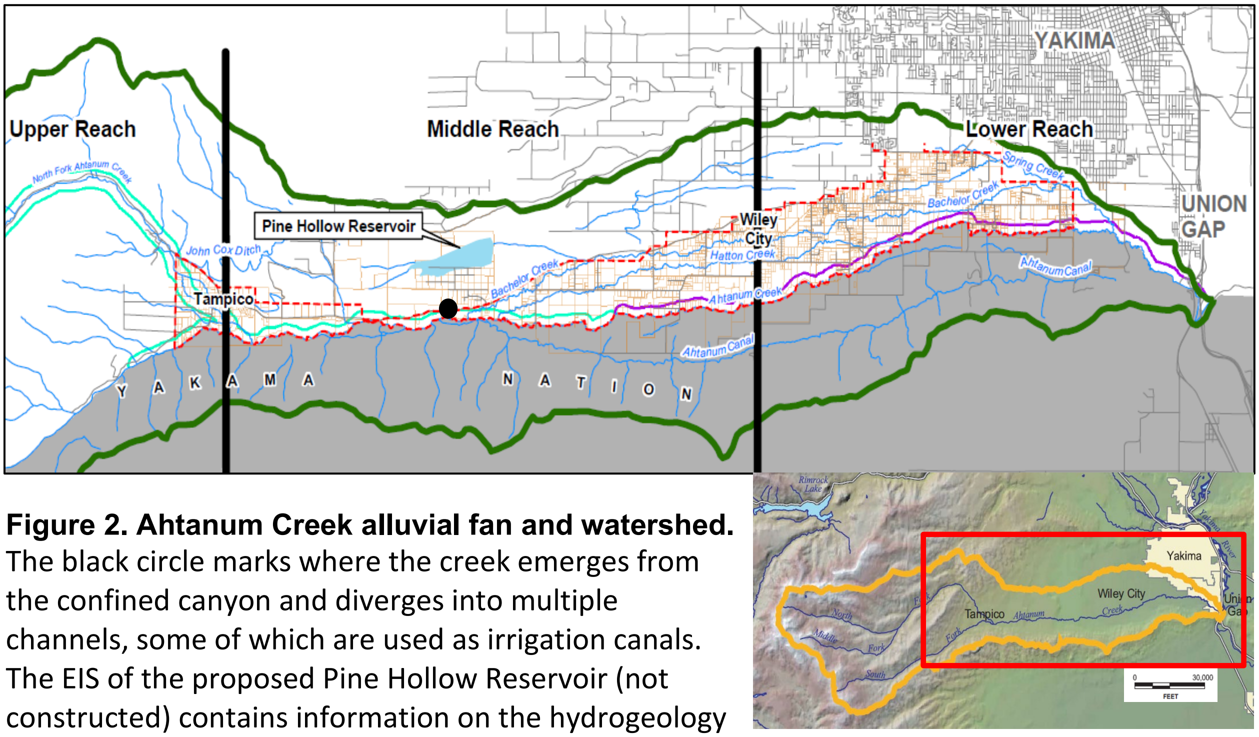

Figure 2. Ahtanum Creek alluvial fan and watershed. The black circle marks where the creek emerges from the confined canyon and diverges into multiple channels, some of which are used as irrigation canals. The EIS of the proposed Pine Hollow Reservoir (not constructed) contains information on the hydrogeology of the area. Inset map shows Ahtanum watershed, red box outlines the area in the close-up map (modified

Manastash Creek is a major tributary to the Yakima River with a drainage of approximately 250 km^2.

The creek forms a large alluvial fan where it enters the southwestern portion of the Kittitas Valley (Figure 3). The stream diverges into multiple branches across the fan, eventually meeting the Yakima River. Collaborative efforts involving multiple stakeholders have resulted in enhanced instream flow in Manastash Creek in recent years.

3.2.1 History of study area

The land to the south of the main branch of Ahtanum Creek on the alluvial fan is part of the Yakama Nation (Figure 2). The area to the north of Ahtanum Creek is mainly farmland owned by individuals (Figure 2). We will request access to wells for sampling from the Yakama Nation hydrogeologist (see Section 4) or individual land owners, as appropriate. Most of the land within the study area for this project north of the creek is within the Ahtanum Irrigation District.

The Washington State Department of Ecology has been measuring groundwater levels annually in Well # DOE-C7 near Wiley City (Figure 2). This well was drilled 450 feet into the sedimentary aquifer in the 1970s. The ECY measurements show that the depth-to-water in this well declined from 50 ft in 1978 to 90 ft in 2022.

The allocation of surface water rights from Ahtanum Creek to the Yakama Nation and the Ahtanum Irrigation District is largely based on a legal decision from Circuit Court Judge Pope in 1964. The legal aspects of water allocation are not within the scope of this project, which is focused on the physical characteristics of the hydrogeology of the alluvial fan. However, the water rights will ultimately have relevance to how, where and by whom MAR could be implemented on the Ahtanum Creek.

Manastash Creek alluvial fan is composed largely of irrigated farmland within the Kittitas Reclamation District (KRD). We have discussed our proposal with the KRD team who are undertaking a YBIP project to assess how the supplementation of Manastash Creek from the KRD South Branch canal has affected groundwater recharge on the upper Manastash fan (Figure 3). The purpose and approach of our two projects are complementary. Our two teams have agreed to share data and collaborate in areas of overlapping interests. The KRD project is centered on the area close to the Manastash channel where the supplemental KRD canal water has been added, while we intend to assess the hydrogeology and recharge/storage potential over a broader area of the Manastash Creek alluvial fan. Because the stable isotope signature of water from the KRD canal is distinct from the water from Manastash Creek (Taylor and Gazis, 2014), we should be able to distinguish which surface water source is recharging the groundwater in different areas on the fan. This leads to a particularly useful intersection between our projects that could illuminate the surface water/groundwater interactions. Dr. Maria Daugherty is our contact person working on the KRD project on the Manastash fan. She is a member of the thesis committee of the CWU graduate student whose Master's thesis is based on the Manastash alluvial fan portion of this project.

Figure 3. Manastash Creek alluvial fan image. Manastash Creek alluvial fan enters the Kittitas Valley from the left. Current and former channels of Manastash Creek diverge down the fan, although not all sustain surface-water flow. The KRD South Branch Canal flows along the base of the hills and crosses Manastash Creek where it exits the canyon. KRD has been diverts water from the canal to supplement low flows in Manastash Creek.

3.2.2 Summary of previous studies and existing data

This project approach expands on previous YBIP investigations by Central Washington University. The YBIP project under Project Manager Carey Gazis and summarized by Sleeper (2020) used geochemical analysis of groundwater to determine potential groundwater storage locations in three alluvial basins within the Yakima River Basin. YBIP projects managed by Carey Gazis assessed the geochemistry of groundwater flow from canals in the Kennewick Irrigation District (Gazis, 2024) and developed a conceptual model for MAR in the Columbia River Basalts (Gazis, in progress).

Additional YBIP projects jointly managed by Lisa Ely and Carey Gazis examined the potential connections between stream restoration and groundwater storage in floodplain aquifers of headwater streams in the Yakima Basin (Ely et al., 2024; Gazis and Ely, 2023). These projects have supported several Master's Degree theses at CWU (Sleeper, 2020; Bartlett, 2022; Petralia, 2022; Henning, 2023; Kharrazi, 2023; Polizzi, 2023; Vlasenko, 2023).

The study areas are on alluvial fans previously identified as having good prospects for groundwater recharge and storage through MAR (Figures 4 and 5; Gibson and Campana, 2018). The basin-wide assessment of MAR potential by Gibson and Campana (2018) was created through a geospatial analysis of criteria conducive to MAR. The current project will build on those results to refine the evidence at two promising areas within the Yakima Basin, Ahtanum Creek and Manastash Creek alluvial fans, using field observations, groundwater-level monitoring and geochemistry.

Previous studies in the Ahtanum watershed will provide historical data for investigating variations and trends in groundwater in the region. Foxworthy (1962) wrote an extensive report on the geology and groundwater resources of the Ahtanum Valley, based on data collected in the 1950s.

An Environmental Impact Statement (Washington Department of Ecology, 2005) explored water management and restoration strategies proposed for the Ahtanum watershed, which included the plans for creation of the Pine Hollow Reservoir near the upstream end of the Ahtanum Creek alluvial fan. The reservoir was not constructed, but the EIS report contains summaries of the geology, geomorphology and hydrology of the site that will be useful background for this study.

The project on Manastash Creek will build on a previous geochemical study that included a portion of the Manastash alluvial fan in a much larger study area across the Kittitas Valley (Taylor and Gazis, 2014). In that research, groundwater samples were collected from 26 wells, analyzed geochemically, and compared to 24 surface water samples. Based on this analysis, they identified seven hydrochemical groups that were interpreted to represent the following:

A – interaction with basalts, no surface water influence
B and C – heavily influenced by Yakima River water or irrigation water

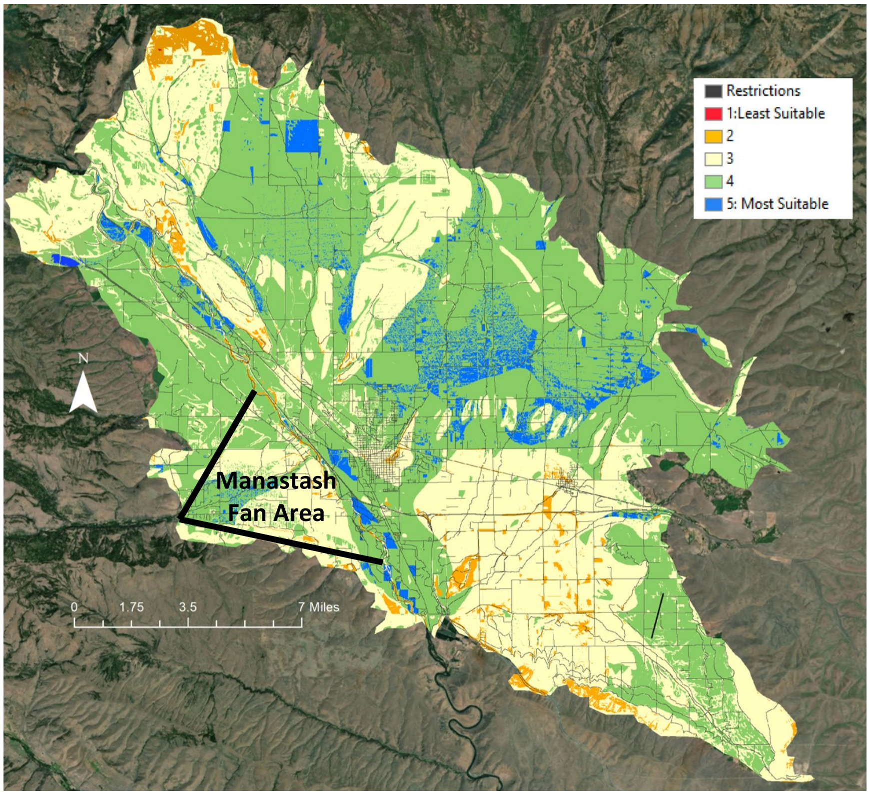

Figure 4. Map of aquifer recharge suitability in the sedimentary basin that includes Manastash Creek alluvial fan. Modified from Gibson and Campana (2018).

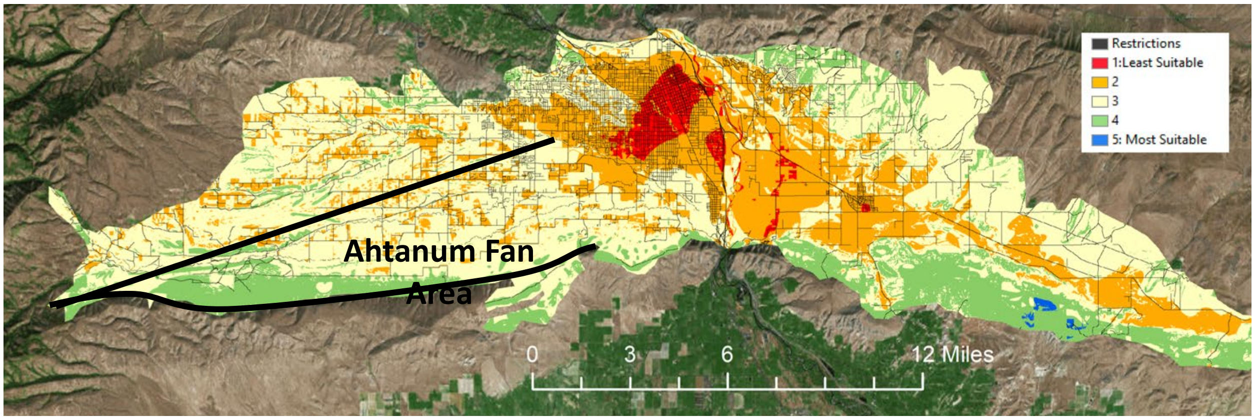

Figure 5. Map of aquifer recharge suitability in the sedimentary basin that includes Ahtanum Creek alluvial fan. Modified from Gibson and Campana (2018).

D and E – interaction with Ellensburg formation with some influence from surface water
F – interaction with Ellensburg formation, no surface water influence

These groups are defined by major ion and stable isotope geochemistry and their seasonal variations. Groundwater from basalt wells is characterized by high Na concentration and light stable isotope signatures (low δD and $\delta^{18}O$). Waters that are heavily influenced by Yakima River water and irrigation water from the Yakima River have heavy stable isotope signatures (high δD and $\delta^{18}O$) and variable and often elevated concentrations of NO_3, SO_4 and Cl. Ellensburg Formation groundwaters have intermediate isotopic signatures and are dominated by Ca, Mg, and HCO_3. In this study, the same methodology will be used on both the Manastash and Ahtanum alluvial fans. We will add more sample sites within the Manastash fan area, and ours will be the first hydrogeochemical study of groundwater flow in the Ahtanum fan. These data will improve our knowledge of surface water infiltration and water mixing and used in combination with the physical aquifer characteristics and water-level data to help identify areas on the fans that represent favorable conditions for MAR. For example, areas where wells show limited recharge from surface water at depth could be poor candidates for MAR.

3.2.3 Parameters of interest and potential sources

This project is not aimed at measuring environmental pollutants. The environmental parameters of interest in this study are:

- Groundwater levels and temperatures at select locations
- Alluvial fan aquifer stratigraphy in relation to groundwater levels, aquifer storage capacity, and groundwater flow
- Stable isotope and major ion geochemistry as a tracer of groundwater flow
- Field measurements of pH, conductivity, and dissolved oxygen to supplement major ion chemistry and ensure stability of groundwater chemistry when sampling

3.2.4 Regulatory criteria or standards

Not applicable.

3.3 Water quality impairment studies

Not applicable.

3.4 Effectiveness monitoring studies

Not applicable.

4.0 Project Description

In this project we aim to quantify the physical properties that indicate the potential for groundwater recharge and storage on the Ahtanum and Manastash Creek alluvial fans, both of which have been identified as promising sites for Managed Aquifer Recharge. We will compile existing data from wells logs, maps and reports, which will be combined with new field observations of sediment characteristics, water levels and geochemistry data. The results will be used to identify areas with suitable permeability rates, head space, and current surface water recharge. The geochemical analysis will identify the degree of surface water/groundwater mixing, which will provide insight into the depth of surface water penetration into the unconfined aquifer. These results will be used to identify sites where additional recharge is most likely to infiltrate and the maximum amount of water can be added during months of surplus. We will estimate directions of groundwater flow, gradient, and quantify the additional aquifer storage capacity at identified locations within these two alluvial fans at different times of the year. Based on our improved understanding of these aquifers and their characteristics, we will use simple groundwater flow equations to predict the travel time of recharged water from the recharge site to nearby streams. The proposed project will produce a detailed assessment of the physical characteristics and hydrology of these sites to provide a necessary foundation for an informed decision about the implementation of MAR projects.

4.1 Project goals

The main goal of this project is to quantify hydrogeologic properties and potential for groundwater recharge and storage on the alluvial fans of two Yakima River tributary watersheds that have been identified as promising sites for MAR in recent YBIP projects (Gibson and Campana, 2018; Kittitas Reclamation District, 2020). Specific questions that this report will address are:

1. Describe physical and hydrogeologic characteristics of the sedimentary aquifers at the study sites from analysis of existing well logs, geologic maps, previous reports and publications. These data will be supplemented with new field observations of the stratigraphy, sedimentology, soil characteristics and geomorphology of the tributary channels and alluvial fans.

2. Document the surface-water and groundwater hydrology. We will collect manual measurements of water levels and install pressure transducers into existing wells to monitor the seasonal groundwater variations and compare water levels among wells across the study sites.

3. Use geochemistry to trace surface water recharge and mixing with groundwater. Geochemical analysis will be used to decipher surface water/groundwater interactions and trace the spatial patterns in infiltration and mixing of surface water within the aquifer (e.g., Taylor and Gazis, 2014; Sleeper, 2020; Petralia, 2022). The resulting details of groundwater/surface water interactions and flow directions will aid in pinpointing the most effective locations for groundwater recharge and predicting the fate of a groundwater mound created by artificial recharge.

4. Quantify aquifer storage capacity and recharge potential within the specific study sites based on the data on the hydrology and aquifer characteristics gathered and measured in Objectives 1 – 3. These include the geologic and geomorphic setting; estimates of porosity and permeability; groundwater elevation data and hydrographs; and geochemical evidence of surface water-groundwater interaction.

4.2 Project objectives

The project objectives are to:

- Document the stratigraphy and geologic context of the Ahtanum and Manastash alluvial fans using well logs from the WA Ecology public online database and the Yakama Nation, geologic maps, and the online Washington State Geology Portal.
- Map relevant surface characteristics of each fan from existing maps and field observations, including 1) surficial soils and geomorphic landforms; 2) springs, wetlands and streams; 3) human-made water infrastructure, e.g. canals, etc. These features will be used to assess infiltration capacity of surface water, groundwater upwelling, and sources or sinks of water in different locations on the alluvial fans.
- Install 3 pressure transducers with data loggers in select wells on each alluvial fan to monitor seasonal groundwater levels and temperatures.
- Take manual measurements of water levels in select wells and surface water streams on each alluvial fan at different times during the year to assess groundwater fluctuations and storage capacity.
- Collect 20 water samples from wells and surface water streams on the Ahtanum Creek alluvial fan for stable isotope and geochemical analysis.
- Collect 20 water samples from wells and surface water streams on the Manastash Creek alluvial fan for stable isotope and geochemical analysis.

4.3 Information needed and sources

Existing data:

- Well log data – well depths, log of sediments, depth to water at time of drilling. These will be obtained from the Washington State well report viewer: https://appswr.ecology.wa.gov/wellconstruction/map/WCLSWebMap/default.aspx

- Geologic data from Washington State Geological Survey Geology Portal: https://www.dnr.wa.gov/geologyportal
- Soil maps from National Resources Conservation Service: https://websoilsurvey.sc.egov.usda.gov/App/WebSoilSurvey.aspx
- Existing characterizations of hydrogeology based on geology, field observations, and well log data (e.g. Foxworthy, 1965; Vaccaro et al., 2009)
- Stream discharge data for Ahtanum Creek from USGS 12502500 Ahtanum Creek at Union Gap, WA https://waterdata.usgs.gov/wa/nwis/inventory/?station=12502500
- Stream discharge data for Manastash Creek from DOE station 39J070 Manastash Creek at Cove Road. https://apps.ecology.wa.gov/ContinuousFlowAndWQ/StationDetails?sta=39J070
- Stable isotope and geochemical data for groundwater in part of Manastash Creek from Taylor and Gazis (2014)
- General maps of promising sites for MAR in the Yakima Basin (Gibson and Campana, 2018)

Data to be generated through this study:

- Descriptions and measurements of Ahtanum and Manastash alluvial fan stratigraphy.
- Groundwater levels from 3 pressure transducers installed in wells on each of the alluvial fans (Lists of priority wells in Appendix A).
- Manual measurements of groundwater levels in select wells on each fan (Appendix A).
- Field and laboratory measurements of pH, dissolved oxygen, conductivity, and alkalinity (bicarbonate + carbonate) for 20 water samples on each of the alluvial fans (total of 40 samples). See Appendix A for lists of well locations.
- Stable isotopes of O and H for 20 water samples on each of the alluvial fans (total of 40 samples). See Appendix A for lists of well locations.
- Major ion concentrations (Ca, Mg, Na, K, Cl, F, sulfate, nitrate, phosphate) for 20 water samples on each of the alluvial fans (total of 40 samples). See Appendix A for lists of well locations.

4.4 Tasks required

- Construct topographic and stratigraphic cross sections on transects across each alluvial fan based on the well logs, geologic maps and exposed stratigraphy in stream banks.
- Acquire streamflow data from Manastash and Ahtanum Creek gaging stations listed in section 4.3 of this QAPP. Consult Yakama Nation, AID, KRD and Kittitas County Conservation District to identify possible additional sources of streamflow data.
- Install pressure transducers in six wells, regular downloading of pressure transducer data.
- Identify sampling sites for groundwater and surface water, including contingency sites if access is not available.

- Collect 40 water samples (≈34 groundwater samples and ≈6 surface water samples).
- Collect field measurements of pH, dissolved oxygen, and conductivity; laboratory measurements of alkalinity.
- Conduct laboratory measurements of stable isotopes and major ion concentrations.
- Compile and analyze new data including graphical and statistical analysis and assessment of spatial patterns.
- Create maps of stratigraphy, geochemistry and hydrogeology of the Ahtanum and Manastash alluvial fans.
- Create conceptual model of alluvial fan hydrogeology and identify feasible locations for MAR.
- Prepare final report and present results.

4.5 Systematic planning process

The QAPP is the systematic planning process for this project.

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

This QAPP was prepared by Lisa Ely and Carey Gazis for Central Washington University (CWU). Dr. Ely, a professor in the Department of Geological Sciences at CWU, is the Project Manager and Principal Investigator; Dr. Gazis, a professor in the Department of Geological Sciences at CWU is the co-Principal Investigator. Much of the project work will be undertaken by Brook Bauer and Elif Myers, M.S. graduate students at CWU, as part of their thesis research. The Principal Investigators and graduate students at CWU will communicate regularly with Jeff Dermond, grant project manager, at the Department of Ecology and other members of the Groundwater Storage Subcommittee of the Yakima Basin Integrated Plan.

Table 1 shows the responsibilities of those who will be involved in this project.

Table 1. Organization of project staff and responsibilities.

Staff	Title	Responsibilities
Lisa Ely Geological Sciences Dept. Central Washington Univ. Phone: 509-963-2177	**Project Manager/ Principal Investigator**	**Write the QAPP. Oversee reporting and project budget. Collaborate on QA review of data. Oversee analysis and interpretation of stratigraphic, geologic and hydrogeologic data. Prepare final report in collaboration with Carey Gazis, with input from Brook Bauer and Elif Myers.**
Carey Gazis Geological Sciences Dept. Central Washington Univ. Phone: 509-963-2820	**Co-Principal Investigator**	**Collaborate on writing the QAPP. Oversee field sampling and transportation of water samples to the laboratory. Collaborate on QA review of data. Oversee analysis and interpretation of geochemical and groundwater data. Collaborate on preparation of final report with Lisa Ely, with input from Brook Bauer and Elif Myers.**
Brook Bauer Geological Sciences Dept. Central Washington Univ.	**Graduate Student Researcher**	**Conduct research on Ahtanum alluvial fan. Compile existing data from well logs, maps and reports. Collect samples and record field information. Enter data into EIM database. Work with Dr. Ely and Dr. Gazis to interpret data and prepare Technical Memorandum.**
Elif Myers Geological Sciences Dept. Central Washington Univ.	**Graduate Student Researcher**	**Conduct research on Manastash alluvial fan. Compile existing data from well logs, maps and reports on. Collect samples and record field information. Enter data into EIM database. Work with Dr. Ely and Dr. Gazis to interpret data and prepare Technical Memorandum.**
Jeff Dermond Office of Columbia River WA Dept. of Ecology Phone: 509-268-1784	**Grant Project Manager**	**Manage the project grant, provide oversight of project, and approve the budget. Provide internal review of the QAPP, approve the final QAPP.**
Scott Tarbutton Office of Columbia River WA Dept. of Ecology Phone: 509-867-6534	**OCR Quality Assurance Coordinator**	**Review and approve the draft and final QAPP**

QAPP: Quality Assurance Project Plan
NEP: National Estuary Program
WQX: Water Quality Exchange

5.2 Special training and certifications

Graduate students Brook Bauer and Elif Myers will receive training from Dr. Ely and Dr. Gazis in field measurement, field sampling and data processing protocols. Individuals performing project tasks will be trained in and experienced with the relevant SOPs for the required instrumentation.

Ms. Bauer and Ms. Myers will receive training in laboratory safety, sample preparation, and use of the Picarro water isotope analyzer and ion chromatograph. These trainings will be given by Dr. Gazis and an engineering technician at Central Washington University.

5.3 Organization chart

Not applicable - See Table 1.

5.4 Proposed project schedule

Tables 2 – 4 list key activities, due dates, and lead staff for this project.

Table 2. Schedule for completing field and laboratory work

Task	Due date	Lead staff
Field work	January 2025	Ely and Gazis
Laboratory analyses	June 2025	Gazis
Contract lab data validation	NA	NA

Table 3. Schedule for data entry

Task	Due date	Lead staff
EIM data loaded	3/1/2026	Gazis
EIM QA	3/1/2026	Gazis
EIM complete	3/1/2026	Gazis

EIM: Environmental Information Management; NA: Not Applicable

Table 4. Schedule for final report

Task	Due date	Lead staff
Draft to Ecology project manager	February 2026	Ely and Gazis
Final report	March 2026	Ely and Gazis

5.5 Budget and funding

This project is funded by the Department of Ecology Office of Columbia River contract IAA No. C2400168, as recommended by Groundwater Storage Subcommittee under the Yakima Basin Integrated Plan. Funding covers summer and academic-year salary, benefits, and tuition costs for the two CWU graduate students, Brook Bauer and Elif Myers; partial summer salary for principal investigators, Dr. Gazis and Dr. Ely; summer funding for student field assistants; travel for field measurements, observations and sample collection; field supplies; and geochemical analyses of 40 water samples. The remainder of Dr. Gazis's and Dr. Ely's effort toward this project is funded by Central Washington University.

Tables 5 and 6 show project and laboratory budget details

Table 5. Project budget and funding

Cost Category	Cost ($)
Salary, benefits, and indirect/overhead	$112,890
Equipment, incl. pressure transducers and supplies	$5600
Travel and other	$1638
Graduate student tuition	$20,484
Laboratory (See Table 6 for details.)	$1800

Table 6. Laboratory budget details

Parameter	Number of Samples	Number of QA Samples	Total Number of Samples	Cost Per Sample ($)	Lab Subtotal ($)
Stable Isotope Analyses	40		40	$15	$600
Stable Isotope Analyses (QA)		12	12	NA	0
Major Ion Analyses	40		40	$30	$1200
Major Ion Analyses (QA)		12	12	NA	0

6.0 Quality Objectives

6.1 Data quality objectives [1]

The main measurement data quality objectives (DQO) for this project are as follows:

1) Collect 40 water samples to represent different groundwater and surface water bodies on the Ahtanum and Manastash alluvial fans and analyze their geochemistry. The analyses will use standard methods to obtain pH, conductivity, DO, alkalinity, major ion, and stable isotope data that meet measurement quality objectives (MQOs) that are described below and are comparable to previous study results.

2) Collect discrete and continuous groundwater elevation and temperature measurements over 12 months from manual measurements and pressure transducers installed in six wells. The study will use standard methods to obtain the groundwater elevations that meet measurement quality objectives (MQOs) that are described below and are comparable to previous study results.

6.2 Measurement quality objectives

One measurement objective of this study is to collect representative geochemical and isotopic data for hydrogeologic characterization. Data quality objectives (DQOs) for this project are based on precision, bias, and sensitivity and are used to establish measurement quality objectives (MQOs) which will be used to assess data quality. Laboratory MQOs for the individual parameters are summarized in Table 7.

A second measurement objective is to install pressure transducers and temperature loggers in three wells to determine seasonal variations in water levels and temperature. Specifications for the data loggers are given in Table 8 and MQOs for the water level and temperature measurements are given in Table 9.

Acceptable data quality for field parameter measurements will be ensured by calibration of instruments according to manufacturer's specifications. The following meters or an equivalent model from another brand will be used: Hanna Instruments HI98196 multiparameter meter, Orion Star A122 portable conductivity meter, YSI 550A dissolved oxygen meter. Meter calibration is accomplished by purchase of appropriate calibration standards when needed and a meter-specific calibration procedure that is described in the meter user's manual. Repeat analyses of these standards as samples are performed periodically after calibration to assure

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[1] 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 do lead to important decisions, 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.

reproducibility, accuracy, and precision. Each meter has a calibration certificate, and a user's manual that addresses calibration procedures, maintenance, and trouble shooting.

6.2.1 Targets for precision, bias, and sensitivity

The MQOs for project results, expressed in terms of acceptable precision, bias, and sensitivity, are described in this section and summarized in the table below.

Table 7. Measurement quality objectives for laboratory analyses of water samples.

Parameter	Laboratory Duplicate (RPD)	Field Duplicate (RPD)	Matrix Spike Duplicate (RPD)	Lab Control Standard (%Recovery)	Matrix Spike (% Recovery)	Internal Standard Recovery (% Recovery)	Lowest Conc. of Interest (Detection Limit*)
Alkalinity	<8%	<10%	<10%	80-120%	75-125%	NA	10 mg/L
Chloride	<8%	<10%	<10%	80-120%	75-125%	NA	0.1 mg/L
Fluoride	<8%	<10%	<10%	80-120%	75-125%	NA	0.1 mg/L
Sulfate	<8%	<10%	<10%	80-120%	75-125%	NA	0.5 mg/L
Nitrate-N	<8%	<10%	<10%	80-120%	75-125%	NA	0.1 mg/L
Phosphate-P	<8%	<10%	<10%	80-120%	75-125%	NA	0.05 mg/L
Calcium	<8%	<10%	<10%	80-120%	75-125%	NA	0.05 mg/L
Magnesium	<8%	<10%	<10%	80-120%	75-125%	NA	0.05 mg/L
Potassium	<8%	<10%	<10%	80-120%	75-125%	NA	0.05 mg/L
Sodium	<8%	<10%	<10%	80-120%	75-125%	NA	0.05 mg/L
Oxygen-18	0.05 per mil	0.1 per mil	NA	NA	NA	NA	NA
Deuterium	0.6 per mil	1.0 per mil	NA	NA	NA	NA	NA

NA Not Applicable

* Although statistically derived, these values represent a realistic estimate of the detection limit rather than a statistical measure of instrument detection; Treatment of measurements below detection limits is discussed in section 14.2 (Treatment of Non-Detects)

Table 8. Specifications of water level data loggers, manual measurements, and surface elevations.

	Measurement	Range	Accuracy	Resolution	Response Time (90%)	Stability (Drift)
HOBO U20-001-01 Data Logger	Pressure	0 to 207 kPa	±0.3% full scale, 0.62 kPa	<0.02 kPa	< 1 sec	
	Water Level Depth	0 to 30 ft at sea level (≈34.4 ft at 5000 ft altitude)	±0.05% full scale, 0.015 ft	0.007 ft	< 1 sec	
	Temperature	-20°C to 50°C	±0.44°C	0.10°C	5 min	0.1°C per yr
Solinst Water Level Meter (Model 101 and 102)	Water Level Depth (Manual)	0.5 to 300 ft	0.03 ft	0.01 ft	< 1 sec	
Garmin GPSMap 64st	Surface Elevation	1200 to 2500 ft	±10 ft	1 ft	n/a	
LiDAR Datasets East Cascades South 2020, Lewis Yakima 2005, Yakima Basin 2018, Manastash Basin 2012	Surface Elevation		0.1 ft			

Table 9. Measurement quality objectives: water levels, temperature, field parameters.

MQO	**Precision**		**Bias**	**Sensitivity**
Parameter	**Duplicate Measurement or Sensor Resolution**		**Based on reported accuracies from user manuals and/or manual measurements**	**Minimum Measurement**
	Relative Percent Difference (%RPD)	In measurement units	in measurement units	in measurement units
Groundwater Level (transducers)	n/a	n/a	0.62 kPa 0.03 ft water	0.01 ft water above sensor
Groundwater Level(manual measurement)	n/a	0.02 ft	0.08 ft	0.02 ft
Temperature	n/a	n/a	0.44°C	0.1°C
pH	n/a	0.01 standard units	0.05 standard units	n/a
Dissolved Oxygen	0.1	0.1 mg/L	0.2 mg/L or 2% of reading (greater value)	0.1 mg/L
Conductivity	0.2	0.2 μs/cm	0.5 μs/cm	0.2 μs/cm

6.2.1.1 Precision

Precision will be determined based on duplicate field measurements and laboratory measurements of duplicate samples. For alkalinity and major ion concentrations, the MQOs require that duplicate samples are within 10% of each other. For stable isotope analyses, measurements are of ratios that are expressed in delta notation[*] (per mil units). For these analyses, in addition to measuring duplicate samples, the laboratory method includes multiple injections and measurements of each sample (typically ten). The first three injections are discarded because of memory effects. The reproducibility of the remaining analyses provides another determination of the precision of the method. Both the duplicate sample

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[*] $\delta = \left(\frac{R_{sam}-R_{std}}{R_{std}}\right) * 1000, \mathit{where}\ R_{sam}\ \mathit{and}\ R_{std}\ \mathit{are\ the\ isotope\ ratios}\ \left(\frac{{}^{18}O}{{}^{16}O}\ \mathit{for}\ \delta^{18}O, \frac{D}{H}\ \mathit{for}\ \delta D\right)$ $\mathit{of\ the\ sample\ and\ the\ standard, respectively}.$

measurements and the multiple analyses of the same sample should meet the MQOs for stable isotopes, 0.1 per mil for Oxygen-18 and 0.6 per mil for deuterium.

For transducer water level and temperature measurements, precision is the sensor resolution. For manual water level measurements using a water level meter, estimated precision is based on duplicate measurements.

6.2.1.2 Bias

Bias will be determined based on measurement of quality control (QC) standards of known ion concentration or isotopic composition. These QC samples are independent from the calibration standards for each measurement. For major ions, the recovery limits for these QC standards should be 90-110%. For stable isotope analyses, these QC standards should measure within 0.1 per mil (oxygen-18) and 0.6 per mil (deuterium) from their known value.

Equipment/filter field blanks will be collected during each sampling round to determine if sampling equipment or filters are introducing bias into the sampling results. Blanks will be used to determine whether the sample tubing, filters, sample containers, preservatives, or transport methods represent a source of bias. If bias is recognized in blank samples early in the project, additional steps will be taken to isolate the source of error, and field procedures or equipment will be modified to eliminate the problem.

For transducer water level and temperature measurements, bias targets are based on the reported accuracies (maximum error) of the sensors. Bias will also be assessed by comparing logger measurements to manual measurements. This comparison is particularly useful for determining if there is any logger drift.

For manual depth-to-water measurements, bias is introduced by any curvature in the measuring tape. The measuring tape will be examined periodically to assure that there are no kinks or bends.

6.2.1.3 Sensitivity

Sensitivity is a measure of signal strength compared to the concentration that creates that signal. It is one measure of the capability of a method to detect a substance. Sensitivity differs from the detection limit in that it does not depend on the signal stability. Detection limits are based on both signal strength (sensitivity) and signal stability. Sensitivity is usually not an issue for major ions in water because they are present in concentrations well above the detection limit and therefore have strong signals and high signal-to-noise ratios. Stable isotope analyses are measurements of ratios not concentrations and therefore sensitivity is not a valid measure for these analyses. Instrumental detection limits for the major ion analyses are given as the lowest concentration of interest in Table 7.

6.2.2 Targets for comparability, representativeness, and completeness

6.2.2.1 Comparability

Comparability is the degree to which data can be compared directly to similar studies. The use of standardized sampling procedures, analytical methods with comparable sensitivity, and units of reporting, and quality control procedures and standards ensure comparability of data. For comparability with existing data, particularly for stable isotope analyses, standards of known concentration will be analyzed and those analyses will either serve as the basis for the measurement calibration or as a check (quality control) standard for the calibration.

The same model of water-level pressure transducer and data logger will be installed in all wells to ensure comparability. Comparison of datalogger depth-to-water measurements with manual measurements will ensure that the absolute measurements between piezometers are comparable and that each data logger is well calibrated within the range of water levels measured.

Standardized sampling procedures will be used as described in this document and informed by the SOPs listed in Section 8.2.

6.2.2.2 Representativeness

Representativeness is the degree to which sample data from the project accurately represent a particular characteristic of the environmental matrix which is being sampled. Representativeness of the samples collected is ensured by adherence to the field sampling protocols and standard laboratory protocols. Sampling locations are selected to represent the groundwater geochemistry in the vicinity of each well.

Groundwater levels can be relatively slow to change compared with surface water. Groundwater fluctuations are expected to occur seasonally in some wells either due to inputs from spring snowmelt or irrigations or withdrawals through pumping in the well or in the region. Transducers that record measurements continually (i.e., every 15 minutes) will allow us to observe changes that might occur in shorter timeframes. Wells will be chosen to represent shallow aquifers that are likely to be influenced by these seasonal effects. Where possible, wells will be chosen that are not being used for pumping so that they are more representative of the regional water level.

The existing streamflow gages on Ahtanum Creek at Union Gap (USGS gage #12502500) and Manastash Creek at Cove Road (WA Dept of Ecology gage #39J070) will provide continual flow measurements that are representative of the surface water fluctuations at the study sites.

6.2.2.3 Completeness

To ensure data completeness, only properly calibrated and maintained equipment will be used. Data logger measurements will be corrected for barometric pressure and compared to manual measurements and any data logger that is not collecting high quality complete data will be replaced. Problems occasionally arise during sample collection that cannot be controlled; thus, a completeness of 95% is acceptable. Example problems are flooding, site access problems, non-linear measurement drift, or equipment failure. For the laboratory analyses, a complete or valid result will include sample documentation and a laboratory analysis report. Greater than 95% completeness is expected for samples collected as part of this project.

6.3 Acceptance criteria for quality of existing data

Existing geochemical data will be used as a comparison to data collected in this project. Existing data will not be used as part of this study unless it has met the same measurement quality outcomes outlined in this QAPP. The quality of existing data from groundwater wells on the Manastash alluvial fan from Central Washington University, published in Taylor and Gazis (2014) has been documented in the laboratory and is available to us. The quality of existing data from the U.S. Geological Survey and the Department of Ecology Environmental Information Management (EIM) database is also well documented . If data quality documentation is not available, existing data will not be used.

6.4 Model quality objectives

Not applicable.

7.0 Study Design

7.1 Study boundaries

A general map of the two study areas is shown in Figure 1. The boundaries of the individual study sites on the Ahtanum and Manastash alluvial fans are shown in Figures 6 and 7. These figures also show the approximate transects of wells from which well logs will be acquired to construct stratigraphic cross sections. The wells do not all fall directly on these straight transect lines, but the stratigraphy will be projected onto the closest locations on the transects. Some of the wells used for the stratigraphy will also be used for water sampling and analysis (See Appendix A).

7.2 Field data collection

Forty water samples plus four field duplicates will be collected during the summer and fall 2024 (~34 wells and ~6 surface water locations) within the two study areas. In addition, water levels and temperatures will be collected from pressure transducers installed in up to six wells. The sampling strategies and field measurement methods are described below.

Geologic and stratigraphic information will mainly rely on existing data from well logs, geologic maps and soil maps. Some of the surface soils and shallow stratigraphic units will be verified in the field at naturally occurring streambank exposures, which will be identified during field reconnaissance.

7.2.1 Sampling locations and frequency

The aquifer stratigraphy will be examined from multiple well logs within the study areas to represent, as much as possible, a range of typical stratigraphic characteristics that could affect the infiltration, storage and mixing of surface water with groundwater. Stratigraphy will initially be described from well logs on transects across the alluvial fans as shown in Figures 6 and 7. Well locations are listed in Appendix A. Information from additional well logs could be added to expand or refine the analysis, based on the initial results.

Final selection of wells for water sampling within the study areas will be based primarily on location and well geology. Surface water sources that potentially recharge the aquifers in the study areas will also be sampled to define their geochemical signatures. Due to time constraints of the project schedule, this QAPP has been prepared in advance of final selection of well locations to be sampled. This QAPP provides a list of candidate wells (Appendix A) and the methods and procedures to be used in sampling and analysis, rather than providing a final list of sampling locations.

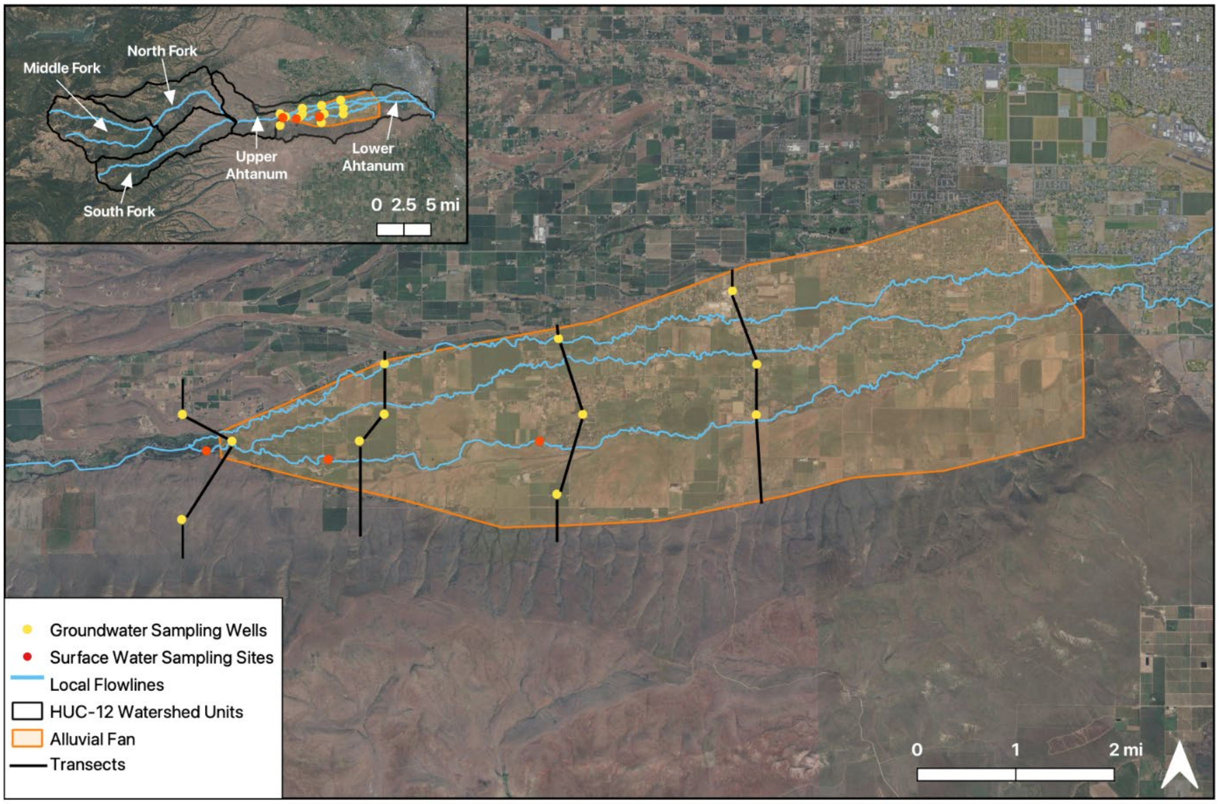

Figure 6. Ahtanum alluvial fan site map. The map shows well log transects and priority sites for groundwater and surface water sampling. Well locations are listed in Appendix A.

The following selection criteria are used to identify potential sampling wells within the study area:

- Candidate wells will have known geology and will represent, as much as possible, the range of lithologies, including both sedimentary and basalt aquifers, within the study area. Priority will be given to wells in the sedimentary basin fill because that is the likely target aquifer.
- Preference will be given to wells with good well logs and construction that indicates sampling from known depth.
- Wells will be selected by location relative to possible surface water recharge sources.
- Wells will be sampled across structures that may be potential conduits or barriers to flow.
- The well must be physically accessible and have a sampling port or other suitable opening. The sampling port will preferably be outside of any residence and wells will have a faucet/hose bib available prior to any reservoir or pressure tank.
- The well owner must give permission for the well to be sampled.

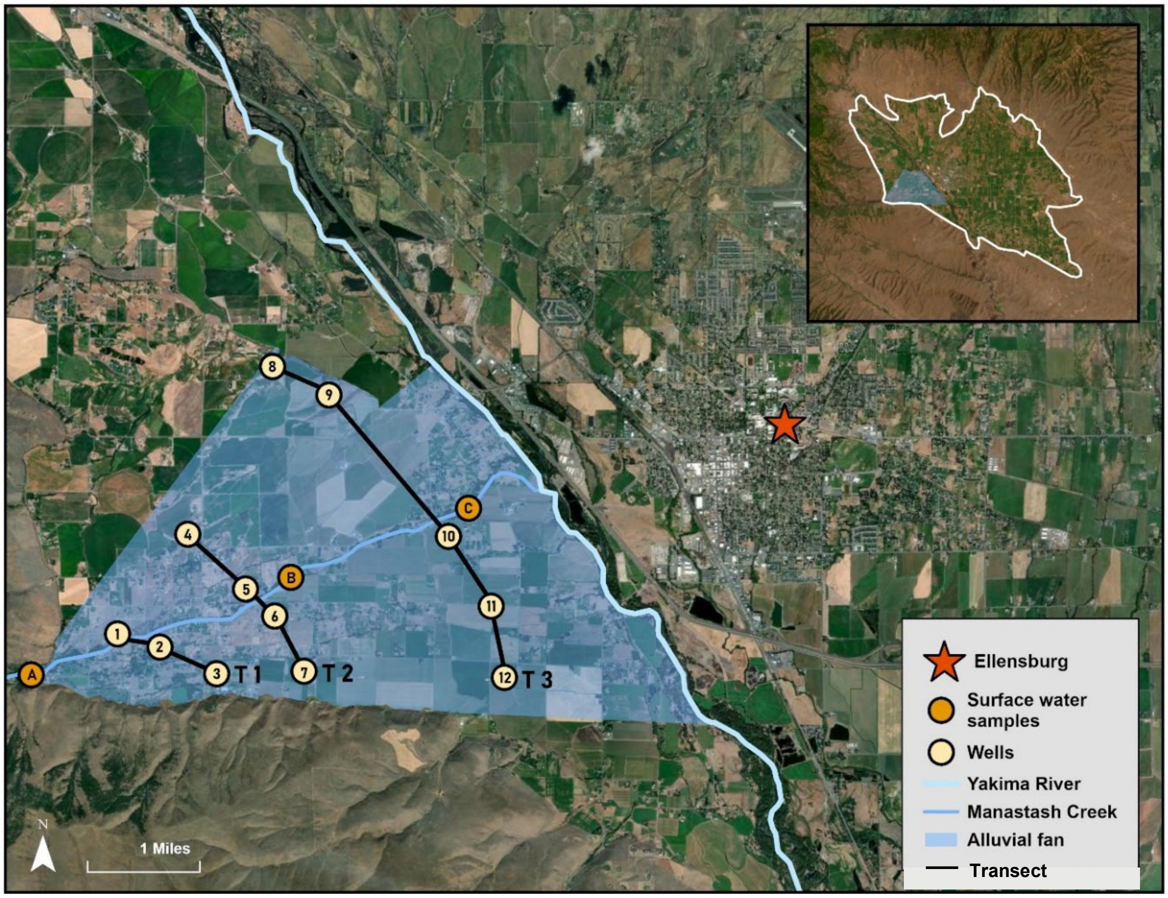

Figure 7. Manastash alluvial fan site map. The map shows well log transects and priority sites for groundwater and surface water sampling. Well locations are listed in Appendix A.

Initial lists of candidate sampling wells from Ahtanum and Manastash alluvial fans, compiled from the USGS and Department of Ecology well log databases in consultation with geologic maps (Washington GIP, 2024), are in Appendix A. The initial lists are based on the first four criteria listed above. The last two criteria will be verified by the investigators during initial site visits. Wells satisfying all six criteria will be scheduled for sampling during summer 2024. It is anticipated that approximately 34 wells will be sampled during the project. This number of wells was chosen partly based on time constraints and budget and partly because it is our experience that this is an adequate number of samples for characterizing the hydrogeochemistry of a region of this size, providing enough spatial distribution (both on the land surface and with depth) and multiple samples from each major aquifer.

The surface water samples will be collected during summer and fall, 2024. Surface water will be collected from Ahtanum Creek upstream of the Yakama Nation irrigation diversion site and at approximately evenly spaced locations along the main Ahtanum Creek down the fan. Sampling locations will be chosen to reflect representative surface water geochemical end members and accessibility (e.g., where roads cross streams). Surface water samples will be collected from Manastash Creek above and below the KRD South Branch Canal augmentation of the Manastash Creek (see Figure 3) and at accessible points along the creek down the alluvial fan. A sample will also be collected from the KRD and Westside irrigation canals that cross the upstream portion of the fan to assess the geochemical signature of these waters, which are diverted from the Yakima River.

Final selection of wells for installing pressure transducers to measure water-level elevations will be based primarily on location and well hydrogeology. Due to time constraints of the project schedule, this QAPP has been prepared in advance of final selection of well locations for installation of the pressure transducers. This QAPP provides the methods and procedures to be used in selecting the wells.

The following selection criteria will be used to identify potential wells within the study area:

- Candidate wells will have known geology and will represent, as much as possible, a geographic range that will document the groundwater elevations across the alluvial fan.
- Preference will be given to wells with good well logs and construction that indicates infiltration from known depth.
- Preference will be given to wells that are not currently being pumped. Secondary preference will be for wells that are not pumped continually throughout the study period.
- The well must be physically accessible and have a suitable opening for installing the pressure transducer.
- The well owner must give permission for the pressure transducer to be installed and for us to retrieve the transducer to download the data.

Wells that meet all criteria will be identified in spring 2024. Pressure transducers will be installed in spring and early summer 2024. At the same time, two barometric loggers will be installed, one on Manastash fan and one on Ahtanum fan. Pressure transducer data will be collected over a 12-month period at 15-minute sampling intervals. Data will be retrieved from the pressure transducers every six weeks. At that time, a manual depth-to-water measurement will be collected from the same wells. Additional manual measurements of depth to water will be taken in the wells where water samples are collected for geochemical analysis, listed in Appendix A, in cases where access is easily available. The ground elevation of each well in which water level is measured will be obtained from hand-held GPS location and elevation measurements taken in the field, which will be refined as needed by deriving the elevation for the latitude/longitude location of the well from lidar imagery (Washington Lidar Portal, 2024; Table 8) or by taking multiple GPS measurements on different days. The distance from the ground surface to the top of the casing (TOC) will be measured manually with measuring tape. These two values (elevation and ground surface to TOC) allow for the conversion of depth from TOC to groundwater measurements to groundwater elevations.

7.2.2 Field parameters and laboratory analytes to be measured

- Water levels and temperatures in wells will be continually recorded by pressure transducers and data loggers. Barometric pressure will be measured at each site on the same time intervals.

Every six weeks, the following manual measurements will be made:

- depth-to-groundwater in all wells with installed pressure transducers

Additional environmental parameters to be measured in the field:

- Stratigraphy in natural exposures along stream banks
- Field measurements of pH, alkalinity, dissolved oxygen, and conductivity of water samples that are collected for geochemical analysis

In the laboratory at CWU, collected water samples will be analyzed for:

- Oxygen isotope ratio (oxygen-18/oxygen-16)
- Hydrogen isotope ratio (deuterium/hydrogen)
- Major element geochemistry (Table 7)

7.3 Modeling and analysis design

Not applicable.

7.3.1 Analytical framework

Not applicable.

7.3.2 Model setup and data needs

Not applicable.

7.4 Assumptions of study design

The study is based on the following assumptions:

- There is connection between the groundwater and surface water in the alluvial fans.
- The sediment and rock units recorded in the well logs accurately represent the stratigraphy of the alluvial fan and its aquifers.
- The water that is sampled from faucets near groundwater wells are geochemically representative of the water from the aquifer(s) in which the wells are screened or perforated. This includes an assumption that any mixtures of end member waters that are observed has occurred in aquifers and not in well casings. This assumption is not met when wells have inadequate seals and there is leakage from the surface. To address this possibility, we will select wells that have good well logs from reliable drillers, including known depths and adequate descriptions of well construction. In interpreting our data, we will remain open to the possibility that waters have been geochemically altered between the aquifer and the sampling point.

7.5 Possible challenges and contingencies

The biggest challenge that we anticipate will be gaining access to wells for sampling. Contingency plans for potential sampling shortfalls are described below. There are no known environmental hazards in the study areas.

7.5.1 Logistical problems

We anticipate that gaining access to wells will constitute a major effort prior to and during sample collection and may present our largest challenge. A variety of approaches will be used to contact owners and request access to their wells: Initial letters to owners, followed by phone calls to owners, word of mouth between neighbors, and visits to houses when owners are home. We have found in similar projects in the past (Gazis, 2023) that connection with well owners through friends, neighbors and known representatives of cooperating organizations such as KRD, Yakama Nation, etc., is especially helpful in identifying wells for sampling. The main contingency plan to mitigate the problem of well access is to identify extra wells in case some are not available or suitable for sampling. In addition, when choosing wells, we will strive to create redundancy in our sampling options.

7.5.2 Practical constraints

There is always the possibility of instrument failure, either in the field or in the laboratory. For field measurements, we have extra meters that can be used in cases of meter failure. In the laboratory, we also have alternative instruments that can be used. There is a Metrohm Ion Chromatograph in the Chemistry Department at CWU that can be used for major ion analyses. An Agilent Inductively Coupled Optical Emission Spectrometer (ICP-OES) can be used for analyses of calcium, magnesium, potassium, sodium, iron, copper, and lead. Finally, there are two operational isotope ratio mass spectrometers that can be used for stable isotope analyses of water if the Picarro water isotope analyzer breaks down.

7.5.3 Schedule limitations

The main people involved in accomplishing the tasks of this study are Brook Bauer and Elif Myers, both graduate students at CWU. Inasmuch as this research constitutes their thesis projects, it will be their top priority. The research stipends that are funded in this project will allow them to devote their time to this research. If the last of the sampling is delayed until the fall, they will have the scheduling flexibility to complete the sampling and analysis.

QAPP review and approval may delay the intended start date for this project. This could affect the installation of pressure transducers before the summer decline in water levels, in which case we will leave them in place through the following spring.

8.0 Field Procedures

8.1 Invasive species evaluation

SOP EAP070, Version 2.2 (Parsons et al 2018) will be followed to minimize any chance of spreading of invasive species.

8.2 Measurement and sampling procedures

Collection of samples and associated field QC samples will follow accepted procedures. The principal investigator will ensure that field sampling personnel will be appropriately trained and thoroughly familiar with these procedures.

Sampling and measurement procedures will be based on the following SOPs:

ASTM Standard Practices for Description and Identification of Soils (Visual-Manual Procedures). International Standard, Designation D2488-17e1 (2017).

Collection and Analysis of pH Samples, Standard Operating Procedure EAP031 (Washington Department of Ecology, 2018)

Collecting Groundwater Samples: Purging and Sampling Monitoring Wells for General Chemistry Parameters, Standard Operating Procedure EAP099 (Washington Department of Ecology, 2023a)

Collecting Groundwater Samples for Metal Analysis from Water Supply Wells, Standard Operating Procedure EAP098 (Washington Department of Ecology, 2019a)

Collection and Analysis of Conductivity Samples, Standard Operating Procedure EAP032 (Washington Department of Ecology, 2017a)

Collection, Processing, and Analysis of Stream Samples, Standard Operating Procedure EAP034 (Washington Department of Ecology, 2017b)

Groundwater Manual Depth to Water Measurements, Standard Operating Procedure EAP052 (Washington Department of Ecology, 2023b)

Use of Submersible Pressure Transducers During Groundwater Studies, Standard Operating Procedure EAP074 (Washington Department of Ecology, 2019b)

The following methods will be used for major ion analyses:

U.S. EPA. 1997. Method 300.1: Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0.

http://quimica.udea.edu.co/~carlopez/cromatoion/ionchro_envir_anal.pdf

Jackson P.E., 2006 Ion Chromatography in Environmental Analysis. Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation. http://quimica.udea.edu.co/~carlopez/cromatoion/ionchro_envir_anal.pdf

Sampling for stable isotope analysis will be done in accordance with protocols developed by the CWU laboratories that have been conducting these analyses. These procedures are documented in internal laboratory SOPs. The general method is documented in Lis et al. (2008).

The procedures for sampling described here are in general agreement with Standard Operating Procedure EAP098 (Washington Department of Ecology, 2019a)

The SOP provides greater detail on many of the steps in purging and sampling.

All wells will be purged prior to sampling using existing pumps and plumbing. Samples will be obtained from a tap as close to the wellhead as possible, and prior to holding or pressure tanks whenever possible. No samples will be collected downstream of filters, water treatment units, hot water tanks, etc. that could modify the water chemistry of the sample. Temperature, specific conductance, pH, and dissolved oxygen will be recorded at intervals during well purging through the use of a metered, closed-atmosphere flow cell. During purging, water from the selected tap will be routed by a clean "Y" fitting directly to the flow cell using a short section of tubing. Discharge from the flow cell will be routed to a suitable location identified by the well owner. Wells that are not routinely pumped will be purged until all field parameters have stabilized over three consecutive readings. Flow rate will be estimated by measuring the time to fill a fixed volume beaker; discharge volume will be calculated by multiplying this rate times the purge time. Table 10 presents the criteria for purge stabilization.

Table 10. Stabilization criteria for well purging

Parameter	Stabilization Criteria (maximum change for 3 successive readings)
Temperature	±0.1°C
pH	±0.1 standard units
Specific conductance	±10 μohms/cm for values < 1000 μohms/cm ±20 μohms/cm for values > 1000 μohms/cm
Dissolved oxygen	±0.1 mg/L for values < 1.0 mg/L ±0.2 mg/L for values > 1.0 mg/L

Once stabilized parameter values have been recorded, water will be re-directed to the second outlet of the "Y" fitting for sample collection. Water samples designated for laboratory analysis will be collected directly into the appropriate containers. Samples requiring filtration will be collected into a clean 60-ml polypropylene syringe connected to a 0.45-micron filter. Samples will then be filtered on site into the appropriate containers. The number and types of containers to be filled for each analysis, as well as holding times and any special sample handling or preservation requirements are listed in Table 11.

Clean latex or nitrile (powder-free) gloves will be worn by sampling personnel during sampling and replaced between wells. The sampler will record the location of the sampling point relative to any treatment units or other in-line hydraulic components such as surge/pressure tanks or cisterns. Upon collection, samples will be labeled and immediately placed on ice in a cooler or otherwise stored as specified in Table 11 until delivery to the laboratory. When necessary, field equipment will be decontaminated using a Liquinox solution and rinsed with deionized water. If a piece of sampling equipment cannot be cleaned, it will be dedicated to the specific well.

Samples from small streams will be collected from the thalweg. For larger streams, samples will be collected from the side of the stream in a location where the water appears to be flowing and in continuity with the thalweg. When needed, an extendable sampling device or a Wildco horizontal alpha sampler will be used.

Water levels and temperatures in wells will be continually recorded by pressure transducers and data loggers. A 15-minute interval will be set for logger measurements. Data will be downloaded via Bluetooth interface at least every eight weeks. Manual measurements of depth-to-groundwater will be made at the time of each visit.

The near-surface stratigraphy will be described at natural exposures along stream banks to assess the range of typical surface sediment characteristics that could affect the shallow groundwater infiltration capacity. Stratigraphic depth from the surface will be measured with a vertically placed measuring tape. Boundaries between major stratigraphic units, if any, will be noted. The average and range of grain sizes, macro organic content, roots, color, and cementation will be described for each major stratigraphic unit or soil horizon following the SOP in ASTM (2017). The location and ground elevation of each stratigraphic site will be obtained from hand-held GPS location and elevation measurements taken in the field, which will be refined as needed by deriving the elevation for the latitude/longitude location of the site from lidar imagery (Washington Lidar Portal, 2024).

8.3 Containers, preservation methods, holding times

Table 11 presents containers, preservation techniques, and holding times for all laboratory geochemical analyses. The container sizes will provide enough sample so that it is possible to make at least five separate measurements of each parameter if needed.

Table 11. Sample containers, preservation, and holding times.

Parameter	Container	Sample Handling and Preservative	Holding Time
Alkalinity	250 mL high density polyethylene (HPDE) bottle	No headspace, store at 4C	3 days
Major Anion: Chloride, Fluoride, Sulfate, Nitrate, Phosphate	60 mL HDPE bottle	Filtered (0.45 micron), store at 4°C	28 days
Major Cation: Calcium, Magnesium, Potassium, Sodium, Ammonium	Acid-washed 60 mL HDPE bottle	Filtered (0.45 microns), store at 4°C, nitric acid to pH < 2	6 months
Stable Isotopes (O and H)	30 mL HDPE bottle sealed with tape	Tightly sealed to prevent evaporation	NA

8.4 Equipment decontamination

It is unlikely that any sample will contain high levels of contaminants or organic materials. In the event that one does, the following SOP will be used to decontaminate equipment: SOP EAP090, Decontamination of Sampling Equipment for Use in Collecting Toxic Chemical Samples (Washington Department of Ecology, 2021).

All non-dedicated, non-disposable field equipment coming into contact with sample water will be cleaned between uses at subsequent sampling locations to prevent cross-contamination of samples. Prior to collection of samples, a rinsing with deionized water followed by rinsing with sample water shall be considered sufficient. The e-tape used for water-level measurements will be sanitized with bleach overnight after sampling. Between well sampling measurements on a single day, the tip of the e-tape that comes into contact with the water will be sanitized with bleach prior to rinsing with deionized water and sample water.

8.5 Sample ID

Sample identification will be based on a format that includes the overall project and year, the site, the type of water, and a sample number. The format will be as follows: YRB24-AHT-type# (for Ahtanum site) and YRB24-MAN-type# (for Manastash site), where YRB24 is this project designation and year, MAN or AHT designates the project site, the type is either G (groundwater) or S (surface water), and the number (#) is the location ID, which will also be used in the EIM database. For each sampling location/date, the following information will be recorded in a field log:

- Sample number
- Sample location
- Well Tag ID
- Sampling date and time
- Sampler's name and names of other field personnel present
- Well purging information (flow rate, duration, total volume purged)
- Field parameter readings during purging
- Final (stabilized) field parameter readings
- Analytes sampled for and number of bottles collected for each analysis
- QA samples collected
- Any other relevant information (field conditions, details of how sample was collected).

Sample bottles will be labeled using self-adhesive labels, which will be completed in indelible ink and include:

- Sample identification number
- Analysis type (cation, anion, isotope)
- Whether acid preservative is added
- Whether field filtered
- Sample date and time

Following completion of each sampling trip, the principal investigator will review the field logs recorded by the samplers for completeness, accuracy, and clarity. The principal investigator will retain a copy of all documentation.

8.6 Chain of custody

Samples will remain within the custody of Carey Gazis and either Brook Bauer or Elif Myers at Central Washington University throughout the project. They will be stored on project-designated shelves in a refrigerator in the Stable Isotope Laboratory in the CWU Geological Sciences Department.

8.7 Field log requirements

Field data will be recorded by field personnel at the time of measurement, sampling or observations in a field notebook (log). Data to be entered into field notebooks includes:

- names of field personnel

- date and location at top of each page in field notebook
- site or data logger identification and description
- well tag ID
- environmental conditions
- sequence of events
- dates and times of measurement, sampling or other activity
- appropriate field measurement values and units of measure
- any observations or unusual circumstances that might affect interpretation of results. This should include observations of surface water use and hydrology (water in tributaries, irrigation on neighboring properties, etc.)
- GPS locations of any stratigraphic descriptions or other field observations
- locations and subjects of photographs
- detailed notes on any deviations from prescribed procedures
- recommended field log practices include:
    - Use bound, waterproof notebooks with pre-numbered pages.
    - Use pencil or permanent, waterproof ink for all entries.

8.8 Other activities

In addition to the standardized procedures described previously in Section 8, the following additional steps will be taken to ensure an adequate level of quality control during sampling:

- Field instruments will be calibrated and/or checked in accordance with the manufacturer's instructions on a daily basis at the beginning of each sampling day, and as needed during the day.
- All non-dedicated, non-disposable field equipment coming into contact with sample water will be cleaned between uses at subsequent sampling locations to prevent cross-contamination of samples. Prior to collection of samples, a rinsing with deionized water followed by rinsing with sample water shall be considered sufficient. The e-tape used for water-level measurements will be sanitized with bleach overnight after sampling. Between well sampling measurements, the tip of the e-tape that comes into contact with the water will be sanitized with bleach prior to rinsing with deionized water and sample water.
- Sources of extraneous contamination (generator fumes, gasoline, sunscreen, wearing of luminescent watches, etc.) will be minimized during sampling. Sampling personnel will employ a "clean hands/dirty hands" approach to sample collection.
- Equipment/filter field blanks will be collected during each sampling round to determine if sampling equipment or filters are introducing bias into the sampling results. Blanks will be used to determine whether the sample tubing, filters, sample containers, preservatives, or transport methods represent a source of bias. If bias is recognized in blank samples early in the project, additional steps will be taken to isolate the source of error, and field procedures or equipment will be modified to eliminate the problem.

Samples will be stored in a CWU refrigerator at 4 degrees C until analysis. Five milliliters of each sample will be archived in break-seal glass ampules.

9.0 Laboratory Procedures

9.1 Lab procedures table

The standard laboratory quality control procedures in place at CWU are adequate to estimate laboratory precision and accuracy, as described in Appendix B. Laboratory quality control samples will include blanks, duplicates, matrix spikes, and check standards (QC standards). Blanks, laboratory control standards, matrix spikes will be used to estimate overall bias due to the combination of the analytical procedure and matrix interferences. Duplicates, laboratory control standard duplicates, and matrix spike duplicates will be analyzed to quantify analytical precision. Check standards will be used to verify analytical precision, to test for instrument drift, and to provide an estimate of bias due to calibration. Laboratory method blanks will be used to ensure that there is no contamination in the laboratory procedures.

Table 13 presents a summary of the types and minimum frequency of field and laboratory quality control samples for this project. If QC results regularly fall outside of the acceptable limits defined in Table 7, the investigators will review the sampling and/or analytical methods to determine an appropriate course of action to obtain the desired data quality and rerun samples as needed. Any changes in procedure will be submitted for approval to Ecology. If these changes are significant, a QAPP addendum will be submitted.

Table 12. Measurement methods (laboratory).

Analyte	Sample Matrix	Samples (Number/ Arrival Date)	Expected Range of Results*	Detection Limit	Sample Prep Method	Analytical (Instrumental) Method**
Alkalinity	water	60/Dec 2020	30 - 500 mg/L	10 mg/L		titration
Chloride	water	60/Dec 2020	0 - 50 mg/L	0.1 mg/L	filtered	IC, EPA 300.1
Fluoride	water	60/Dec 2020	0 - 10 mg/L	0.1 mg/L	filtered	IC, EPA 300.1
Sulfate	water	60/Dec 2020	0 - 50 mg/L	0.5 mg/L	filtered	IC, EPA 300.1
Nitrate-N	water	60/Dec 2020	0 - 20 mg/L	0.1 mg/L	filtered	IC, EPA 300.1
Phosphate-P	water	60/Dec 2020	0 - 5 mg/L	0.05 mg/L	filtered	IC, EPA 300.1
Calcium	water	60/Dec 2020	0 - 100 mg/L	0.05 mg/L	filtered	IC, EPA 300.1
Magnesium	water	60/Dec 2020	0 - 50 mg/L	0.05 mg/L	filtered	IC, EPA 300.1
Potassium	water	60/Dec 2020	0 - 50 mg/L	0.05 mg/L	filtered	IC, EPA 300.1
Sodium	water	60/Dec 2020	0 - 100 mg/L	0.05 mg/L	filtered	IC, EPA 300.1

Analyte	**Sample Matrix**	**Samples (Number/ Arrival Date)**	**Expected Range of Results***	**Detection Limit**	**Sample Prep Method**	**Analytical (Instrumental) Method****
Oxygen-18	water	60/Dec 2020	–5 to –25‰	NA	filtered	CRS
Deuterium	water	60/Dec 2020	–30 to –170‰	NA	filtered	CRS

* Treatment of measurements below detection limits is discussed in section 14.2 (Treatment of Non-Detects)

The equipment and instrumentation that will be used in these analyses are:

- Ion chromatograph – Thermo Scientific Dionex ICS-5000+ IC
- Cavity ring down spectroscope – Picarro L2130-I Isotopic H2O Analyser

In most cases, there is alternative instrumentation to perform each type of analyses in cases where equipment or instrumentation are malfunctioning.

9.2 Sample preparation method(s)

For major ion analyses, two samples are collected, one for cations and one for anions. Both samples are filtered in the field using a clean 60-ml polypropylene syringe connected to a 0.45 micron polypropylene filter. The cation sample is placed in a 60 ml acid-washed high-density polyethylene (HDPE) bottle. Upon return to the laboratory, cation samples are acidified with 2% ultrapure nitric acid. The anion sample is placed in a clean 60 ml HDPE bottle that has not been acid washed.

For stable isotope analysis water sample is collected directly into a clean, dry 30 mL HDPE bottle, filling it almost to the top, and capping it tightly. The main objective is to protect the sample from evaporation and exchange with atmospheric water vapor. Samples need not be filtered unless they contain abundant particulate matter.

All samples are stored at in a refrigerator at 4 degrees C in the Stable Isotope Laboratory at CWU.

9.3 Special method requirements

Not applicable.

9.4 Laboratories accredited for methods

The Central Washington University Chemistry Department has been accredited for major ion analyses as part of a long term project studying precipitation chemistry on Mount Rainier. Dr. Gazis now oversees that project. Documentation for the laboratory certification methods is provided in Appendix B. As of January 24, 2024, the certification is on hold as we transfer the methods to a newer ion chromatograph in the Murdock Analytical Laboratory at CWU. We have initiated the recertification process and will provide the certificate to the Department of Ecology when it is complete. If the recertification is not completed by the time the samples for this project are collected, we will send the samples to AmTest Laboratories in Kirkland for analysis or an equivalent certified laboratory.

Stable isotope analyses is a specialized type of geochemical analysis that does not have EPA accreditation criteria. Dr. Gazis's laboratory in the Geological Sciences Department has been performing this type of analyses for over twenty years, including over 350 analyses for an Ecology-funded project in the Columbia Basin Groundwater Management Area (Vlassopoulos, 2009) and four previous YBIP projects funded by Ecology (Sleeper, 2020; Gazis, 2023; Gazis and Ely, 2023; Ely et al., 2024). We regularly (at least annually) calibrate our instruments and internal isotope standards using international reference materials. We also perform cross laboratory measurements of internal standards with other isotope laboratories periodically.

10.0 Quality Control Procedures

The quality control procedures for field and laboratory measurements are outlined above. Field notebooks and field data will be reviewed after each sampling trip. Laboratory results will be reviewed immediately to ensure that quality control standards are within accepted range and that there are no problems with the blanks, duplicates, or matrix spikes. One of the co-principal investigators, Carey Gazis or Lisa Ely, will meet weekly with the graduate student researchers to review quality control results and discuss any problems that have arisen and will accompany them regularly to the field sites.

Most stratigraphy will be determined from existing well logs. The quality control for this information will be to assess the detail provided in the well log; those with minimal detail will not be used. The stratigraphy from others will be compared among logs across a transect for reasonable correlations in elevations of major stratigraphic units as well as compared with published geologic maps. The quality control procedure for documenting the locations of near-surface stratigraphy measured in the field will be to compare the relative elevations and locations with landmarks and benchmarks from aerial photographs and satellite imagery.

10.1 Table of field and laboratory quality control

Table 13 shows a plan for frequency and types of quality control samples.

Table 13. Quality control samples, types, and frequency.

Parameter	Field Blanks	Field Duplicates	Laboratory Check Standards	Laboratory Method Blanks	Analytical Duplicates	Laboratory Matrix Spikes
pH	NA	1/10	NA	NA	1/6	NA
conductivity	NA	1/10	NA	NA	1/6	NA
DO	NA	1/10	NA	NA	1/6	NA
Alkalinity	NA	1/10	1/12	NA	1/6	NA

Parameter	Field Blanks	Field Duplicates	Laboratory Check Standards	Laboratory Method Blanks	Analytical Duplicates	Laboratory Matrix Spikes
Chloride	1/20	1/10	1/6	1/12	1/6	1/20
Fluoride	1/20	1/10	1/6	1/12	1/6	1/20
Sulfate	1/20	1/10	1/6	1/12	1/6	1/20
Nitrate-N	1/20	1/10	1/6	1/12	1/6	1/20
Phosphate-P	1/20	1/10	1/6	1/12	1/6	1/20
Calcium	1/20	1/10	1/6	1/12	1/6	1/20
Magnesium	1/20	1/10	1/6	1/12	1/6	1/20
Potassium	1/20	1/10	1/6	1/12	1/6	1/20
Sodium	1/20	1/10	1/6	1/12	1/6	1/20
Oxygen-18	NA	1/10	1/6	NA	1/6	NA
Deuterium	NA	1/10	1/6	NA	1/6	NA

Each type of QC sample listed has 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

If there is a problem with a single sample or a set of samples, a series of steps will be taken to correct any faulty data:

- A series of standards will be run through the instrument to ensure that it is accurate.
- If there is a problem with the instrument, the instrument technicians at CWU will help with any trouble-shooting to solve the problem.
- Once the instrument is running properly, the samples will be rerun and checked again for quality of analysis.
- If necessary, samples will be recollected in the method described in this QAPP.

For water depth measurements, the following corrective actions will be taken:

- Repeat manual measurement of depth-to-water.
- Repair or replace a faulty transducer as soon as possible if there is evidence of mid-deployment failures.
- Faulty transducers that cannot be repaired will be replaced if resources are available.

For field data collection with handheld GPS, the following steps will be taken to correct any faulty data:

- If there is a problem with the instrument or software, the instrument technicians at CWU will help with any trouble-shooting to solve the problem, which could include replacing the instrument.
- Once the instrument is running properly, the affected portion of the survey will be recalculated or resurveyed as appropriate using the method described in this QAPP.

11.0 Data Management Procedures

11.1 Data recording and reporting requirements

All field data will be recorded in a field notebook. Field notebooks will be checked for missing or improbable measurements before leaving each site. Field-generated sampling and survey data will be entered into Excel spreadsheets or other instrument-specific formats as soon as practical after returning from the field. Data entry will be checked by the field staff against the field notebook data for errors and omissions. Missing or unusual data will be brought to the attention of the project manager for consultation.

Raw pressure transducer data (pressures and temperatures) and corrected pressure transducer data (depth-to-water, groundwater elevation) will be archived for each sampling interval on the Department of Geological Sciences computers and server at Central Washington University. The raw and corrected pressure transducer data will be made available through a database management system on the CWU Geology server and will also be provided to the Department of Ecology through the EIM system under Study ID: CWUFAN-001.

Laboratory-generated data will be managed by the Laboratory Information Management Systems (LIMS) at CWU and backed up on the Geological Sciences Department's server. In addition to sample results, the laboratory data package will include all relevant calibration standards and QC results needed for data validation. Following evaluation of the analytical data against the project data quality objectives, the investigators will incorporate the results into a master Excel spreadsheet database. For each sample, the spreadsheet database will record station identification, coordinates, sampling date, and associated field and laboratory analytical data. The documentation for each sampling location will include the completed field notebook (log) entry, a copy of the analytical results, as well as analytical results for associated field and laboratory QC samples. Full documentation for all samples will be compiled and stored at the investigator's office at CWU. The geochemical data will also be entered into the Department of Ecology EIM system.

Results of quality control checks and calibrations will be recorded on electronic forms to allow for quality assurance review. Quality assurance records will be saved on CWU computers until Ecology's final approval of the project report so they may be accessed for post-project analysis and audits.

11.2 Laboratory data package requirements

The laboratory data will initially be transferred into an Excel workbook and sorted into the following worksheets:

1. Raw data
2. Results for calibration standards and calibrations
3. Results for QC standards with graph of results with time and comparison to quality control thresholds
4. Results of duplicates and any other QC samples and comparison with expected values
5. Results for unknown samples

11.3 Electronic transfer requirements

Data will be transferred to Ecology's EIM system using Study ID CWUFAN_001 according to the timeline approved for this project per online submittal guidelines. Only applicable project data, verified through the project QA process, will be uploaded into EIM.

11.4 Data upload procedures

Data will be transferred to Ecology's EIM system using Study ID CWUFAN_001 according to the timeline approved for this project per online submittal guidelines. Only applicable project data, verified through the project QA process, will be uploaded into EIM. The EIM data coordinator will be consulted if data submittal problems arise. The graduate student researchers will complete EIM training offered by Ecology and follow all existing Ecology business rules and the EIM User's Manual for loading, data quality checks, and editing.

11.5 Model information management

Not applicable.

12.0 Audits and Reports

12.1 Audits

Not applicable.

12.2 Responsible personnel

See Table 1 in Section 5.1.

12.3 Frequency and distribution of reports

The data collected under this project will be summarized in a formal peer-reviewed report that includes results, methods, and data quality assessment. This final report will be submitted in March 2026.

12.4 Responsibility for reports

Carey Gazis, Lisa Ely, Brook Bauer and Elif Myers will co-author the final report.

13.0 Data Verification

All data collected are subject to review by the principal investigator to determine if the data meet QAPP objectives. Decisions to reject or qualify data are made by the principle investigator in conjunction with the other investigators. Data may be rejected because of inadequate or deficient documentation or because the QC sample results fail to meet the MQOs identified in Section 4.

13.1 Field data verification, requirements, and responsibilities

Field personnel will review data recorded in field notebooks for correctness, clarity and completeness at the end of each sampling day. Field notebooks will be scanned, reviewed by the one of the principal investigators, and archived in the project database on the CWU Geological Sciences server.

13.2 Laboratory data verification

All laboratory data will undergo an initial quality assurance review by Brook Bauer or Elif Myers to verify that laboratory quality control samples met acceptance criteria as specified in the laboratory's standard operating procedure for that method. The co-principal investigator, Carey Gazis, will provide a follow-up quality assurance review. Appropriate qualifiers will be attached to results that do not meet requirements. An explanation for the data qualification will be attached with the data package.

13.3 Validation requirements, if necessary

Not applicable.

13.4 Model quality assessment

Not applicable.

13.4.1 Calibration and validation

Not applicable.

13.4.1.1 Precision

Not applicable.

13.4.1.2 Bias

Not applicable.

13.4.1.3 Representativeness

Not applicable.

13.4.1.4 Qualitative assessment

Not applicable.

13.4.2 Analysis of sensitivity and uncertainty

Not applicable.

14.0 Data Quality (Usability) Assessment

14.1 Process for determining project objectives were met

After all field data are verified, the field lead or project manager will thoroughly examine the data to determine if MQOs have been met. The project manager will examine the data 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. The project manager will decide how any qualified data will be used in the technical analysis.

Upon receipt of the verified laboratory data, the co-principal investigator, Carey Gazis, will determine if the results meet the MQOs for bias, precision, and accuracy for that sampling episode. These values provide an indication of the degree of random variability introduced by sampling and analytical procedures. Analytical bias is assumed to be within acceptable limits if laboratory quality control limits are met for quality control and check standards. Sampling bias will be checked by verifying that the correct sampling and handling procedures were used.

To ensure that we are on track to meet the project objectives (Section 4.2), the PIs and graduate students will meet weekly during the data collection phase to review the progress towards these objectives. All of the objectives can be measured with a number (e.g. number of samples collected) or the percentage completion can be estimated. For each objective, we will review the percent completion and discuss any challenges that have been encountered in the field or laboratory. This will include a discussion of the sample location choices and the usefulness of the data for answering the research questions. In this way, we will track our progress to ensure that the project objectives are met. It will also allow us to adjust our sample or data collection as needed.

14.2 Treatment of non-detects

When a major ion is not detected, it will be entered as “nd” on the data table. This value will be converted to half of the detection limit for purposes of graphing and statistical analyses when necessary.

14.3 Data analysis and presentation methods

Stratigraphic data will be correlated and plotted in geologic cross sections. Locations will be presented in tabular form, plotted on geologic cross sections, and mapped.

Groundwater elevations derived from pressure transducer data over the time period of the study will be graphically displayed along with manual depth-to-water measurements. Once these have been plotted, comparisons can be made between wells and nearby streams (Manastash and Ahtanum Creeks) to estimate how hydraulic pressure is transmitted through time and space.

Geochemical data will be analyzed by a variety of means. To obtain a first-order view of geochemical variations, major ion data will be plotted on Piper diagrams and Stiff plots; stable isotope data will be displayed on a plot of $\delta^{18}O$ versus δD. Multivariate analyses will be performed using SPSS software. Initially, a matrix scatter plot will be examined to find first order correlations between variables. Based on that result, simple x-y plots of data pairs will be examined to quantify correlations between variables and any clustering among samples. Next, two main multivariate analysis methods, hierarchical cluster analysis and principal component analysis, will be applied to the entire data set and subsets of the data in order to determine the defining characteristics of distinct groundwater chemistries at each study site. If necessary, this will be repeated with subsets of samples to determine the robustness of the results.

14.4 Sampling design evaluation

The sampling design is based on existing information, and the actual conditions at the site may be more complex than indicated. The spatial distribution of the sampling locations is partially pre-determined by the locations of the existing wells at the study sites. If we identify deficiencies in our sampling design, we will evaluate the potential consequences on the project. We may recommend additional work or activities to resolve such problems.

The geochemical sampling design targets 34 groundwater samples and 6 surface water samples. For multivariate methods such as principal component analysis, a greater number of samples is always preferable, especially if one intends to document multivariate normality in principal component analysis. However, this is not our intent. In our experience, 40 samples should be sufficient for exploratory purposes to determine end member and mixed groundwater chemistries. Even if the multivariate analysis proves to be difficult to interpret, it is likely that the combined graphical and statistical analyses of the geochemical data will provide important insight into the details of the hydrogeology.

14.5 Documentation of assessment

The project manager will include a section in the final technical report summarizing the findings of the data quality assessment.

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16.0 Appendices

Appendix A. Sampling Locations

Identified locations for groundwater and surface water samples in Ahtanum and Manastash alluvial fan study areas. Maps showing the study areas, transects of priority wells for stratigraphy and groundwater sampling, and surface-water sampling locations are in Figures 6 and 7 in the main text.

Table A-1. Ahtanum well locations for stratigraphy, groundwater sampling and surface water sampling. Priority locations for water sampling are also marked on Figure 6. Additional back-up well locations are included in this table in case the priority sites are not available.

STRAT	**COLUMNS**								
Intent No.	ID	Depth	Diameter	Static Water Level	Owner	Address	Tax Parcel	Drill Yr	Use
W357644	BIN409	540	6	315	Kurt L & Heidi Sutton	51 Sisotow Belle Ln	161213_21403	2015	Domestic
WE22443	BIF299	133	6	75	Catholic Bishop of Yakima Corp.	17740 Ahtanum Rd.	161213_14004	2015	Domestic
176939	AKJ715	413	6	312	Yakama Reservation	18171 Ahtanum Rd	NR	2005	Stockwater
W255649	APG343	465	6	145	Travis J & Kasey M Oneal	100 Carson Rd	171208_31003	2008	Domestic
W355692	BIN956	543	8	183	Bruce Ball	15210 Rutherford Rd, Yakima	181433_34413	2017	Irrigation
WE24633	BJB534	514	12	71	Russell Wilkenson	710 Lynch Lane, Union Gap	171218_24005	2016	Irrigation
WE32558	BLD302	283	6	145	Jerry Stover	3203 Marks Road	171210-23002	2018	Domestic
W170170	AGM765	221	6	109	Jason Adams	Lone Dove Lane, Yakima	171215_21408	2004	Domestic
W355946	BJA230	233	6	135	Daniel Trenkenshuh	Lone Dove Lane, Yakima	171215_23408	2017	Domestic
W26588	ABJ087	95	6	14	Jim Record	11501 Gilbert Road	171202-34014	1995	Domestic
W355691	BIN595	290	6	48	Tyson Paul	3509 S Wiley Road	171212_32403	2017	Domestic
W272641	AGM847	325	6	20	Impact Construction	3801 S Wiley Road.	171213_22005	2012	Domestic
WELLS:	**SAMPLING**								
Intent No.	**Well ID**	**Depth**	**Diameter**	**Static Water Level**	**Well Owner**	**Address**	**Tax Parcel**	**Drilling Date**	**Use**
WE24633	BJB534	514	12	71	Russell Wilkenson	710 Lynch Lane, Union Gap	171218_24005	2016	Irrigation
W355692	BIN956	543	8	183	Bruce Ball	15210 Rutherford Rd, Yakima	181433_34413	2017	Irrigation
WE17843	BHT985	357	8	208	Borton & Sons Inc	2309 Borton Rd	171203_22005	2014	Domestic
W255649	APG343	465	6	145	Travis J & Kasey M Oneal	100 Carson Rd	171208_31003	2008	Domestic
W161039	AGM847	153	6	46	Paula Wales	10740 S Ahtanum Rd, Yakima	NR	2003	Domestic
W26588	ABJ087	95	6	14	Jim Record	11501 Gilbert Road	171202-34014	1995	Domestic
WE49633	BLD597	665	6	422	Casey Thaxton	1211 Hubbard Rd	171205_14002	2022	Domestic
WE22443	BIF299	133	6	75	Catholic Bishop of Yakima Corp.	17740 Ahtanum Rd.	161213_14004	2015	Domestic
176939	AKJ715	413	6	312	Yakama Reservation	18171 Ahtanum Rd	NR	2005	Stockwater
W272641	BAF734	160	6	82	Jerry Reynolds	271 E Pine Hollow, Yakima	171218_21402	2010	Domestic
WE32558	BLD302	283	6	145	Jerry Stover	3203 Marks Road	171210-23002	2018	Domestic
W267309	BAF898	285	6	106	Gary Mcinnis	3408 Marks Rd, Yakima	171209_41405	2009	Domestic
W355691	BIN595	290	6	48	Tyson Paul	3509 S Wiley Road	171212_32403	2017	Domestic
W272641	AGM847	325	6	20	Impact Construction	3801 S Wiley Road.	171213_22005	2012	Domestic
W357644	BIN409	540	6	315	Kurt L & Heidi Sutton	51 Sisotow Belle Ln	161213_21403	2015	Domestic
W318200	BLD243	427	6	310	John & Nancy Lippolis	51 W Ponderosa Dr	161212_34403	2019	Domestic
W003903	ABJ039	108	6	35	Stan Childers	52nd Ave & Ahtanum	NR	1993	Domestic
W047459	ACT745	225	6	80	Rob & Carolyn Dresker	80 American Fruit Rd.	171215_21404	1998	Domestic
DE01905	BIN560	287	6	125	Rick Wagner	9408 Occidental Road	W355653	2015	Domestic
W170170	AGM765	221	6	109	Jason Adams	Lone Dove Lane Yakima	171215_21408	2004	Domestic
W355946	BJA230	233	6	135	Daniel Trenkenshuh	Lone Dove Lane, Yakima	171215_23408	2017	Domestic
WELLS:	**TRANSDUCERS**								
Intent No.	**Well ID**	**Depth**	**Diameter**	**Static Water Level**	**Well Owner**	**Address**	**Tax Parcel**	**Drilling Date**	**Use**
AE23694	BHK729	20	2	NR	PCF Acquisitions Co LLC	207 Ahtanum Rd, Yakima 98903	181201_13020	2012	Monitoring
AE23694	ACG206	15	2	NR	PCF Acquisitions Co LLC	207 Ahtanum Rd, Yakima 98903	181201_13020	2013	Monitoring
AE34211	BHW550	25	2	16	Tiger Oil Site	1614 E Nob Hill Blvd, Yakima	NR	2015	Monitoring
8147	ABR063	230	8	10	West Valley School	3006 S WILEY RD 150W & 380S NE SEC COR	NR	1966	Domestic
PWS04410502	AFL770	365	8	145	Borton & Sons Inc	2550 Borton Rd., Yakima, 98903	NR	1973	Domestic

Table A-2. Manastash priority well locations for stratigraphy and groundwater sampling. Priority locations for surface and groundwater sampling are also marked on Figure 7.

Transect ID	#	Well Tag ID	Depth (ft)	Diameter (in)	Static Water Level (ft)	Proposed Use	Date	Well Location	Tax Parcel	Well Owner	Address
PNO1	1	ACE959	201	6	116	Domestic	6/10/1996	W 1/4 SW 1/4 Sec 12 T 17 N R 17 WM	N/A	Dean Allen	N/A
PAC2	2	AGL510	240	6	20	Domestic	8/28/2001	SW 1/4 SE 1/4 Sec 12 T 17 N.R 17 WM	N/A	Steve Herman	N/A
PSO3	3	APG972	185	6	130	Not labeled	4/10/2008	NW 1/4-1/4 NW Sec 18 T 17 R 18	1.71818E+12	R.J. Hayes Construction	Orion Rd. Ellensburg, Kittitas
MFNO4	4	AEQ979	280	6	75	Domestic	4/30/2000	SE 1/4 SE Sec 1 T 17 N.R. 17	N/A	Marasha Parks	620 West Columbia St
MFAC5	5	BJB081	220	8	105	Domestic	9/21/2018	SE1/4 - 1/4 NW Sec 7 Twn 17N R 18E EWM	14214	Cole Satterlund	N/A
MFAC5	6	BJA293	200	6	110	Domestic	1/21/2019	NW 1/4-1/4 SE 1/4 Sec 7 Twn 17 R 18 EWM	14213	Steve Hansen	Sawbuck Lane
MFSO6	7	APG119	420	6	280	Domestic	9/23/2013	NE 1/4-1/4 NE 1/4 Sec 18 Twn 17 R 18	12579-171818010-0015	Mike Stougard	Blazing Sky Lane
DNO7	8	APT555	420	6	90	Domestic	5/7/07	SW 1/4-1/4 NE 1/4 Sec 31 Twn 18 R 18	18-18-31000-0015	Steve Lathrop	1572 Robinson Cnayon Rd
DNO7	9	BAN942	404	6	64	Domestic	4/28/2008	NW 1/4-1/4 SW 1/4 Sec 32 Twn 18 R 18	181832055-0004	Ben Faubion	Weaver Road
DAC8	10	AKW573	110	6	11.5	Domestic	5/25/2003	SW 1/4 1/4 SW Sec 4 Twn 17 R 18 EWM	17-18-04030-0034	Bob Tuck	Barnes Rd
DAC8	11	BBJ475	240	6	35	Domestic	10/28/2010	NW 1/4-1/4 NW 1/4 Sec 9 Twn 17 R 18 EWM	17-18-0905-00004	Loman Blankenship	751 Strande Road
DSO9	12	BLG423	100	8	15	Domestic	10/30/19	NW 1/4 -1/4 , NE 1/4, sec, 16 T 17N R 18E	388833	Bart Bland	1160 Manastash Rd

Table A-3. Manastash additional well locations for stratigraphic descriptions. These wells will also be used for water sampling if the priority wells in Table A-2 are not available.

Well Tag ID	Depth	Diameter	Static Water Level (ft) below top of well	Land Surface Elevation (ft)	Proposed Use	Date	Well Location	Tax Parcel	Lat/Long	Well Owner	Address
NO ID 1	100ft	6in	60ft	N/A	Domestic	7/30/1990	SE 1/4 SE 1/4 Section 11 Township 17 Range 17	N/A	N/A	Mitch Williams	Richards Rd (no number)
NO ID 2	120ft	6in	40ft	N/A	Domestic	4/29/91	SW 1/4 SE 1/4 Section 11 Township 17 Range 17	N/A	N/A	WM Allen	Richards Rd (no number)
BJB178	279ft	6in	94.5ft	1,889ft	Domestic	2/11/2020	NW 1/4-1/4 of the SW 1/4 Sec 12 T 17 R 17	17-17-12058-0004	46.98072, -120.06536	Daniel G. and Teressa A. Freighner	381 Allegro Way
AEG485	162ft	6in	30ft	N/A	Domestic	5/4/2020	SW 1/4 SW 1/4 Section 12 Township 17 Range 17	N/A	N/A	Alex Drake Williams	5750 Cove Rd
BJB180	232ft	6in	26ft	1,968ft	Domestic	2/17/2020	SW 1/4-1/4 Section 12 Township 17 Range 17	17-17-12030-0008	46.47120, -120.66342	William and Courtney Allenbaugh	7041 Manastash Rd
BIW690	163ft	6in	80ft	N/A	Domestic	2/14/2020	SE 1/4-1/4 of the SW 1/4 Section 12 Township 17 Range 17	955760	N/A	Dominic Dannian	Cove Rd
ABW887	280ft	6in	N/A	N/A	Domestic	10/17/1995	SE-SW 1/4 Section 12 Township 17 Range 17	N/A	N/A	Roberta Clarkson	610 Quail Run Lane
BIW689	203ft	6in	95ft	1,950ft	Domestic	2/10/2020	SE 1/4 of the SE 1/4 Section 12 Township 17 Range 17	955761	N/A	Karrie and Micheal Higgins	Cove Road (no address number)
AGB220	310ft	6in	102ft	1,950ft	Domestic	6/12/2001	S 1/4 SE 1/4 Section 12 Township 17 Range 17	17-17-12040-00012	N/A	Bruce Wilson	6111 Manastash Road
NO ID 3	160ft	6in	35ft	1,950ft	Domestic	11/10/1997	NW 1/4 SE Section 12 Township 17 Range 17	N/A	N/A	Douglas Streccker	1010 Serentiy Lane
AFH683	200ft	6in	40ft	N/A	Domestic	10/26/01	NW 1/4 NW Section 13 Township 17 Range 17	N/A	N/A	Brent Renfrow	7500 Manastash Roaad
ALC953	143ft	6in	3ft	N/A	Domestic	6/10/2005	NE 1/4 NE 1/4 Section 13 Township 17 Range 17	171713010-0007	N/A	Larry Whitlitch	6370 Manastash Road
BIN865	143ft	6in	32ft	N/A	Domestic	9/16/15	NE 1/4-1/4 NE 1/4 Section 12 Township 17 Range 17	171713056-0002	N/A	Joe Lombardi	6732 Manastash Road
W256006	133ft	6in	18ft	N/A	Domestic	3/23/2007	NE 1/4-1/4 NW 1/4 Section 12 Township 17 Range 17	171712020-0001	N/A	Bill Rowley	Hansen Road (No address number)
AWK756	200ft	6in	89ft	N/A	Domestic	6/23/2003	NE 1/4-1/4 NW Section 12 Township 17 Range 17	1717120200023	N/A	Mike and Linda Baker	Hansen Road (No address number)
BKB388	227ft	6in	102ft	1,885ft	Domestic	3/13/18	SW 1/4-1/4 NE 1/4 Section 12 Township 17 Range 17	1717120580010	N 46 58'49.54 W 120 39'20.72	Marcello Martinez	Next to 530 Allegro Way
BIN863	200ft	6in	121ft	N/A	Domestic	9/7/15	NW 1/4 SW 1/4 Section 07 Twonship 17 Range 18	171807057-0002	N/A	Padi Pierce	Manastash Road, No address number
BJA293	223ft	6in	110ft	1,800ft	Domestic	1/21/19	NW 1/4 1/4 SE Section 7 Township 17 Range 18	14213	N/A	Steve Hansen	Sawbuck Lane (no address number)
ALF414	220ft	6in	98ft	1,800ft	Domestic	3/11/05	SE 1/4-1/4 NW 1/4 Section 7 Township 17 Range 18	17-18-07040-0018	N/A	Steve and Mandi Laurent	1461 Susan Road
W361160	230ft	6in	111ft	1,800ft	Domestic	5/9/13	NW 1/4-1/4 NW 1/4 Section 7 Township 17 Range 18	955748/17-18-070580001	N/A	Randy Willett	Cover Road (no address number)
APG119	420ft	6in	280 ft	N/A	Domestic	9/14/2013	NE 1/4 NE Section 18 Township 17 Range 18	12579-171717010-0015	N/A	Mike Stougard	Blazing Sky Lane (No number address)
NO ID 4	200ft	6in	35ft	N/A	Domestic	11/28/97	NE 1/4 SW 1/4 SEction 6 Township 17 Range 18	N/A	N/A	Jim Andrews	1107 Arnold Dr.
ABW780	102ft	6in	30ft	N/A	Domestic	6/21/95	SW 1/4 SW 1/4 Section 05 Township 17 Range 18	N/A	N/A	David Wright	921 Hanson Rd
W351746	133ft	6in	34ft	1,700ft	Domestic	5/20/14	SW 1/4 SW 1/4 Section 08 Township 17 Range 18	17180800-0022	N/A	Kevin Hansen	Susan Road (no street address)
BIN193	265ft	6in	72ft	1,700ft	Domestic	6/3/15	SE 1/4-1/4 NW Section 8 Township 17 Range 17				
ALC801	132ft	6in	55ft	1,700ft	Domestic	6/20/05	NW 1/4-1/4NW Section 8 Twonship 17 Range 18	17-18-08000-0005	N/A	Steve Linse	2990 Hansen Road
ACL947	162ft	6in	53ft	N/A	Domestic	12/21/1998	SW 1/4 SE 1/4 Section 08 Township 17 Range 18	N/A	N/A	Jason Smith	409 W 12th St

Appendix B. Laboratory Quality Assurance/Control Manual

The following pages contain the relevant parts of the Quality Assurance/Quality Control Manual for the Environmental Testing Laboratory in the Chemistry Department at Central Washington University. The Geological Sciences and Chemistry Departments share instruments and QA/QC methods.

QUALITY ASSURANCE/QUALITY CONTROL MANUAL

CENTRAL WASHINGTON UNIVERSITY

CHEMISTRY DEPARTMENT ENVIRONMENTAL TESTING

Topics Covered in Quality Assurance/Quality Control Manual

Organization / QA Policy
CWU Environmental Laboratory Standard Operation Procedures
  Mt. Rainier Sample Processing S.O.P.
  pH Measurement S.O.P.
  Conductivity Measurement S.O.P.
  Ion Chromatograph Anion S.O.P.
  Ion Chriomatograph Cation S.O.P.
Quality Control Procedures
References

Organization / QA Policy

Laboratory Purpose:

The laboratory is a teaching and service laboratory which accepts samples from local, federal, and state agencies for analysis. We are concerned with environmental monitoring and the implications of the laboratory findings.

Laboratory Organization:

The laboratory is housed in the chemistry department at Central Washington University, and it is managed by Anne Johansen. The manager is responsible for the Quality Assurance and Quality Control.

Sample receiving, storage, and analytical work is performed by the manager as well as staff. The manager and staff may participate in QC work and data logging. The manager reviews all data and reports before release.

Staff:

The laboratory staff primarily consists of CWU students. Students who perform analytical work are required to meet a minimum course work qualification of junior status with one year general chemistry, one quarter quantitative analysis, and one quarter instrumental analysis. Students involved in analyses have been given training on analytical QA/QC as part of their analytical chemistry curriculum and qualified students are then trained to accomplish the particular analyses assigned to them. Students will be required to satisfactorily analyze check standards before they are given the responsibility of working on environmental samples. This manual serves as a procedure manual.

QA/QC Policy Statement:

It is our goal that the analytical results from this laboratory will be reported with defined accuracy limits and with stated estimates of uncertainty and minimum detection limits. Sample handling, sample analysis, data manipulation, and data storage procedures are documented in this QA/QC manual.

The actual laboratory work is documented in laboratory notebooks. The analytical results of precipitation chemistry studies are archived in the computer file S:\Chemistry Research\Johansen Research\Mt Rainier.

Sample Management:

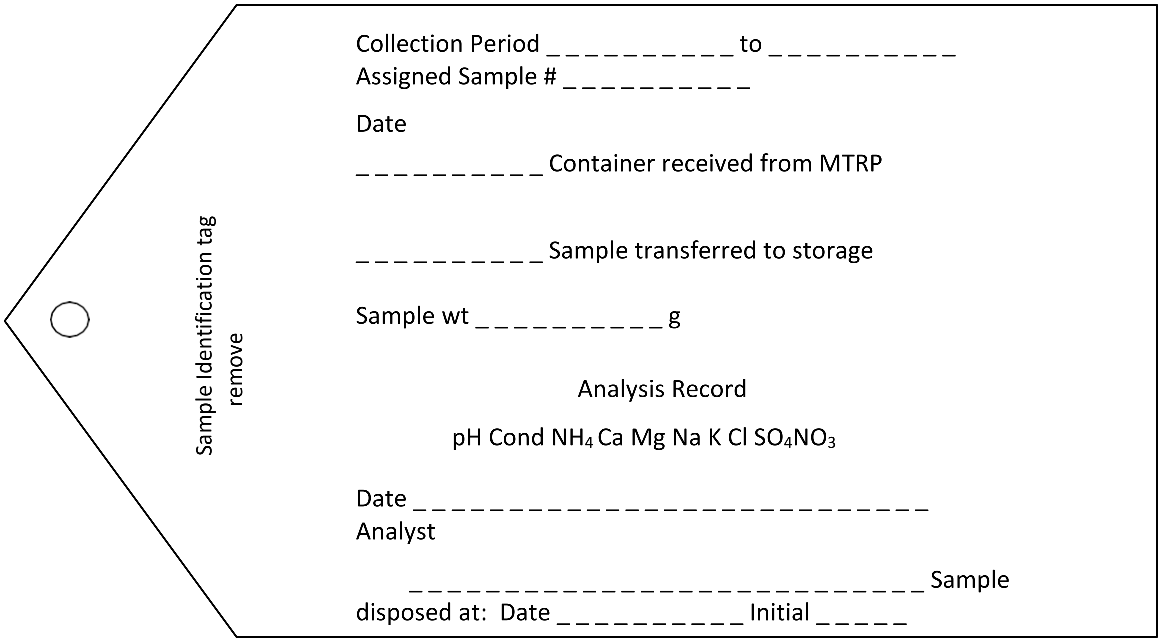
Procedures for requesting analysis: Samples are usually accepted as part of a defined study. For instance: Weekly bulk precipitation samples which have been collected at Mt. Rainier Paradise Station as a result of a working agreement with the National Park Service are analyzed for pH, conductivity, and major cations and anions. Filtered lake water samples which have been collected at lakes around Mt. Rainier and North Cascade National Park are also sent in to our lab annually for cation and anion analyses.

Procedure for receipt: Individual staff is assigned responsibility for receipt of samples for particular studies. On receipt, samples are to be inspected for container breakage, container integrity, and sample condition. The sample log sheet should be marked to show the observation of each parameter. If sample integrity has been compromised the sample will be rejected or a notation will be attached to the reported results for that sample.

Procedure for logging: The samples are logged in a notebook or binder dedicated to the particular study. Sample identity, size, condition, and processing date are logged. Sample containers are labeled with a sequential number to assure identification of those samples during all steps in the analysis. The identification number is also to be recorded on the sample log sheet.

Procedure for storage: If it is necessary to transfer samples from shipping containers to storage containers, the final containers and transfer equipment should be treated to avoid introduction of outside contaminants. The treatment procedure is described in the section of this manual titled: “Requirements: A; Container Requirements”. Samples should be well mixed before transfer.

Aliquots for analysis are poured from the sample storage containers. Containers are then returned to the storage site.



Sample Identification tag
remove

Collection Period _ _ _ _ _ _ _ _ _ _ _ to _ _ _ _ _ _ _ _ _ _ _
Assigned Sample # _ _ _ _ _ _ _ _ _ _ _

Date

_ _ _ _ _ _ _ _ _ _ _ Container received from MTRP

_ _ _ _ _ _ _ _ _ _ _ Sample transferred to storage

Sample wt _ _ _ _ _ _ _ _ _ _ _ g

Analysis Record

pH Cond NH_4 Ca Mg Na K Cl SO_4NO_3

Date _
Analyst

_ Sample
disposed at: Date _ _ _ _ _ _ _ _ _ _ _ Initial _ _ _ _ _

Figure 8 Sample ID Tag

Procedure for chain-of custody: Procedures should be practiced to ensure that samples are traceable from time of collection through data collection to sample disposal. A designated person is responsible for receiving and logging-in all samples. In addition to assigning a sample number and recording the data concerning each sample into a logbook, the receiving person will affix a sample identification tag to each sample container. The tag will serve as chain of custody record. See the sample tag for the Mt. Rainier Precipitation Study. Figure 1.

Criteria for sample acceptance/rejection: Sample is not accepted for analysis if: (in all cases tag the samples and notify the lab manager)

a) Field log sheets indicate vandalism or accidental contamination.
b) Samples have been retained beyond "maximum holding times for parameters of interest" (see section on holding times).
c) Samples have not been cooled as prescribed.
d) Samples have not been preserved as prescribed*.

* Precipitation samples may be handled differently. Changes will be defined with the user.

Requirements:

A. Container requirements: Plastic collection buckets are scrubbed and rinsed with deionized water until the conductivity of the rinse is less than 1μS/cm. The conductivity of the collection buckets are logged before they are sent back to the collection site.

TraceClean™ High-density polyethylene bottles are used for sample storage container to ensure to meet U.S. EPA Specifications and Guideline for Contamination-Free Sample Container.

B. Holding times: Samples are held in a refrigerator at approximately 4°C until analysis to retard biological activity which might change analyte concentrations. Unless otherwise noted, the maximum holding times are:

Parameter	**Maximum Holding Time**
pH*	Analyze immediately
Nitrate + Nitrite**	28 days
Conductivity	28 days
Ammonia	28 days
Sulfate	28 days
Chloride	28 days
Calcium	6 months
Magnesium	6 months
Sodium	6 months
Potassium	6 months

*In the case of precipitated sample that have been collected over extended period, the holding time for the pH sample is irrelevant and pH is usually measured alongside with conductivity.

**If Nitrite is present in samples, it is assumed to be oxidized to Nitrate within the holding time.

C. Preservation requirements: Unless otherwise noted, metal samples (Ca, Mg, Na, K) should be preserved to pH < 2 with nitric acid, and ammonia samples should be preserved to pH < 2 with sulfuric acid.

Analytical Methods:

Analytical methods used are listed below:

Analyte	**Technique**	**Method #**
pH	Electrochemical	EPA 150.1
Conductivity	Electrochemical	EPA 120.1
Cation (Na, NH_4, K, Mg, Ca)	Ion Chromatography with Electrochemical Detector	EPA 300.7
Anion (Cl, NO_3, SO_4)	Ion Chromatography with Electrochemical Detector	EPA 300.1

Mt. Rainier Bucket Processing S.O. Ps

Sample Receiving Procedure

A bucket should be arriving at the Chemistry main office at approximately the same time of day on the same day of the week each week (usually every Thursday by noon). When the bucket arrives, the sample water either needs to be transferred to storage containers or the whole bucket needs to be placed in the lab refrigerator at below 4 °C immediately.

Failure to do so may cause unwanted evaporation and/or change the chemical content of the sample, i.e. biological, thermal decomposition, and to minimize evaporation.

Check the log sheet to make sure name on the bucket matches with the "Bucket ID" on the log sheet. Fill out the "Bucket Record Sheet", which is in the front of Mt. Rainier three-ring binder, with the date of bucket arrival to the Chemistry main office, and date of the water sample transfer to the storage bottles.

Sample Transferring Procedure

1. Wear plastic gloves to handle a bucket. Open the box and take the bucket out. Set the box aside until the next batch of buckets are shipped out. Reuse the plastic bag for as long as possible. If the plastic bag is torn, full of debris, or is wet, throw it away, and get new one from a waste can in the lab.
2. Use the aluminum bucket opener to get the lid off of the bucket. Take extra caution not to spill the contents, because the lid might be difficult to open.
3. If the bucket is empty, skip to the **Bucket Cleaning Procedure**. If there is water in the bucket, proceed to the Step 4.
4. Using the large Mettler balance, weigh the bucket and its contents. Write it down on the log sheet (See **Log Sheet**).
5. Get three unused 120 mL "Pre-Clean" HDPE bottles. Using a permanent marker, label each bottle with the sample name (See **Sample Name**) with analyses methods (one for "pH, Conductivity, and Anions", one for "Cations", and one for "Ammonia"). Rinse bottles with small amount of sample water from the bucket. It is ideal to rinse each bottle three times in this manner. If there is not enough sample to spare, they can be rinsed less than three times (or no rinsing); on the log sheet, make sure to note the reason for not rinsing three times.
6. Fill bottles with the sample water. If the water sample is large enough that you can let some of the water go down the drain, make an effort to dump out any debris in the water sample. At least 15-20 mL sample water must be present to be considered a useful amount for "pH, Conductivity, and Anions" analyses, and at least 2-3 mL sample water is needed for "Cations" and "Ammonia" analyses.
7. Once all three bottles are filled, the rest of water sample in the bucket can go down in the drain. Drain as much water as possible, and then place the empty bucket on the Mettler balance. Record it on the log sheet.

8. Subtract the mass of the empty bucket from the mass of the full bucket with rain water to get the sample weight and record this on the log sheet. Initial the log sheet, write down any comments that you may have. (When in doubt, write it down.) Also be sure to write down the sample's identification name/number on the log sheet.
9. Now, "Cations" and "Ammonia" samples need to be treated with acid for preservation. Concentrated nitric acid and sulfuric acid dropper bottles are stored in the cabinet under the fume hood. Add the concentrated nitric acid drop by drop to the "Cation" sample until pH < 2. Check the pH with pH papers. Repeat this procedure for the "Ammonia" sample with the concentrated sulfuric acid.
10. Before these bottles are stored in the refrigerator, a sample tag is filled out and attached to one of the bottles. Blank tags are stored in the drawer by the Mettler balance along with the Mt. Rainier Sample stamp and an ink pad. Make a tag, and transfer information of first half of the tag (Collection Period to Sample wt; highlighted with grey) from the bucket log sheet (Figure 1).

Bucket Cleaning Procedure

1. Turn on the deionized water faucet 5 to 10 minutes (if the deionized water has not been used for a while, wait a little bit longer) before starting the cleaning procedure. Take out the cleaning brush from the drawer (right side of the sink) and rinse it well with deionized water.
2. Rinse the lid of the bucket with deionized water for at least 2 minutes. Try to hold the lid by the edge or on the outside of the lid. Shake it well and set aside.
3. Rinse the inside and outside of the bucket with deionized water 3 times to remove any debris and dirt. Next using the cleaning brush, scrub the inside bottom of the bucket and rinse. Repeat this procedure 3 times. Then scrub the inner bucket wall and rinse 3 times. Finally rinse the bucket for 3 times. Each rinsing is carried out with about 1 to 1.5 L. Always hold outside of bucket while cleaning, and try not to touch inside of the bucket as much as possible.
4. The bucket has to be clean until the **conductivity** of the rinse water is below 1µs/cm. The Solomat MPM 1000 conductivity meter (usually kept by the sink) is used to measure the rinse conductivity, and the setting for our measurement is 0.1Cell, 160µS. The probe is kept in the test tube with deionized water. A plastic cup, such as a nalgene bottle with the top cut off, is used for sample container. Do not use the sample container for anything else. The hole on the probe must be submerged completely in the water, and to remove any air trapped within the hole swish the probe in the water. The probe should not touch the bottom or the wall of the container to obtain accurate measurements.
5. To measure the rinse water conductivity, first measure conductivity of deionized water. The reading should be below 0.5µS. Then place the bucket on the edge of the sink and use the hose coming from the deionized water faucet to rinse all surfaces of the inside of the bucket. Rotate the bucket to make sure all surfaces

are equally rinsed. Rinse the plastic cup, described in Step 4, with the bucket rinse water three times, then, fill the cup with the rinse water. Take a conductivity measurement. The reading should be less than 1 µS (more like 0.5 to 0.8 µS). If the reading is higher, rinse the bucket with deionized water until the reading is in the acceptable range. Record the conductivity reading on the new log sheet and the bucket record sheet.

6. Empty the bucket and dry outside of bucket with paper towel. Place the lid on the bucket, but DO NOT SEAL.

Bucket Shipping Procedure

Put the clean bucket and lid in the clean plastic bag. Fill out the "DEPARTURE" section of a new log sheet, and put it in an envelope. Place the bucket and envelope in the box and tape the box. If a new box is used, make sure the address label with budget number (the current address label is *S:\Chemistry Research\Johansen Research\Mt Rainier\Mt. Rainier SOP's\Mt Rainier Address Label*) is pasted on the box, and "This way is up" sign is drawn on each side of the box. Take the box to the Facility Management building (across from the science building) for shipment.

Sample Names

A sample name for Mt. Rainier precipitation water has been **M-Last two digits of year-Sample number for the year**. M stands for Mt. Rainier. For example, the 22nd sample collected in the year 2007 is named **M-07-22**.

Log Sheet

Log sheets are used to exchange valuable information between the lab personnel and the person in charge of collecting buckets at Mt. Rainier. This information is useful for annual reports, so it is very important to fill them out correctly. The log sheet should be stored in the designated three-ring binder.

Before a bucket is processed, review the log sheet carefully. Make sure that the name of the bucket and the name on the log sheet matches, and the person who collected the bucket filled out all the necessary information. If some information is missing and/or it is not making sense, contact the responsible Mt. Rainier sample collector immediately (currently Rebecca Lofgren is in charge of collecting buckets. Her contact information can be found in *S:\Chemistry Research\Johansen Research\Mt Rainier\Mt. Rainier SOP's\Mt Rainier Contact Information*).

If there was no sample, check the box on the log sheet for "No Sample" and put it in the binder. If there was water in the bucket, fill out the Sample ID and DATA section of the log sheet. Write down any comments on the log sheet if unusual conditions are noted, i.e. some water leaked in the plastic bags, the bucket sat at room temperature overnight.

Ship the bucket with new log sheet with DEPARTURE section filled out.

Blank log sheets can be printed out from *S:\Chemistry Research\Johansen Research\Mt Rainier\Mt. Rainier SOP's\bucketlog*.

pH S.O.Ps

Instrument

Instrument:

pH Meter: Orion Model 420A

Electrode: Ross Electrode Model 81-02, combination pH Electrode
Storage Solution: 1.0g KCl/200mL pH7.00 buffer solution

Analytical Procedure

Calibration:

1. Pour approximately 12mL of pH 4.00 buffer solution and pH 7.00* buffer solution to clean and labeled plastic containers.
2. Turn on the instrument main switch. Remove the electrode from the storage solution, and rinse it with Milli-Q water and gently tap with paper towel (do not over dry). Remove the filling hole cover during measurement to ensure uniform flow of filling solution.
3. Insert the probe into pH 4.00 buffer solution. Swirl the solution gently and wait until the reading stabilizes. Adjust the meter to read pH 4.00. Rinse and wipe the electrode. Insert the probe into pH 7.00 buffer solution. Adjust the meter to read pH 7.00.

Instrument Check:

1. Turn on the instrument's main power switch.
2. Rinse a small sample container twice with pH 5.00** buffer check standard (CS) solution and pour CS solution to the container.
3. Rinse the pH probe with Milli-Q water and gently remove water with Chem wipe (avoid rubbing or wiping electrode bulb, to reduce chance of error due to polarization) before placing it into the solution. Insert the electrode to the pH 5.00 CS solution and stir. The ceramic reference junction of the electrode must be submerged. Wait until the display is stable (a beep should go off). The pH reading should stabilize within few minutes to 5.00

   ± 0.1.

* If the pH of sample(s) is (are) known to be larger than pH 7.00, use pH 4.00 and pH 10.00 buffer solution to calibrate the electrode.

** The pH 7.00 buffer solution or other known pH solutions could be used as the CS when pH 10.00 buffer was used for calibration.

Sample Analysis:

1. Allow samples to come to room temperature. Rinse the electrode with Milli-Q water between data collection of samples. If the same sample container is used for all measurements or containers are not dry, rinse the sample container twice with sample before filling again for analysis.
2. Place the electrode into the sample and observe pH.
3. Run CS solution, blank, and samples in the following order. After every 6th sample measure conductivity of the CS solution and a duplicate of the sample.
    1. CS 1
    2. Blank
    3. Sample 1
    4. Sample 2
    5. Sample 3
    6. Sample 4
    7. CS 2
    8. Duplicate of Sample 4
    9. Sample 5

Data Recording:

All pH data should be recorded in the designated notebook in the following form: Date of Measurement: Initial or name of personal: ______________________

pH of Buffer used for the calibration: ______________________

pH of Buffer used for the Check Standard: ______________________

Samples:

Run #	Sample ID	pH	Temperature (Cº)
1	CS1		
2	Blank		
3	Sample 1		
4	Sample 2		
5	Sample 3		
6	Sample 4		
7	CS2		
8	Sample 4-2		
9	Sample 5		
…	…		

Conductivity S.O.Ps

Instrument

YSI 3200 with a model 3252 conductivity cell constant (K): 0.964

Temperature correction: 2.00%/°C (Converted to 25°C)

Analytical Procedure

Check Standard Solution:

1. Dry ~2g of potassium chloride at 105°C for 2 hours, and cool it in a desiccator to room temperature (at least 20 min).
2. The 0.01000M KCl stock solution is prepared by placing 0.7456g of KCl in a 1.000L volumetric flask and diluting to the mark with Milli-Q water.
3. To prepare the $1.000X10^{-4}$M KCl working check standard solution, dilute 10.00mL of the KCl stock solution in a 1.000L volumetric flask.

Instrument Check:

1. Turn on the instrument's main power switch and make sure temperature compensation is on.
2. Rinse a small sample container twice with $1.000X10^{-4}$M KCl working check standard (CS) solution and pour CS solution to the container.
3. Rinse the conductivity cell with Milli-Q water and gently remove water with Kimwipes™ before placing it into the solution. Insert the cell to the CS solution and gently tap it to remove any air bubbles. The cell electrode must be submerged completely (the solution line must be above the holes). Wait until the temperature stabilizes. Gently move the cell side to side or up and down in the solution. Be careful that the cell does not touch the bottom or side of the solution container. The conductivity reading should stabilize within few minutes to 14.90µS/cm ±10%.

Sample Analysis:

1. Allow samples to equilibrate to room temperature. It is advisable to perform pH and Conductivity analysis on the same day to prevent samples from going through the temperature change twice. Rinse the conductivity cell with Milli-Q water between data collection of samples. If one sample container is used for all measurements or containers are not dry, rinse the sample container twice with analyte before filling again for analysis.
2. Place the conductivity cell into the analyte and observe the conductivity. Record temperature of the analyte after reading has stabilized. The conductivity reading should stabilize to < 0.2 µS/cm change over 1 minute.
3. Run CS solution, blank, and samples in the following order. After every 6th sample measure conductivity of the CS solution and a duplicate of the sample.
    1. CS 1
    2. Blank
    3. Sample 1
    4. Sample 2
    5. Sample 3
    6. Sample 4
    7. Sample 5
    8. CS 2
    9. Duplicate of Sample 5
    10. Sample 6
    11. Sample 7
    12. Sample 8
    13. Sample 9
    14. Sample 10
    15. CS 3

Data Recording:

All conductivity data should be recorded in the designated notebook in the following form:

Date of Measurement: ______________________

Initial or name of personal: ______________________

Cell Constant (K): ______________________

Temperature Correction: ______________________

Samples:

Run #	Sample ID	Conductivity (µS/cm)	Temperature (Cº)
1	CS1		
2	Blank		
3	Sample 1		
4	Sample 2		
5	Sample 3		

Ion Chromatograph Anions S.O.P’s

SO_4^{2-}, NO_3^-, Cl^-

Instrument

Instrument and Parts:

Chromatography System:	DX500 Electrochemical Detector ED40 Gradient Pump GP50 Automated Sampler AS40
Column:	Ion Pac AS14 4mm Analytical Column with AG14 4mm Guard Column
Suppressor:	ASRS-ULTRA 4mm, run in Auto-suppression Mode
Injection Loop:	50µL
Program Software:	Chromeleon® Version 6.80

Operation Procedure:

1. Check the reservoir for the sodium carbonate-sodium bicarbonate eluent. To prevent introducing air bubbles into the system, do not let eluent drop below 200mL. The eluent is prepared by following these procedures:

   Stock Solutions:

   Prepare the 0.25M stock solutions by placing 26.4903g Na_2CO_3 in a 500.0mL volumetric flask and diluting to the mark with Milli-Q water. Also place 21.0001g $NaHCO_3$ in a separate 500.0mL volumetric flask and dilute to the mark with Milli-Q water.

   Working Eluent:

   Prepare the 1.75mM Na_2CO_3 / 0.50mM $NaHCO_3$ working eluent by pipetting 7.00mL of the Na_2CO_3 stock solution and 2.00mL of the $NaHCO_3$ stock solution into the same 1.000L volumetric flak. Dilute to the mark with Milli-Q water.

   Open the needle valve by the HCO_3^-/CO_3^{2-} eluent bottle and make sure that all the other needle valves are closed.

2. Turn on the ED40 and GP50 power switches.
3. Open the He gas main valve, and check that the He pressure to the system is at least 90psi.
4. Open the eluent flow valve, and adjust it to 80psi.
5. Load an anion method (usually saved as “as12_size of vial_date of calibration”, e.g., “as12_small_06December05”). Let the instrument equilibrate to about

1400psi, and conductivity 17.6µs/cm (takes 30 minutes to 2 hours).

Method parameters:

Pump Rate:	1.2mL/min
Eluent:	100% 1.75mM Na_2CO_3 / 0.50mM $NaHCO_3$
Suppressor Current:	50 mA
Sample Loop:	50µL

6. Turn on the AS40, and place sample trays into the slot. Press “Hold/Run” on the AS40 to position the first sample for the injection. Load the schedule and start run.

7. After completion of the full schedule, turn off the switches on ED40, GP50, and AS40, then close the eluent flow valve and He gas valve.

Analytical Procedure

Instrument: See Instrument.

Reagents:

1. Reagents must be ACS reagent grade or better.

2. Milli-Q water is used as the deionized water. It must have a conductance of less than 1µs/cm.

Stock Standard Solution (Prepare monthly):

1. Dry ~2g of sodium chloride, potassium sulfate, and sodium nitrate at 105°C for 30 minutes, and let them cool for at least 20 minutes in a desiccator to room temperature.

2. To make the $1.000X10^4$µeq/L (= 10.00mg/L) stock solution, weigh 0.5844g NaCl, 0.8713g K_2SO_4, and 0.8499g $NaNO_3$ in a 1.000L volumetric flask and dilute to the mark with deionized water.

   Store stock standard solution in a labeled and rinsed (with deionized water and subsequently the stock standard solution) 500mL HDPE bottle in the refrigerator.

Calibration Standards (Prepare weekly):

1. Since there is a small amount of chloride ion present in the Milli-Q water, 100% Milli-Q water (Blank) is used for the first calibration point. All other calibration standards are prepared by diluting the stock standard solution in 500.0mL or 100.0mL volumetric flasks. If stock standard solution was stored in the refrigerator, let it warm up to room temperature before use (preferably overnight). Use automatic pipetter to measure accurate volumes of the stock solution and follow the table below.

Volume of Stock Solution (mL)	Diluted to	Concentration of calibration standards (µeq/L)
0.000	Use Blank	0.000
0.100	500mL	2.000
0.250	500mL	5.000
0.750	500mL	15.00
1.500	500mL	30.00
3.000	500mL	60.00
6.000	500mL	120.0
2.400	100mL	240.0
3.600	100mL	360.0

Quality Control Solution: (Prepare weekly)

1. Dionex Five Anion Standard (at room temperature) is used as the QC stock solution. To prepare the working QC solution, 10.00mL of the QC stock solution is diluted to 1.000L with deionized water. The target value (µeq/L) of each anion is calculated from the manufacturer's data sheet.

Cleaning Automated Sampler Vials and Caps (as recommended by manufacturer):

1. During sample preparation and collection, or when handling clean vials and caps, always wear poly gloves (not latex gloves) to prevent contamination.

2. Rinse the filter caps with deionized water using a small syringe. Place vials and caps in a large pre-cleaned plastic container and rinse them for 3 to 5 times. Soak them for 4 hours in deionized water.

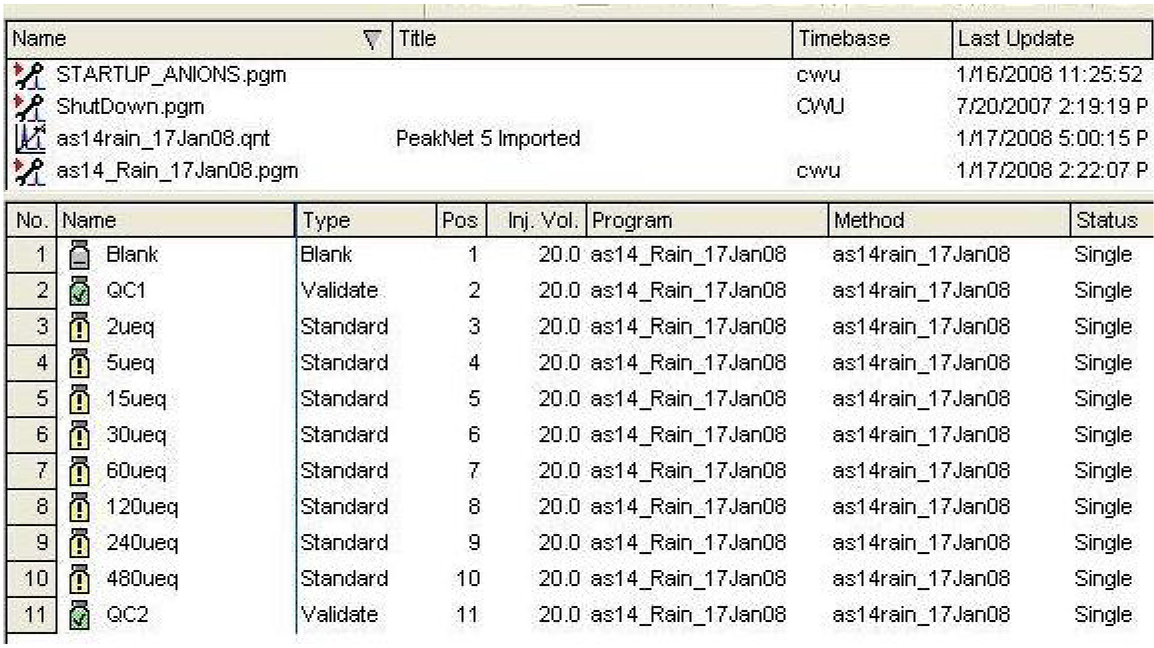
3. Drain the container and refill with deionized water. Soak the vials and caps for an additional 24 hours before use.

4. Plunge deionized water through each filter cap with the syringe before drying.

Solution Analysis:

1. Pour room temperature samples, calibration standards, and working QC solution in clean labeled 0.5mL automated sample vials. Fill the vial with analysis solution until it overflows, and insert the clean filter caps. If the vials are not dry, rinse the vial twice with the analysis solution before filling.

2. To obtain the calibration curve for each anion, run blank, calibration standards, and the QC standard in the following order.

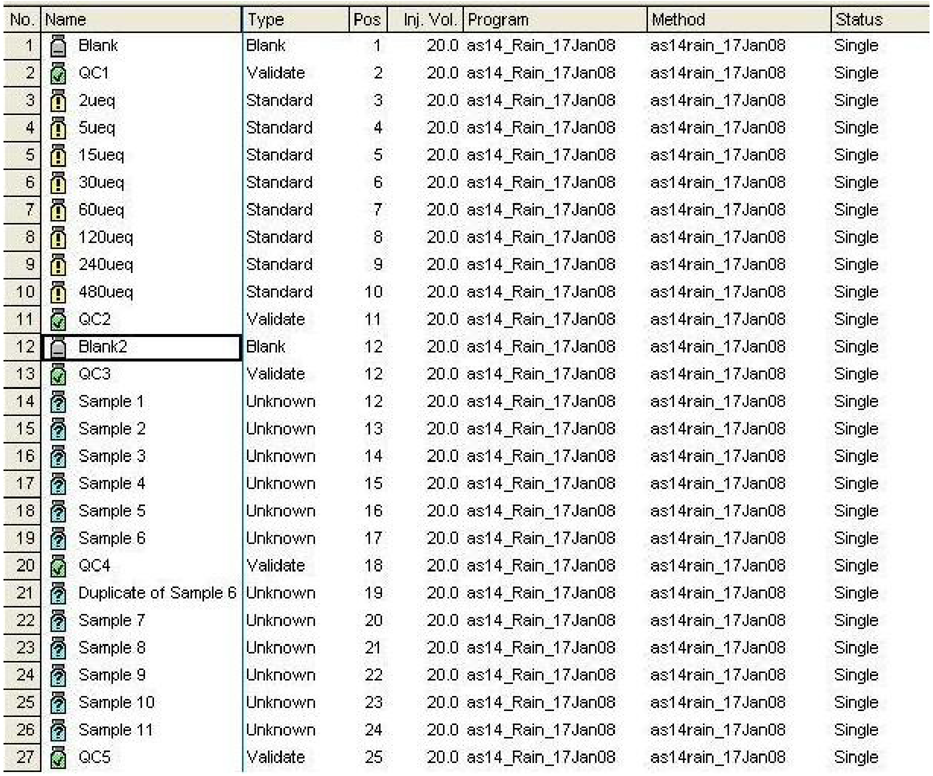


Name	Title	Timebase	Last Update
STARTUP_ANIONS.pgm		cwu	1/16/2008 11:25:52
ShutDown.pgm		CWU	7/20/2007 2:19:19 P
as14rain_17Jan08.qnt	PeakNet 5 Imported		1/17/2008 5:00:15 P
as14_Rain_17Jan08.pgm		cwu	1/17/2008 2:22:07 P

No.	Name	Type	Pos	Inj. Vol.	Program	Method	Status
1	Blank	Blank	1	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
2	QC1	Validate	2	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
3	2ueq	Standard	3	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
4	5ueq	Standard	4	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
5	15ueq	Standard	5	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
6	30ueq	Standard	6	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
7	60ueq	Standard	7	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
8	120ueq	Standard	8	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
9	240ueq	Standard	9	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
10	480ueq	Standard	10	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
11	QC2	Validate	11	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single

Within the instrument software plot concentration (µeq/L) vs. peak area using the data from the calibration standards. Choose linear curve fit type; force origin through zero, and record the equation and R^2 value. Print out each calibration graph. Update the method file.

3. Proceed with sample analysis. Run blank, QC standards, and samples in the following order. After every 6th sample determine a QC standard and a duplicate of the sample.



No.	Name	Type	Pos	Inj. Vol.	Program	Method	Status
1	Blank	Blank	1	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
2	QC1	Validate	2	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
3	2ueq	Standard	3	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
4	5ueq	Standard	4	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
5	15ueq	Standard	5	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
6	30ueq	Standard	6	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
7	60ueq	Standard	7	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
8	120ueq	Standard	8	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
9	240ueq	Standard	9	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
10	480ueq	Standard	10	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
11	QC2	Validate	11	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
12	Blank2	Blank	12	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
13	QC3	Validate	12	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
14	Sample 1	Unknown	12	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
15	Sample 2	Unknown	13	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
16	Sample 3	Unknown	14	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
17	Sample 4	Unknown	15	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
18	Sample 5	Unknown	16	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
19	Sample 6	Unknown	17	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
20	QC4	Validate	18	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
21	Duplicate of Sample 6	Unknown	19	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
22	Sample 7	Unknown	20	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
23	Sample 8	Unknown	21	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
24	Sample 9	Unknown	22	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
25	Sample 10	Unknown	23	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
26	Sample 11	Unknown	24	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single
27	QC5	Validate	25	20.0	as14_Rain_17Jan08	as14rain_17Jan08	Single

Performance Report

Method Detection Limits (MDL) and Linear Range:

Analyte	Retention Time (min)	MDL		Linear Range	
		(μeq/L)	(mg/L)	(μeq/L)	(mg/L)
Chloride	3.1	1.42	0.0502	1.4 – 360	0.050 – 12.8
Nitrate	4.6	1.07	0.0665	1.0 – 360	0.067 – 22.3
Sulfate	6.1	1.35	0.0650	1.4 – 360	0.065 – 17.3

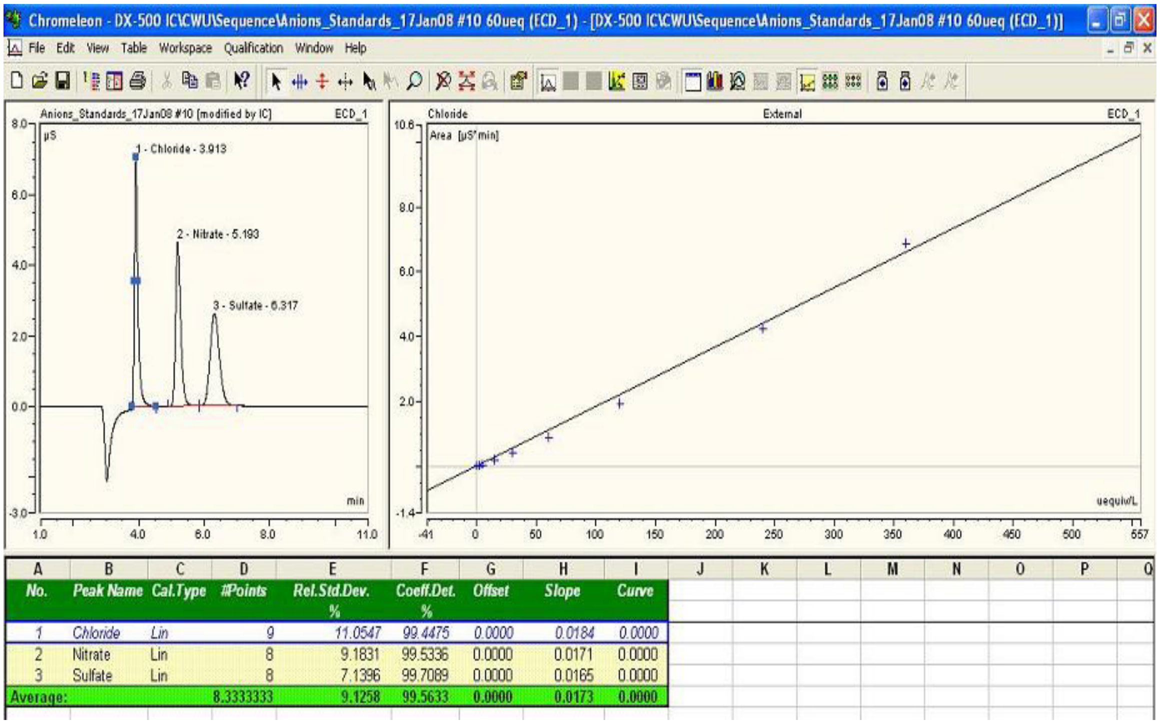
Standard Conditions:

Refer to Instrument section.

MDL calculated from 41 replicates of QC run from different days. MDL = t·std (t = 2.42 for 41 replicates with 98% confidence level). See attached spreadsheet in Appendix.

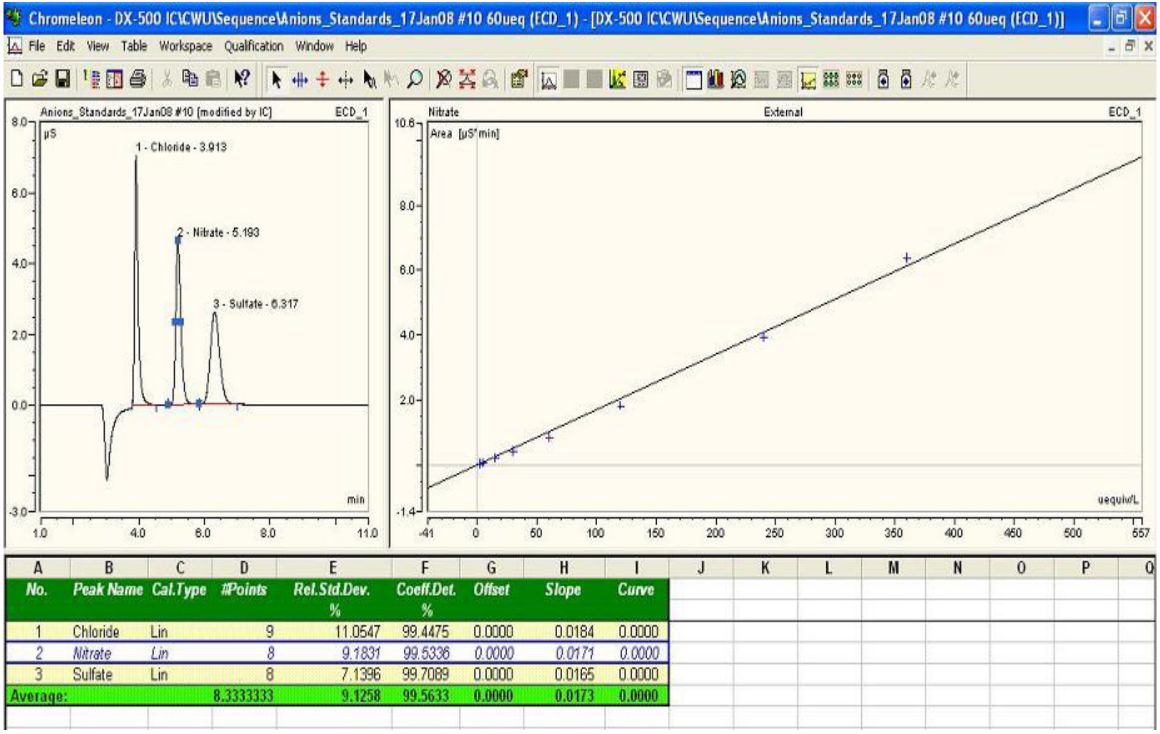
Calibration Curves:

1. Chloride standards 0.00 to 360μeq/L



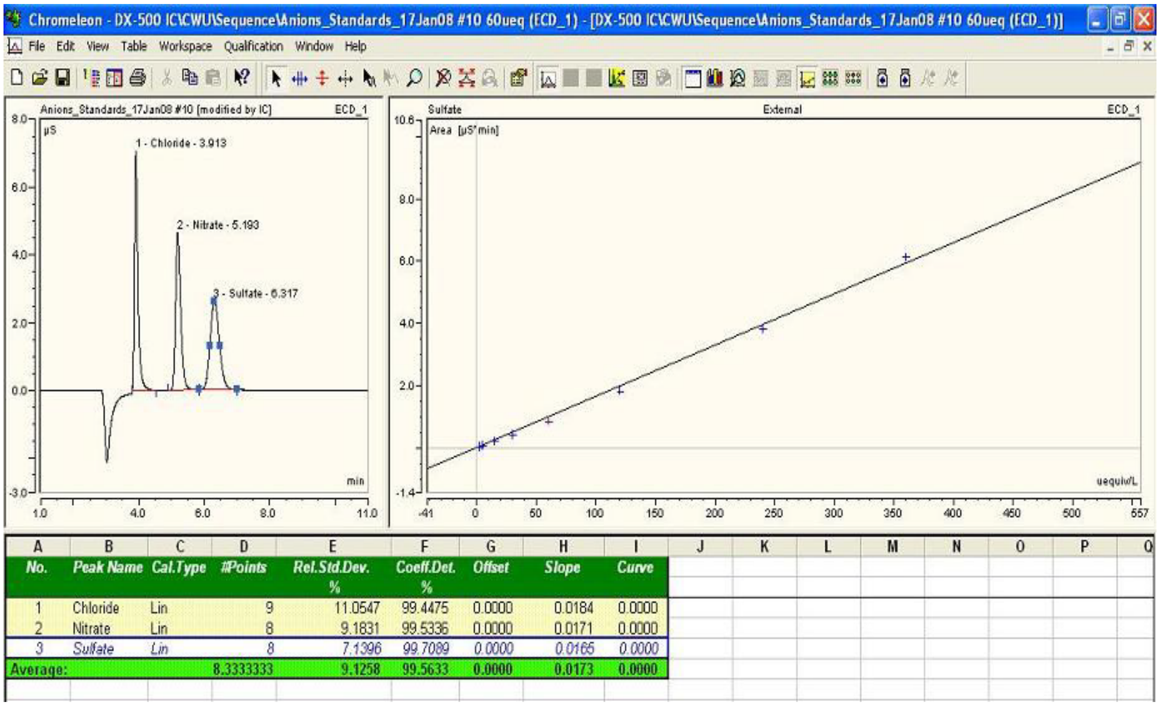
No.	Peak Name	Cal.Type	#Points	Rel.Std.Dev. %	Coeff.Det. %	Offset	Slope	Curve
1	Chloride	Lin	9	11.0547	99.4475	0.0000	0.0184	0.0000
2	Nitrate	Lin	8	9.1831	99.5336	0.0000	0.0171	0.0000
3	Sulfate	Lin	8	7.1396	99.7089	0.0000	0.0165	0.0000
Average:			8.3333333	9.1258	99.5633	0.0000	0.0173	0.0000

2. Nitrate standards 2.00 to 360μeq/L



No.	Peak Name	Cal.Type	#Points	Rel.Std.Dev. %	Coeff.Det. %	Offset	Slope	Curve
1	Chloride	Lin	9	11.0547	99.4475	0.0000	0.0184	0.0000
2	Nitrate	Lin	8	9.1831	99.5336	0.0000	0.0171	0.0000
3	Sulfate	Lin	8	7.1396	99.7089	0.0000	0.0165	0.0000
Average:			8.3333333	9.1258	99.5633	0.0000	0.0173	0.0000

3. Sulfate standards 2.00 to 360μeq/L



Chromeleon - DX-500 IC\CWU\Sequence\Anions_Standards_17Jan08 #10 60ueq (ECD_1) - [DX-500 IC\CWU\Sequence\Anions_Standards_17Jan08 #10 60ueq (ECD_1)]

A	B	C	D	E	F	G	H	I
No.	Peak Name	Cal.Type	#Points	Rel.Std.Dev. %	Coeff.Det. %	Offset	Slope	Curve
1	Chloride	Lin	9	11.0547	99.4475	0.0000	0.0184	0.0000
2	Nitrate	Lin	8	9.1831	99.5336	0.0000	0.0171	0.0000
3	Sulfate	Lin	8	7.1396	99.7089	0.0000	0.0165	0.0000
Average:			8.3333333	9.1258	99.5633	0.0000	0.0173	0.0000

Appendix to IC Anion SOP:

1. Spreadsheet used to calculate MDLs

QC deom 06-Dec-05 to 28-Feb-06

	QCD	Cl	NO3	SO4
6-Dec-05	1	8.39	15.37	31.30
	2	8.07	15.29	31.67
	3	8.11	15.48	31.71
	4	8.44	15.85	31.81
	5	7.93	15.80	32.00
	6	8.78	15.79	31.61
	7	8.01	15.65	31.90
	8	7.22	15.59	31.93
	9	7.70	16.18	32.19
	10	7.36	15.73	32.45
	11	10.26	16.57	33.07
	12	8.71	15.86	32.55
	13	8.38	15.70	32.54
8-Dec-05	14	8.39	15.86	32.25
	15	8.33	15.74	32.15
	16	8.47	15.73	32.16
	17	8.37	15.70	31.51
	18	8.50	15.74	32.11
	19	8.62	15.86	31.74
	20	7.76	15.70	32.04
	21	9.07	16.27	33.25
	22	7.46	15.13	31.43
	23	8.62	15.94	32.22
	24	7.70	15.89	32.15
	25	7.88	16.30	33.57
	26	7.53	15.95	32.24
9-Dec-05	27	8.16	15.82	32.17
	28	7.96	15.95	32.61

	QCD	**Cl**	**NO3**	**SO4**
9-Dec-05	29	7.70	16.06	32.96
	30	7.76	16.02	31.99
	31	7.75	16.30	31.65
	32	7.70	16.29	31.85
	33	7.55	16.19	32.99
	34	7.84	16.27	32.57
	35	7.73	16.48	32.41
	36	7.62	16.47	31.99
	37	8.93	16.84	32.49
	38	7.72	17.27	32.46
	39	7.46	16.46	32.72
28-Feb-06	40	7.29	16.68	30.72
	41	7.71	15.19	31.51
Std Dev		0.58	0.44	0.56
MLD(ueq/L)		1.42	1.07	1.35
MLD(mg/L)		0.0502	0.0665	0.0650
Mean (ueq/L)		8.07	15.97	32.16
Actual Value (ueq/L)		8.55	16.00	31.00
M.W.		35.45	62.00	96.06
Charge		1	1	2

Ion Chromatograph Cations S.O.P's

Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}

Instrument

Instrument and Parts:

Chromatography System: DX500

Electrochemical Detector ED40 Gradient Pump GP50
Automated Sampler AS40

Column: Ion Pac CS12A 4x250mm Analytical Column with CG 12A 4mm Guard Column

Suppressor: CSRS-ULTRA 4mm, run in Auto-suppression Mode

Injection Loop: 50µL

Program Software: Chromeleon® Version 6.80

Operation Procedure:

1. Check the reservoir for the 20.0mM Methanesulfonic acid (MSA) eluent. To prevent introducing air bubbles into the system, do not let eluent drop below 200mL. The 20.0mM MSA is prepared by pipetting 2.590mL MSA into a 2.000L volumetric flask and diluting with deionized water to the mark. Open the needle valve by the MSA eluent bottle and make sure that all the other needle valves are closed.
2. Turn on the ED40 and GP50 power switches.
3. Open the He gas main valve, and check that the He pressure to the system is at least 90 psi.
4. Open the eluent flow valve, and adjust it to 80psi.
5. Load a cation method (usually saved as "cs12_size of vial date of calibration", e.g., "cs12_small_24Jan06"). Let the instrument equilibrate to about 1150psi, and conductivity 1.0 to 1.3µs/cm (takes 30 minutes to 2 hours).

   Method parameters:

   Pump Rate: 1.0mL/min

   Eluent: 100% 20mM
   MSA Suppressor Current: 50mA

   Sample Loop: 50µL

6. Turn on the AS40, and place sample trays into the slot. Press “Hold/Run” on the AS40 to position the first sample for the injection. Load the schedule and start run.
7. After completion of the full schedule, turn off the switches on ED40, GP50, and AS40, then close the eluent flow valve and He gas valve.

Analytical Procedure

Instrument: See Instrument.

Reagents:

1. Reagents must be ACS reagent grade or better.
2. Milli-Q water is used as the deionized water. It must have a conductance of less than 1µs/cm.

Stock Standard Solution (Prepare monthly):

1. Dry ~2g of sodium chloride, ammonium chloride, potassium chloride, and
2. calcium carbonate at appropriate temperatures (NaCl, NH4Cl, and KCl at 105°C, CaCO3 at 180°C) for 1 hour, and let them cool for at least 20 minutes in a desiccator to room temperature.
3. To make the 1.000X104µeq/L (= 10.00 mg/L) stock solution, weigh 0.5844g NaCl, 0.5349g NH4Cl, 0.7455g KCl, and 0.5005g CaCO3. For magnesium, sand the magnesium ribbon to remove any oxide and dissolve 0.1216g of it in a minimal volume of 6N HCl (approximately less than 2mL).
4. Add all reagents in a 1.000L volumetric flask, and dissolve them in approximately 600mL of deionized water. Add a minimal amount of concentrated HCl to the solution until all the CaCO3 has dissolved (approximately less than 1mL). Dilute to the 1.000L mark with deionized water and mix well.
5. Store stock standard solution in a labeled and rinsed (with deionized water and subsequently the stock standard solution) 500mL HDPE bottle in the refrigerator.

Calibration Standards (Prepare weekly):

1. All calibration standards are prepared by diluting the stock standard solution in 500.0mL or 100.0mL volumetric flasks. If stock standard solution was stored in the refrigerator, let it warm up to room temperature before use (preferably overnight). Use automatic pipetter to measure accurate volumes of the stock solution and follow the table below.

Volume of Stock Solution (mL)	Diluted to	Concentration of calibration standards (µeq/L)
0.100	500mL	2.000
0.250	500mL	5.000
0.750	500mL	15.00
1.500	500mL	30.00
3.000	500mL	60.00
6.000	500mL	120.0
2.400	100mL	240.0
4.800	100mL	480.0

Quality Control Solution: (Prepare weekly)

1. Dionex Six Cation-II Standard (at room temperature) is used as the QC stock solution. To prepare the working QC solution, 1.000mL of the QC stock solution is diluted to 1.000L with deionized water. The target value (µeq/L) of each cation is calculated from the manufacturer's data sheet.

Cleaning Automated Sampler Vials and Caps (as recommended by manufacturer):

1. During sample preparation and collection, or when handling clean vials and caps, always wear poly gloves (not latex gloves) to prevent contamination.

2. Rinse the filter caps with deionized water using a small syringe. Place vials and caps in a large pre-cleaned plastic container and rinse them for 3 to 5 times. Soak them for 4 hours in deionized water.

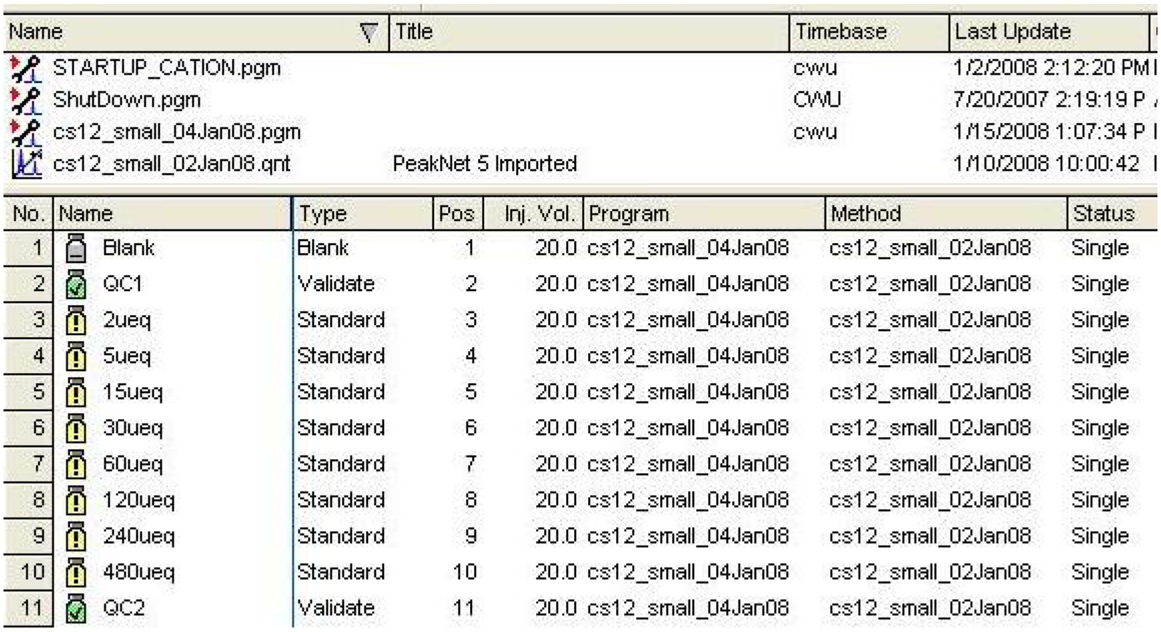
3. Drain the container and refill with deionized water. Soak the vials and caps for an additional 24 hours before use.

4. Plunge deionized water through each filter cap with the syringe before drying.

Solution Analysis:

1. Pour room temperature samples, calibration standards, and working QC solution in clean labeled 0.5mL automated sample vials. Fill the vial with analysis solution until it overflows, and insert the clean filter caps. If the vials are not dry, rinse the vial twice with the analysis solution before filling.

2. To obtain the calibration curve for each cation, run blank, calibration standards, and the QC standard in the following order.

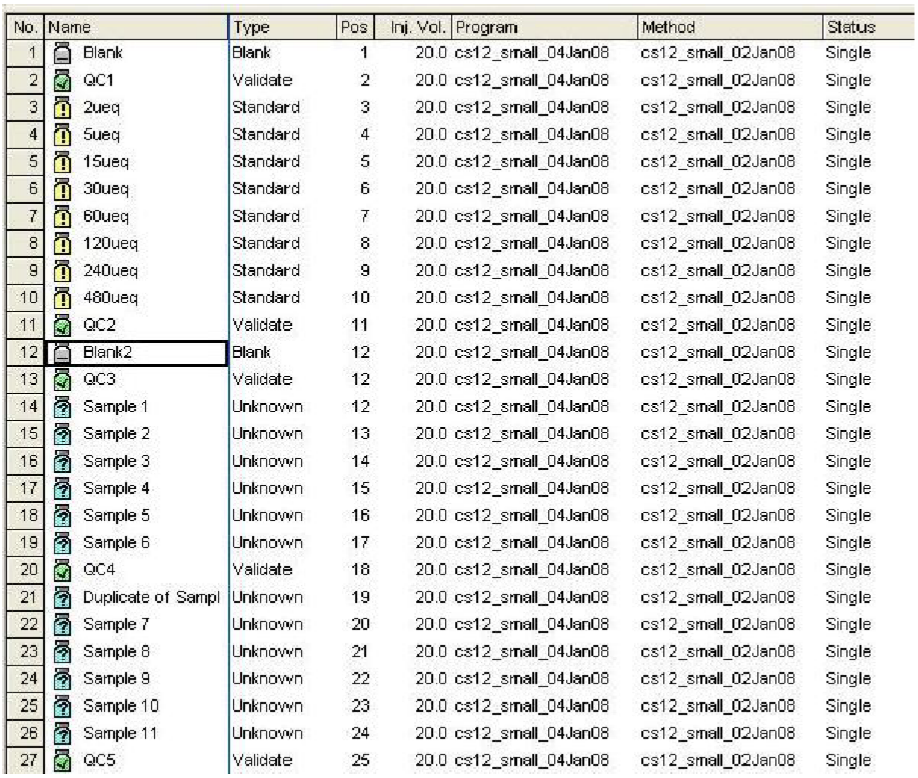


Name	Title	Timebase	Last Update
STARTUP_CATION.pgm		cwu	1/2/2008 2:12:20 PM
ShutDown.pgm		CWU	7/20/2007 2:19:19 P
cs12_small_04Jan08.pgm		cwu	1/15/2008 1:07:34 P
cs12_small_02Jan08.qnt	PeakNet 5 Imported		1/10/2008 10:00:42

No.	Name	Type	Pos	Inj. Vol.	Program	Method	Status
1	Blank	Blank	1	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
2	QC1	Validate	2	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
3	2ueq	Standard	3	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
4	5ueq	Standard	4	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
5	15ueq	Standard	5	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
6	30ueq	Standard	6	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
7	60ueq	Standard	7	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
8	120ueq	Standard	8	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
9	240ueq	Standard	9	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
10	480ueq	Standard	10	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
11	QC2	Validate	11	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single

3. Within instrument software plot concentration (µeq/L) vs. peak area using the data from the calibration standards. Choose linear curve fit type; force origin through zero, and record the equation and R2 value. Print out each calibration graph. Update the method file.

4. Proceed with sample analysis. Run blank, QC standards, and samples in the following order. After every 6th sample determine a QC standard and a duplicate of the sample.



No.	Name	Type	Pos	Inj. Vol.	Program	Method	Status
1	Blank	Blank	1	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
2	QC1	Validate	2	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
3	2ueq	Standard	3	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
4	5ueq	Standard	4	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
5	15ueq	Standard	5	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
6	30ueq	Standard	6	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
7	60ueq	Standard	7	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
8	120ueq	Standard	8	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
9	240ueq	Standard	9	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
10	480ueq	Standard	10	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
11	QC2	Validate	11	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
12	Blank2	Blank	12	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
13	QC3	Validate	12	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
14	Sample 1	Unknown	12	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
15	Sample 2	Unknown	13	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
16	Sample 3	Unknown	14	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
17	Sample 4	Unknown	15	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
18	Sample 5	Unknown	16	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
19	Sample 6	Unknown	17	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
20	QC4	Validate	18	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
21	Duplicate of Sampl	Unknown	19	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
22	Sample 7	Unknown	20	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
23	Sample 8	Unknown	21	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
24	Sample 9	Unknown	22	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
25	Sample 10	Unknown	23	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
26	Sample 11	Unknown	24	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single
27	QC5	Validate	25	20.0	cs12_small_04Jan08	cs12_small_02Jan08	Single

Performance Report

Method Detection Limits (MDL) and Linear Range:

Analyte	Retention Time (min)	MDL (µeq/L)	MDL (mg/L)	Linear Range (µeq/L)	Linear Range (mg/L)
Sodium	3.2	4.73	0.109	4.7 – 480	0.109 - 11.0
Ammonium	3.7	3.23	0.0583	3.2 – 120	0.0583 - 2.16
Potassium	4.9	2.47	0.0967	2.5 – 480	0.0967 – 18.8
Magnesium	8.1	3.11	0.0378	3.1 – 480	0.0378 – 5.83
Calcium	10.3	3.87	0.0775	3.9 - 480	0.0775 – 9.62

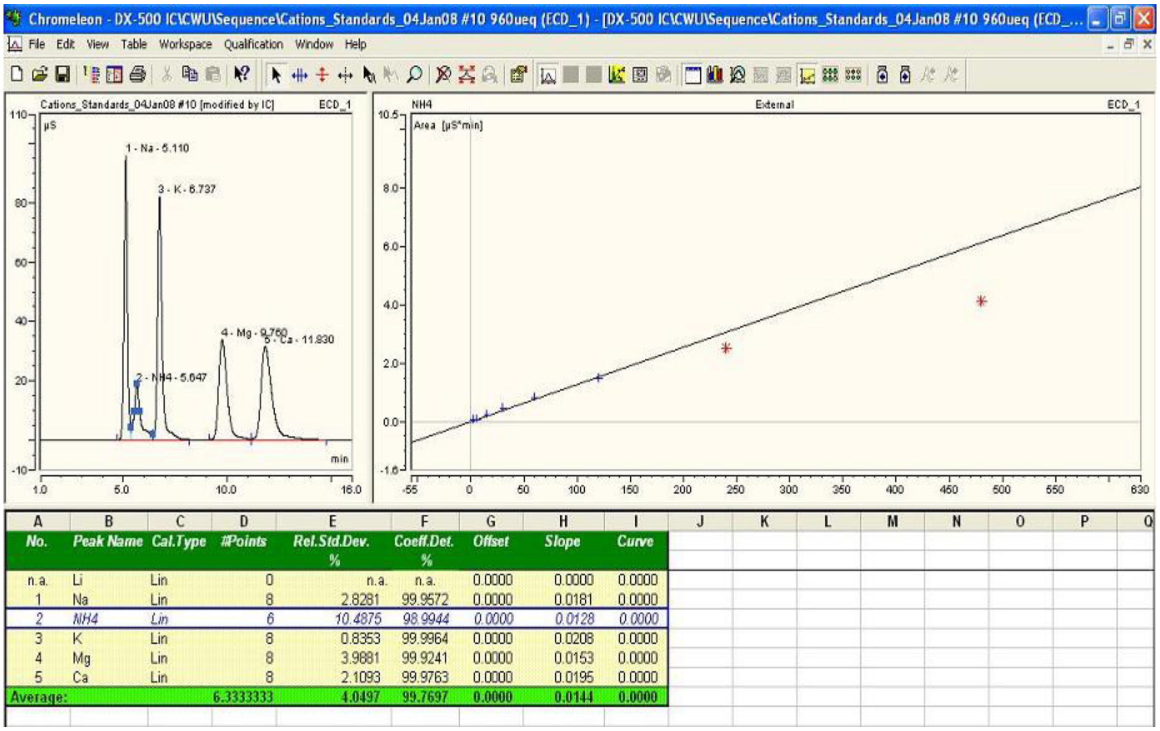
Standard Conditions:

Refer to Instrument section.

MDL calculated from 41 replicates of QC run from different days. MDL = t·std (t = 2.42 for 41 replicates with 98% confidence level). See attached spreadsheet in Appendix.

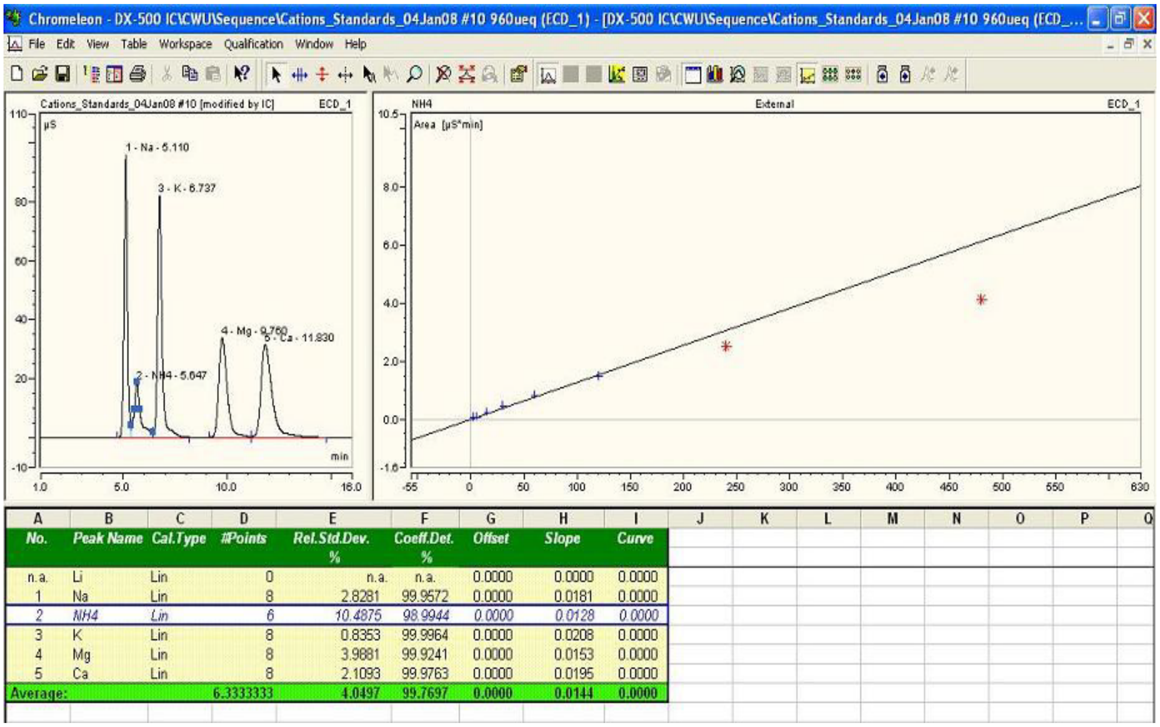
Calibration Curves:

1. Sodium standards 2.00 to 480µeq/L



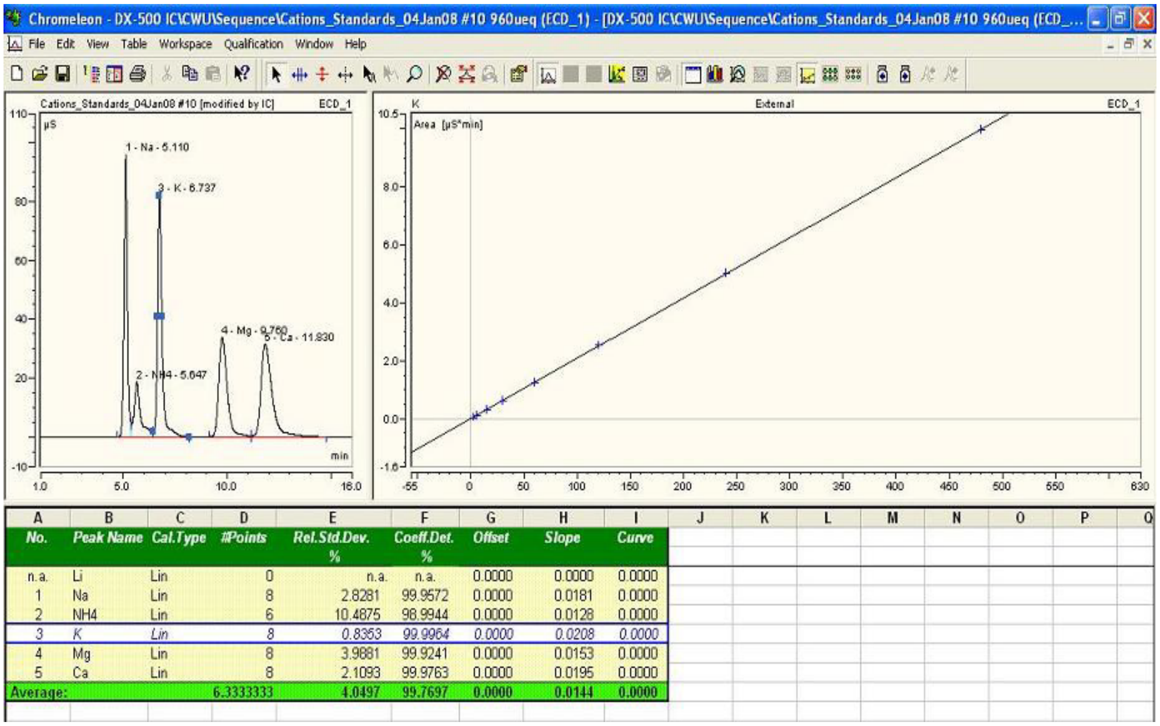
No.	Peak Name	Cal.Type	#Points	Rel.Std.Dev. %	Coeff.Det. %	Offset	Slope	Curve
n.a.	Li	Lin	0	n.a.	n.a.	0.0000	0.0000	0.0000
1	Na	Lin	8	2.8281	99.9572	0.0000	0.0181	0.0000
2	NH4	Lin	6	10.4875	98.9944	0.0000	0.0128	0.0000
3	K	Lin	8	0.8353	99.9964	0.0000	0.0208	0.0000
4	Mg	Lin	8	3.9881	99.9241	0.0000	0.0153	0.0000
5	Ca	Lin	8	2.1093	99.9763	0.0000	0.0195	0.0000
Average:			6.3333333	4.0497	99.7697	0.0000	0.0144	0.0000

2. Ammonium standards 2.00 to 120µeq/L



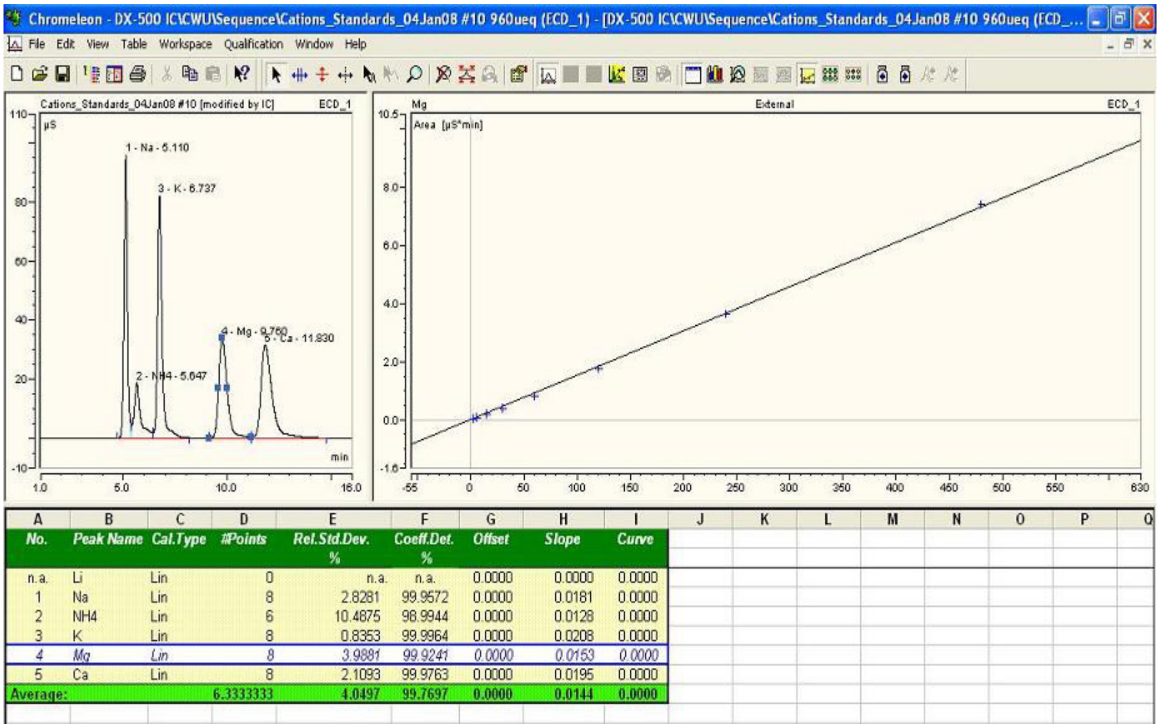
No.	Peak Name	Cal.Type	#Points	Rel.Std.Dev. %	Coeff.Det. %	Offset	Slope	Curve
n.a.	Li	Lin	0	n.a.	n.a.	0.0000	0.0000	0.0000
1	Na	Lin	8	2.8281	99.9572	0.0000	0.0181	0.0000
2	NH4	Lin	6	10.4875	98.9944	0.0000	0.0128	0.0000
3	K	Lin	8	0.8353	99.9964	0.0000	0.0208	0.0000
4	Mg	Lin	8	3.9881	99.9241	0.0000	0.0153	0.0000
5	Ca	Lin	8	2.1093	99.9763	0.0000	0.0195	0.0000
Average:			6.3333333	4.0497	99.7697	0.0000	0.0144	0.0000

3. Potassium standards 2.00 to 480µeq/L



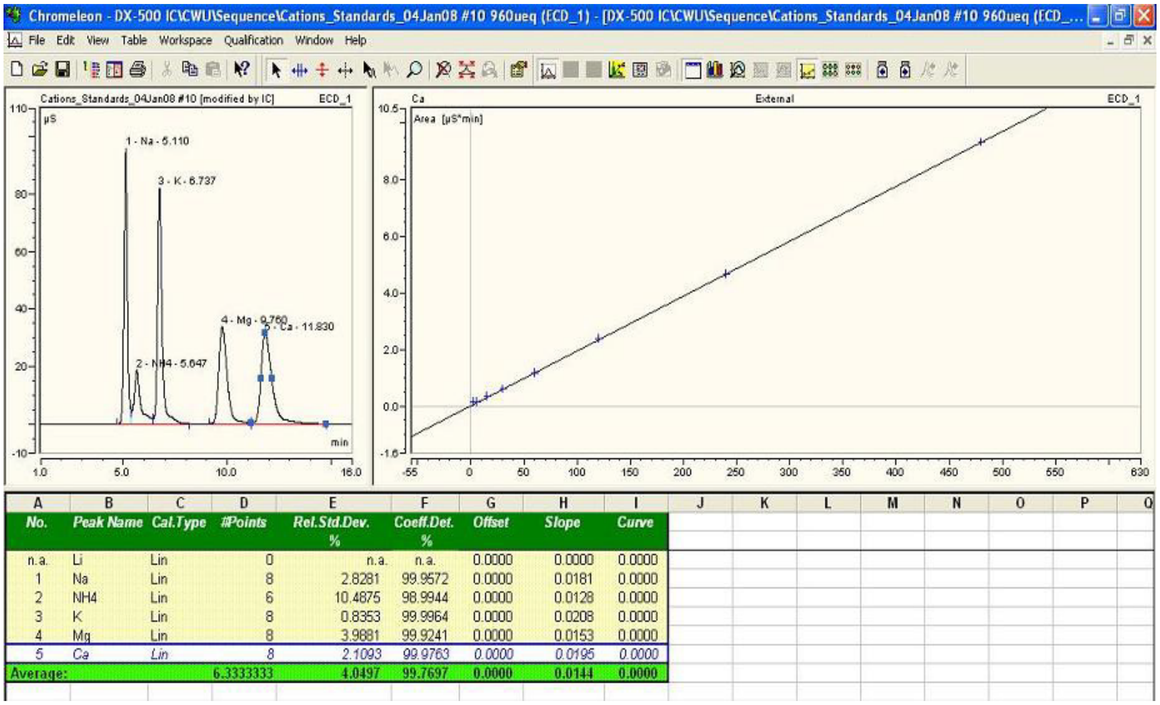
A	B	C	D	E	F	G	H	I
No.	Peak Name	Cal.Type	#Points	Rel.Std.Dev. %	Coeff.Det. %	Offset	Slope	Curve
n.a.	Li	Lin	0	n.a.	n.a.	0.0000	0.0000	0.0000
1	Na	Lin	8	2.8281	99.9572	0.0000	0.0181	0.0000
2	NH4	Lin	6	10.4875	98.9944	0.0000	0.0128	0.0000
3	K	Lin	8	0.8353	99.9964	0.0000	0.0208	0.0000
4	Mg	Lin	8	3.9881	99.9241	0.0000	0.0153	0.0000
5	Ca	Lin	8	2.1093	99.9763	0.0000	0.0195	0.0000
Average:			6.3333333	4.0497	99.7697	0.0000	0.0144	0.0000

4. Magnesium standards 2.00 to 480µeq/L



A	B	C	D	E	F	G	H	I
No.	Peak Name	Cal.Type	#Points	Rel.Std.Dev. %	Coeff.Det. %	Offset	Slope	Curve
n.a.	Li	Lin	0	n.a.	n.a.	0.0000	0.0000	0.0000
1	Na	Lin	8	2.8281	99.9572	0.0000	0.0181	0.0000
2	NH4	Lin	6	10.4875	98.9944	0.0000	0.0128	0.0000
3	K	Lin	8	0.8353	99.9964	0.0000	0.0208	0.0000
4	Mg	Lin	8	3.9881	99.9241	0.0000	0.0153	0.0000
5	Ca	Lin	8	2.1093	99.9763	0.0000	0.0195	0.0000
Average:			6.3333333	4.0497	99.7697	0.0000	0.0144	0.0000

5. Calcium standards 2.00 to 4



A	B	C	D	E	F	G	H	I
No.	**Peak Name**	**Cal.Type**	**#Points**	**Rel.Std.Dev. %**	**Coeff.Det. %**	**Offset**	**Slope**	**Curve**
n.a.	Li	Lin	0	n.a.	n.a.	0.0000	0.0000	0.0000
1	Na	Lin	8	2.8281	99.9572	0.0000	0.0181	0.0000
2	NH4	Lin	6	10.4875	98.9944	0.0000	0.0128	0.0000
3	K	Lin	8	0.8353	99.9964	0.0000	0.0208	0.0000
4	Mg	Lin	8	3.9881	99.9241	0.0000	0.0153	0.0000
5	*Ca*	*Lin*	*8*	*2.1093*	*99.9763*	*0.0000*	*0.0195*	*0.0000*
Average:			**6.3333333**	**4.0497**	**99.7697**	**0.0000**	**0.0144**	**0.0000**

Appendix to IC Cation SOP:

1. Spreadsheet used to calculate MDLs
QC from 24, 25, 27, 31-Jan-06

		Na	NH4	K	Mg	Ca
24-Jan-06	1	8.38	15.05	9.94	21.67	23.94
	2	9.63	14.07	10.62	19.76	25.30
25-Jan-06	3	15.66	14.62	13.21	20.20	28.61
	4	15.51	14.69	15.60	20.04	28.04
	5	11.05	12.35	10.97	21.62	26.77
	6	15.13	14.19	10.27	18.05	24.50
	7	11.62	14.37	11.38	20.16	27.56
	8	13.50	14.54	11.66	20.07	26.47
	9	9.97	13.60	11.27	20.38	25.84
	10	12.76	14.90	10.95	20.19	23.32
	11	13.66	13.17	10.96	19.52	24.72
	12	13.65	13.69	11.19	21.44	26.34
	13	12.56	15.85	11.24	21.13	28.16
	14	11.16	13.00	11.80	23.99	26.86
	15	10.87	14.74	11.21	21.21	25.58
	16	12.54	14.93	9.96	21.70	26.48
	17	13.10	13.44	10.67	19.74	23.42
	18	13.84	15.16	10.38	20.29	25.14
	19	12.79	14.26	10.74	19.01	24.19
	20	11.72	14.24	10.52	19.07	25.84
	21	10.03	14.55	10.91	20.06	26.64
	22	10.68	14.05	10.42	20.42	24.28
	23	9.07	15.13	10.42	20.60	26.20
	24	9.98	14.40	10.60	20.35	27.84
	25	12.35	14.24	10.77	17.68	24.60
	26	9.11	14.03	10.34	21.67	25.93
	27	11.57	15.20	9.80	18.45	24.26
27-Jan-06	28	9.47	12.58	10.79	20.49	24.27
	29	11.41	14.60	9.93	20.91	28.32
	30	11.53	14.23	11.40	19.94	25.89
	31	11.95	16.30	9.73	21.87	28.98
	32	8.01	14.03	10.20	20.60	25.04
	33	9.40	16.15	9.86	20.19	24.44
	34	15.18	14.84	10.66	19.34	24.78
	35	11.96	14.73	10.23	20.32	24.86
	36	12.76	14.64	10.74	20.24	24.31
	37	9.80	14.36	10.06	19.61	23.68
	38	11.50	16.30	11.27	20.01	23.01
	39	12.39	15.55	10.38	20.63	24.23
31-Jan-06 Redo	40	9.88	8.21	10.44	16.84	24.71
	41	9.55	12.75	9.55	17.83	23.26
Std Dev		1.96	1.34	1.02	1.29	1.60
MLD(ueq/L)		4.73	3.23	2.47	3.11	3.87
MLD(mg/L)		0.1088	0.0583	0.0967	0.0378	0.0775
Mean (ueq/L)		11.63	14.29	10.81	20.18	25.53
Actual Value (ueq/L)		8.79	14.03	12.76	20.98	25.45
M.W.		22.99	18.03	39.1	24.31	40.08
Charge		1	1	1	2	2

Quality Control Procedures

The following Quality Control (QC) Procedures are employed to assess and insure that the error associated with the reported analytical results is known.

a) **Determination of Blanks**: A blank determination is intended to estimate the analytical response attributable to all factors other than the analyte in the sample. Blanks are analyzed identically to samples but do not contain the analyte (e.g., in water analyses, 18 MΩ Milli-Q water would be analyzed to determine the blank). Blank determinations will be carried out for each analyte, except pH, each time those specific determinations are carried out. A sample of deionized water will be treated in the same manner as analyte for each determination. An out-of-control blank could suggest laboratory contamination or instrumental malfunction, and appropriate action will be taken to eliminate problems before sample analyses.

b) **Check Standards (i.e., Quality Control (QC) Standards)**: Check standard solutions of known concentration are analyzed with each batch of analyte. These standards have to be from a different source than the calibration standards as results are used to monitor the precision of any bias of analysis. The results of the check standard determinations will be followed and documented using the technique of control charting. Actions will be taken as described in the section on Control Procedures: Control Charts. Check standards are to be determined at a frequency of one check sample determination before analyses, then one after every sixth sample. Check standard concentrations are listed in the SOP procedure for each analyte.

c) **Duplicates**: Duplicate determinations of analytes are determined to track precision of analysis on real samples, and are performed every sixth sample (before and after the check standard). The two results will be compared during the analysis, and if they differ more than 5% from each other, the sample will be reanalyzed.

d) **Performance Evaluation (Proficiency Testing)**: Performance evaluation samples will be analyzed semiannually as part of the EPA certification program. The sources and procedures for PE sample acquisition and result submission are described in the Procedural Manual For The Environmental Laboratory Accreditation Program, Washington State Department of Ecology, 98353-0488, Manchester, Washington, November 2002. The results of the PE (PT) determination will be documented for laboratory users.

e) **Procedure for the use of Control Charts**: Control charts will be used to document the results of repetitive analyses and to signal the need for corrective action as a result of analyses of check standards. “Control Charts” document the relationship of particular analytical results with respect to the mean and standard deviation of a statistically valid set of previous determinations of a reproducible sample (see Appendix III for example). The control chart presentation documents the mean and standard deviation of previous determination of sample as well as the value of the determination in question. Actions are taken if the values under consideration differ from the mean by specified amounts. If

the determination under consideration differs from the mean by ±2σ it is likely, at the 5% level, that the method analytical precision has changed or a determinant error has been introduced into the result. This level is defined as the Warning Limit. If the determination differs from the mean by more than ±3σ it is likely, at the .3% level, that the method analytical precision has changed or a determinant error has been introduced into the results. This level is defined as the Action Limit.

A procedure is considered "out of control" (EPA) if:

1) Any result is beyond the action limit.

2) Any three consecutive results fall beyond the warning limit.

3) Any seven consecutive results are either above or below the mean of previous determinations.

The control chart technique will be used to document the running average of determinations of check standards (which can be compared to the expected value to determine bias).

f) **Guidelines for corrective action when data is "out of control":**

   1) Analytical results acquired after the procedure is discovered to be "out of control" will not be considered valid.

   2) New samples of blank, check standard, or duplicate sample (whichever was "out of control") will be re-determined. If the results do not fall within the acceptable ranges, instrumentation and method will be examined to determine and correct the cause of result error.

g) **Procedures for preparation and storage of standards**: See SOP for particular analyses.

h) **Definitions**: See the Glossary of Quality Assurance/Quality Control terms. Appendix IV.

i) **QA/QC Reports**: The laboratory will compile, review, and prepare a summary report describing the QA performance once a year. The report will describe laboratory activity including; number of determinations, staffing, performance on CRM samples, control chart results with respect to blanks, check standards, and duplicates. The corrective actions that were taken will be documented.

j) **Quantitation**: Calibration equations will be derived for those methods where a physical signal is recorded that is proportional in magnitude to the analyte concentration. If the relationship between concentration and physical signal is linear with $R^2 > 99\%$ the equation will be used to calculate subsequent analyte sample concentrations. The standard deviation of slope and intercept will be recorded.

Data Management:

a) **Recording**: All laboratory data is entered in laboratory notebooks as acquired. Integrator printouts are reduced and affixed to the notebooks.

b) **Calculations**: Calculations are performed using computer software (e.g., in the case of anions and cations it is instrument specific). The calculation method is entered in the lab notebook with summary copies of the computer printout.

c) **Archived data**: Analytical results of precipitation and lake studies are retained on a shared server, e.g., S:\Chemistry Research\Johansen Research\Mt Rainier.

d) Laboratory notebooks and records will be maintained for at least three years from the date of last entry. Records will be maintained for longer periods if the requirement is defined with a particular user.

References

Duncan, L.C., Quality Assurance/Quality Control Manual, Central Washington University, Ellensburg, WA, 1992

Kirchmer, C.J., Analytical Control Charting, Department of Ecology, Quality Assurance Section, Manchester, WA

Standard Practice for Sampling Chain of Custody Procedures, ASTM International, West Conshohocken, PA, 1988

Procedure Manual for the Environmental Laboratory Accreditation Program, Publication No. 02-03-055, Washington State Department of Ecology, Manchester, WA, 2002

Appendix C. Glossaries, Acronyms, and Abbreviations

Glossary of General Terms

Ambient: Background or away from point sources of contamination. Surrounding environmental condition.

Anthropogenic: Human-caused.

Bankfull stage: Formally defined as the stream level that "corresponds to the discharge at which channel maintenance is most effective, that is, the discharge at which moving sediment, forming or removing bars, forming or changing bends and meanders, and generally doing work that results in the average morphologic characteristics of channels (Dunne and Leopold, 1978).

Baseflow: The component of total streamflow that originates from direct groundwater discharges to a stream.

Char: Fish of genus *Salvelinus* distinguished from trout and salmon by the absence of teeth in the roof of the mouth, presence of light-colored spots on a dark background, absence of spots on the dorsal fin, small scales, and differences in the structure of their skeleton. (Trout and salmon have dark spots on a lighter background.)

Chronic critical effluent concentration: The maximum concentration of effluent during critical conditions at the boundary of the mixing zone assigned in accordance with WAC 173-201A-100. The boundary may be based on distance or a percentage of flow. Where no mixing zone is allowed, the chronic critical effluent concentration shall be 100% effluent.

Clean Water Act: 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.

Conductivity: A measure of water's ability to conduct an electrical current. Conductivity is related to the concentration and charge of dissolved ions in water.

Critical condition: When the physical, chemical, and biological characteristics of the receiving water environment interact with the effluent to produce the greatest potential adverse impact on aquatic biota and existing or designated water uses. For steady-state discharges to riverine systems, the critical condition may be assumed to be equal to the 7Q10 flow event unless determined otherwise by the department.

Designated uses: Those uses specified in Chapter 173-201A WAC (Water Quality Standards for Surface Waters of the State of Washington) for each water body or segment, regardless of whether or not the uses are currently attained.

Diel: Of, or pertaining to, a 24-hour period.

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

Dilution factor: The relative proportion of effluent to stream (receiving water) flows occurring at the edge of a mixing zone during critical discharge conditions as authorized in accordance with the state's mixing zone regulations at WAC 173-201A-100.
http://apps.leg.wa.gov/WAC/default.aspx?cite=173-201A-020

Diurnal: Of, or pertaining to, a day or each day; daily. (1) Occurring during the daytime only, as different from nocturnal or crepuscular, or (2) Daily; related to actions which are completed in the course of a calendar day, and which typically recur every calendar day (e.g., diurnal temperature rises during the day, and falls during the night).

Effective shade: The fraction of incoming solar shortwave radiation that is blocked from reaching the surface of a stream or other defined area.

Effluent: An outflowing of water from a natural body of water or from a human-made structure. For example, the treated outflow from a wastewater treatment plant.

Enterococci: A subgroup of the fecal streptococci that includes *S. faecalis*, *S. faecium*, *S. gallinarum,* and *S. avium*. The enterococci are differentiated from other streptococci by their ability to grow in 6.5% sodium chloride, at pH 9.6, and at 10 degrees C and 45 degrees C.

Eutrophic: Nutrient rich and high in productivity resulting from human activities such as fertilizer runoff and leaky septic systems.

Existing uses: Those uses actually attained in fresh and marine waters on or after November 28, 1975, whether or not they are designated uses. Introduced species that are not native to Washington, and put-and-take fisheries comprised of non-self-replicating introduced native species, do not need to receive full support as an existing use.

Extraordinary primary contact: Waters providing extraordinary protection against waterborne disease or that serve as tributaries to extraordinary quality shellfish harvesting areas.

Fecal coliform (FC): That portion of the coliform group of bacteria which is present in intestinal tracts and feces of warm-blooded animals as detected by the product of acid or gas from lactose in a suitable culture medium within 24 hours at 44.5 plus or minus 0.2 degrees Celsius. Fecal coliform bacteria are "indicator" organisms that suggest the possible presence of disease-causing organisms. Concentrations are measured in colony forming units per 100 milliliters of water (cfu/100 mL).

Fish Tissue Equivalent Concentration (FTEC): The FTEC is a tissue contaminant concentration used by Ecology to determine whether the designated uses of fishing and drinking from surface waters are being met. The FTEC is an interpretation of Washington's water quality criterion for a specific chemical for the protection of human health: the National Toxics Rule (40 CFR 131.36). Fish tissue sample concentrations that are lower than the FTEC suggest that the uses of fishing and drinking from surface waters are being met for that specific contaminant. Where an FTEC is not met (i.e., concentration of a chemical in fish tissue is greater than the FTEC), that water body is then placed into Category 5 during Washington's periodic Water Quality Assessment (WQA and 303d List). Category 5 listings become part of Washington's 303(d) list during the assessment process. The FTEC is calculated by multiplying the contaminant-specific Bio-Concentration Factor (BCF) times the contaminant-specific Water Quality Criterion found in the National Toxics Rule.

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.

Hyporheic: The area beneath and adjacent to a stream where surface water and groundwater intermix.

Load allocation: The portion of a receiving water's loading capacity attributed to one or more of its existing or future sources of nonpoint pollution or to natural background sources.

Loading capacity: The greatest amount of a substance that a water body can receive and still meet water quality standards.

Margin of safety: Required component of TMDLs that accounts for uncertainty about the relationship between pollutant loads and quality of the receiving water body.

Municipal separate storm sewer systems (MS4): A conveyance or system of conveyances (including roads with drainage systems, municipal streets, catch basins, curbs, gutters, ditches, manmade channels, or storm drains): (1) owned or operated by a state, city, town, borough, county, parish, district, association, or other public body having jurisdiction over disposal of wastes, stormwater, or other wastes and (2) designed or used for collecting or conveying stormwater; (3) which is not a combined sewer; and (4) which is not part of a Publicly Owned Treatment Works (POTW) as defined in the Code of Federal Regulations at 40 CFR 122.2.

National Pollutant Discharge Elimination System (NPDES): National program for issuing, modifying, revoking and reissuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements under the Clean Water Act. The NPDES program regulates discharges from wastewater treatment plants, large factories, and other facilities that use, process, and discharge water back into lakes, streams, rivers, bays, and oceans.

Near-stream disturbance zone (NSDZ): The active channel area without riparian vegetation that includes features such as gravel bars.

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities, including but not limited to atmospheric deposition, surface-water runoff from agricultural lands, urban areas, or forest lands, subsurface or underground sources, or discharges from boats or marine vessels not otherwise regulated under the NPDES program. Generally, any unconfined and diffuse source of contamination. Legally, any source of water pollution that does not meet the legal definition of "point source" in section 502(14) of the Clean Water Act.

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.

Pathogen: Disease-causing microorganisms such as bacteria, protozoa, viruses.

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.

Phase I stormwater permit: The first phase of stormwater regulation required under the federal Clean Water Act. The permit is issued to medium and large municipal separate storm sewer systems (MS4s) and construction sites of five or more acres.

Phase II stormwater permit: The second phase of stormwater regulation required under the federal Clean Water Act. The permit is issued to smaller municipal separate storm sewer systems (MS4s) and construction sites over one acre.

Point source: Source of pollution that discharges at a specific location from pipes, outfalls, and conveyance channels to a surface water. Examples of point source discharges include municipal wastewater treatment plants, municipal stormwater systems, industrial waste treatment facilities, and construction sites where more than 5 acres of land have been cleared.

Pollution: Contamination or other alteration of the physical, chemical, or biological properties of any waters of the state. This includes change in temperature, taste, color, turbidity, or odor of the waters. It also includes discharge of any liquid, gaseous, solid, radioactive, or other substance into any waters of the state. This definition assumes that these changes will, or are likely to, create a nuisance or render such waters harmful, detrimental, or injurious to (1) public health, safety, or welfare, or (2) domestic, commercial, industrial, agricultural, recreational, or other legitimate beneficial uses, or (3) livestock, wild animals, birds, fish, or other aquatic life.

Primary contact recreation: Activities where a person would have direct contact with water to the point of complete submergence including, but not limited to, skin diving, swimming, and water skiing.

Reach: A specific portion or segment of a stream.

Riparian: Relating to the banks along a natural course of water.

Salmonid: Fish that belong to the family *Salmonidae*. Species of salmon, trout, or char.

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

Stormwater: The portion of precipitation that does not naturally percolate into the ground or evaporate but instead runs off roads, pavement, and roofs during rainfall or snow melt. Stormwater can also come from hard or saturated grass surfaces such as lawns, pastures, playfields, and from gravel roads and parking lots.

Streamflow: Discharge of water in a surface stream (river or creek).

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.

Synoptic survey: Data collected simultaneously or over a short period of time.

System potential: The design condition used for TMDL analysis.

System-potential channel morphology: The more stable configuration that would occur with less human disturbance.

System-potential mature riparian vegetation: Vegetation which can grow and reproduce on a site, given climate, elevation, soil properties, plant biology, and hydrologic processes.

System-potential riparian microclimate: The best estimate of air temperature reductions that are expected under mature riparian vegetation. System-potential riparian microclimate can also include expected changes to wind speed and relative humidity.

System-potential temperature: An approximation of the temperatures that would occur under natural conditions. System potential is our best understanding of natural conditions that can be supported by available analytical methods. The simulation of the system-potential condition uses best estimates of *mature riparian vegetation, system-potential channel morphology, and system-potential riparian microclimate* that would occur absent any human alteration.

Thalweg: The deepest and fastest moving portion of a stream.

Total Maximum Daily Load (TMDL): A distribution of a substance in a water body designed to protect it from not meeting (exceeding) water quality standards. A TMDL is equal to the sum of all of the following: (1) individual wasteload allocations for point sources, (2) the load allocations for nonpoint sources, (3) the contribution of natural sources, and (4) a margin of safety to allow for uncertainty in the wasteload determination. A reserve for future growth is also generally provided.

Total suspended solids (TSS): Portion of solids retained by a filter.

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

Wasteload allocation: The portion of a receiving water’s loading capacity allocated to existing or future point sources of pollution. Wasteload allocations constitute one type of water quality-based effluent limitation.

Watershed: A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

1-DMax or 1-day maximum temperature: The highest water temperature reached on any given day. This measure can be obtained using calibrated maximum/minimum thermometers or continuous monitoring probes having sampling intervals of thirty minutes or less.

303(d) list: Section 303(d) of the federal Clean Water Act, requiring Washington State to periodically prepare a list of all surface waters in the state for which beneficial uses of the water – such as for drinking, recreation, aquatic habitat, and industrial use – are impaired by pollutants. These are water quality-limited estuaries, lakes, and streams that fall short of state surface water quality standards and are not expected to improve within the next two years.

7-DADMax or 7-day average of the daily maximum temperatures: The arithmetic average of seven consecutive measures of daily maximum temperatures. The 7-DADMax for any individual day is calculated by averaging that day's daily maximum temperature with the daily maximum temperatures of the three days before and the three days after that date.

7Q2 flow: A typical low-flow condition. The 7Q2 is a statistical estimate of the lowest 7-day average flow that can be expected to occur once every other year on average. The 7Q2 flow is commonly used to represent the average low-flow condition in a water body and is typically calculated from long-term flow data collected in each basin. For temperature TMDL work, the 7Q2 is usually calculated for the months of July and August as these typically represent the critical months for temperature in our state.

7Q10 flow: A critical low-flow condition. The 7Q10 is a statistical estimate of the lowest 7-day average flow that can be expected to occur once every ten years on average. The 7Q10 flow is commonly used to represent the critical flow condition in a water body and is typically calculated from long-term flow data collected in each basin. For temperature TMDL work, the 7Q10 is usually calculated for the months of July and August as these typically represent the critical months for temperature in our state.

90th percentile: An estimated portion of a sample population based on a statistical determination of distribution characteristics. The 90th percentile value is a statistically derived estimate of the division between 90% of samples, which should be less than the value, and 10% of samples, which are expected to exceed the value.

Acronyms and Abbreviations

Delete all of the following that aren't used in this QAPP.

BMP	Best management practice
DO	Dissolved oxygen
DOC	Dissolved organic carbon
e.g.	For example
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management database
EPA	U.S. Environmental Protection Agency
et al.	And others
FC	Fecal coliform
GIS	Geographic Information System software
GPS	Global Positioning System
i.e.	In other words
MEL	Manchester Environmental Laboratory
MQO	Measurement quality objective
NAF	New Approximation Flow
NPDES	National Pollutant Discharge Elimination System
NSDZ	Near-stream disturbance zones
NTR	National Toxics Rule
PBDE	Polybrominated diphenyl ethers
PBT	Persistent, bioaccumulative, and toxic substance
PCB	Polychlorinated biphenyls
QA	Quality assurance
QC	Quality control
RM	River mile
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SRM	Standard reference materials
TIR	Thermal infrared radiation

TMDL	Total Maximum Daily Load
TOC	Total organic carbon
TSS	Total suspended solids
USFS	United States Forest Service
USGS	United States Geological Survey
WAC	Washington Administrative Code
WDFW	Washington Department of Fish and Wildlife
WQA	Water Quality Assessment
WRIA	Water Resource Inventory Area
WSTMP	Washington State Toxics Monitoring Program
WWTP	Wastewater treatment plant

Units of Measurement

°C	degrees centigrade
cfs	cubic feet per second
cfu	colony forming units
cms	cubic meters per second, a unit of flow
dw	dry weight
ft	feet
g	gram, a unit of mass
kcfs	1000 cubic feet per second
kg	kilograms, a unit of mass equal to 1,000 grams
kg/d	kilograms per day
km	kilometer, a unit of length equal to 1,000 meters
L/s	liters per second (0.03531 cubic foot per second)
m	meter
mm	millimeter
mg	milligram
mgd	million gallons per day
mg/d	milligrams per day
mg/kg	milligrams per kilogram (parts per million)
mg/L	milligrams per liter (parts per million)

mg/L/hr	milligrams per liter per hour
mL	milliliter
mmol	millimole or one-thousandth of a mole
mole	an International System of Units (IS) unit of matter
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)
psu	practical salinity units
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)
µm	micrometer
µM	micromolar (a chemistry unit)
µmhos/cm	micromhos per centimeter
µS/cm	microsiemens per centimeter, a unit of conductivity
ww	wet weight

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 (Kammin, 2010). For Ecology, it is defined according to WAC 173-50-040: "Formal recognition by [Ecology] that an environmental laboratory is capable of producing accurate and defensible analytical data."

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* (USEPA, 2014).

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: Discrepancy between the expected value of an estimator and the population parameter being estimated (Gilbert, 1987; USEPA, 2014).

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, 2014; USEPA, 2020).

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, 2014; USEPA 2020).

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: The process of determining that the data satisfy the requirements as defined by the data user (USEPA, 2020). There are various levels of data validation (USEPA, 2009).

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, 2014).

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)/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. Monitors a lab's performance for bias and precision (USEPA, 2014).

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).

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 (USEPA, 2001).

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): The minimum measured concentration of a substance that can be reported with 99% confidence that the measured concentration is distinguishable from method blank results (USEPA, 2016). MDL is a measure of the capability of an analytical method of distinguished samples that do not contain a specific analyte from a sample that contains a low concentration of the analyte (USEPA, 2020).

Minimum level: Either the sample concentration equivalent to the lowest calibration point in a method or a multiple of the method detection limit (MDL), whichever is higher. For the purposes of NPDES compliance monitoring, EPA considers the following terms to be synonymous: “quantitation limit,” “reporting limit,” and “minimum level” (40 CFR 136).

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:

$$RPD = [Abs(a-b)/((a + b)/2)] * 100\%$$

where “Abs()” is absolute value and a and b are results for the two replicate samples. RPD can be used only with 2 values. Percent Relative Standard Deviation is (%RSD) is used if there are results for more than 2 replicate samples (Ecology, 2004).

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).

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).

Reporting level: Unless specified otherwise by a regulatory authority or in a discharge permit, results for analytes that meet the identification criteria (i.e., rules for determining qualitative presence/absence of an analyte) are reported down to the concentration of the minimum level established by the laboratory through calibration of the instrument. EPA considers the terms “reporting limit,” “quantitation limit,” and “minimum level” to be synonymous (40 CFR 136).

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, 1992).

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, 2014).

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, 2014).

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).

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