PACIFIC groundwater GROUP

INTERIM FINAL GROUNDWATER MONITORING PLAN LOWER YAKIMA VALLEY GWMA INITIAL CHARACTERIZATION

August 15, 2014

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Prepared for:

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MONITORING PLAN APPROVALS

This Groundwater Monitoring Plan, developed (insert final date), 2014 for the Lower Yakima Valley Groundwater Management Area, has been reviewed and approved by the undersigned. Copies of the completed and signed Groundwater Monitoring Plan shall be distributed to the undersigned and all field personnel.

Lower Yakima Valley Groundwater Advisory Committee	Date
Project Manager	Date
QC Coordinator	Date
Field Manager	Date



This work was performed under HDR contract #CON0082545 and partially fulfills scope Item 2c. The Groundwater Monitoring Plan was prepared in accordance with hydrogeologic practices generally accepted at this time in this area, for the exclusive use of the Lower Yakima Valley Groundwater Advisory Committee and HDR, for specific application to the Initial Characterization. No other warranty, express or implied, is made.

1.0 PROJECT BACKGROUND

The Lower Yakima Valley (LYV) Groundwater Management Area (GWMA) was formed in 2011 in response to elevated nitrate concentrations in groundwater in the LYV. The GWMA project is a multi-agency, citizen-based, coordinated effort to reduce groundwater nitrate concentrations in the LYV to below Washington State drinking water standards. To achieve this goal, activities contributing to elevated groundwater nitrate concentrations must be identified based on scientific data and evaluation, and strategies for implementing best management practices must be developed. The GWMA extends from Union Gap southeast to the Yakima County boundary, minus the Yakama Reservation (Figure 1).

The LYV Groundwater Advisory Committee (GWAC) through Yakima County Public Services, selected HDR Engineering (HDR) and Pacific Groundwater Group (PGG) to perform two Scopes of Work under HDR contract #CON0082545. The first scope, led by HDR, is a study to identify applicable local, state, and federal regulatory requirements that control and manage nitrate in groundwater, identify Best management Practices (BMPs), and evaluate the effectiveness of these BMPs. The second scope, led by PGG, focuses on development of this Groundwater Monitoring Plan to establish a network of wells and field procedures to evaluate current and future nitrate concentrations in groundwater.

This interim final Groundwater Monitoring Plan addresses:

- Sampling Procedures
- Sampling Schedule (developed following identification of the sampling network)
- Sampling Network (sampling network has not been established as of the date of issue for the interim final Groundwater Monitoring Plan)
- Quality Assurance/Quality Control
- Reporting (frequency developed following identification of the sampling network and schedule)

While this Monitoring Plan is intended to be comprehensive, revisions and/or amendments may be required as the project evolves.

1.1 OBJECTIVES

The objectives of this Groundwater Monitoring Plan are to establish procedures for the collection and analysis of representative groundwater samples for nitrate and nitrate-related analytes. In accordance with objectives established in the Potential Groundwater Monitoring Stations Report (PGG, December 2014), the data should be used to:

- Evaluate BMP effectiveness
- Evaluate groundwater trends
- Identify nitrate hotspots

• Calculate basin-wide average nitrate concentrations

The GWAC will use analytical results from these samples to make administrative decisions and policy recommendations; therefore, the data inputs must be reliable and defensible. Following the sampling protocols and methods described in this Monitoring Plan will facilitate collection of samples that accurately represent the groundwater and minimize sampling artifacts.

1.2 PROJECT DESCRIPTION/SCOPE OF WORK

This project is designed for the GWAC to collect representative nitrate and nitrate-related groundwater data to assess current and future conditions and to meet the objectives summarized in Section 1.1.

The study boundaries for the groundwater monitoring program are the GWMA boundaries minus the area covered by the consent order between the United States Environmental Protection Agency and several dairies ("dairy cluster", Figure 1).

The sampling program described in this Groundwater Monitoring Plan involves collecting groundwater samples from a network of wells for analyses of nitrate, nitrite, ammonia, and the sum of organic nitrogen + ammonia + ammonium (Total Kjeldahl Nitrogen). The network is assumed to include wells that already have pumps (private, public, and irrigation supply wells), and monitoring wells that require use of sampling pumps.

Groundwater samples will be analyzed by labs accredited by the Washington State Department of Ecology (Ecology). To avoid data entry errors, PGG recommends that preference be given to labs that can provide electronic data deliverables (EDDs) to the GWAC for direct upload to a database. Data will be managed in the project database and evaluated for trends, effectiveness of BMPs, hotspots, etc.

1.3 PROJECT SCHEDULE

Once the Groundwater Monitoring Plan is approved, field personnel will be identified, associated training will be completed, and equipment purchases or rental arrangements (field instruments, etc.) will be made. Following completion of these tasks, the initial sampling event under this Monitoring Plan will be performed at the next occurring interval established by the sampling schedule (Section 3.5).

Reports summarizing monitoring data will be prepared and submitted to the GWAC (Section 5).

2.0 PARAMETERS OF CONCERN AND ANALYTICAL LABS

Based on previous investigations and the purpose for establishing the GWMA, the parameters of concern for this study are:

- Nitrate
- Ammonia-nitrogen
- Sum of organic nitrogen + ammonia + ammonium (Total Kjeldahl Nitrogen)

Recommended and alternative analytical methods and holding times (from sample collection to analysis) are summarized in Table 1. The analytical method list in Table 1 was derived from Ecology's *Methods and Analytes Table* on their environmental lab accreditation website. The recommended analytical methods in Table 1 meet the PQL requirements, are common analytical methods, and have frequently been used by PGG in characterization studies. Alternative analytical methods are listed so that multiple labs (which may use acceptable but different methods of analysis from the recommended methods) could be contracted to analyze the parameters of concern. If there are discrepancies regarding preservation or holding time between Table 1 and the analytical method, the analytical method shall be considered correct.

Samples will be analyzed by a Washington State accredited chemical laboratory. A list of labs accredited for the GWMA parameters of concern is presented in Table 2, which was derived from Ecology's Lab Search website. Lab-prepared sample bottles should be acquired from the selected analytical lab prior to mobilizing to the field. Since nitrate and nitrite will be analyzed individually, rather than combined as nitrate+nitrite, the sample bottles will not have a sulfuric acid preservative. When sulfuric acid preservative is added to a sample, only nitrate+nitrite concentrations can be measured and not individual concentrations of nitrate or nitrite.

Considerations for selecting a lab from Table 2 should include price, logistics in delivering or shipping samples to the lab within 45 hours of collection, and EDD availability.

3.0 SAMPLING PROTOCOLS

Before mobilizing to the field, consult data collected during the Field Verification survey for information regarding well access. Note and meet any access notice requested by the well owner or operator. It is also important that a member of the sampling team can communicate effectively with well owners who are Spanish speakers.

Samples may be collected from either pre-existing, privately-owned supply wells, or project-specific monitoring wells. Sampling methods for both well types are given below.

3.1 WATER QUALITY METER CALIBRATION

Water quality instruments will be used to measure pH, electrical conductivity, temperature, and dissolved oxygen in the field during sampling. Flow through cells and multi-parameter meters are preferred; however, it may not be practical to use flow through cells at domestic and irrigation wells because unknown fittings may be required. In those cases, single-use CHEMetrics CHEMets may be used to measure dissolved oxygen.

Water quality instruments will be calibrated at the beginning (prior to sampling) and middle of each sampling day for pH and electrical conductivity following manufacturer's instructions. Readings will also be taken at the end of the day to evaluate drift.

Rented multi-parameter meters should be calibrated for dissolved oxygen by the rental company prior to delivery to the sampling team. Purchased multi-parameter meters should be calibrated for dissolved oxygen in the office prior to the sampling event. At the beginning (prior to sampling), middle, and end of each sampling day, partially fill the manufacturer supplied calibration cup or sensor storage container with enough tap water to submerge the dissolved oxygen probe and record the reading, it should be about 10-12 mg/L if the probe is well calibrated. If not, all dissolved oxygen readings should be J-flagged in the field notes. The relative values will be useful to monitor stabilization; however, the absolute values will not be accurate. Alternatively, CHEMets may be used, which do not require calibration.

Calibration data will be recorded in the field notes. An example Field Instrument Calibration Form is presented in Appendix A.

3.2 WATER SUPPLY WELL SAMPLES FROM SPIGOTS

The following tasks will be performed at each domestic, irrigation, and water supply well to be sampled. An example Groundwater Monitoring – Supply Well Sampling Field Form is presented in Appendix A. Field forms or notebooks should be weather-resistant (e.g. Rite in the Rain paper).

- 1. Confirm that water quality instruments have been calibrated according to the schedule presented in Section 3.0.
- 2. Record date, time, Ecology well ID, well owner and number where applicable (e.g. City of Sunnyside Well #10), appearance and condition of the wellhead, and weather conditions.
- 3. Groundwater samples should be collected from a sampling port on the well or the nearest tap to the wellhead and upstream of any tank or treatment device. Any tank or treatment device upstream of the sampling location should be noted on the field form. The well owner should observe and approve of modifications and operations.
- 4. Inspect the sampling port to assess if it is possible to connect a flow through cell with available fittings. If so, open the spigot and allow water to run for approximately 1 minute to flush out any particulates. If sampling in a well house, this water may be collected in buckets. Close the spigot and connect the flow through cell outfitted with a calibrated multi-parameter meter. If it is not possible to connect a flow through cell with available fittings, record in field notes what additional fittings would be required for future sampling events.
- 5. Start purging the well by opening the spigot. Record the time purging began in the field notes. Purge water should be routed to the ground or a floor drain. A length of polyethylene (PE) tubing (typically 1/2 by 3/8 inch diameter) and female threaded metal clamp hose may be used if necessary to route water outside well houses to ground surface. The pump should be running when samples are collected, even

though a pressure tank could cause the sampling port to flow even when the pump is off.

- 6. Record the make/model of water quality instrument(s) in the field notes. During purging, monitor the following field parameters at regular intervals (2 to 5 minutes): temperature, pH, specific conductivity, and dissolved oxygen. Record the time and measurements in the field sheets. Also note on field sheets any observed color or odor in purge water.
- 7. Continue purging until field parameters have stabilized according to:
 - $pH: \pm 0.1$ standard units
 - Specific conductance: ±10.0 umhos/com for values less than 1,000 umhos/cm, or ±20 umhos/cm for values greater than 1,000 umhos/cm
 - Dissolved oxygen if using a probe (multi-parameter meter): ± 0.05 mg/L for values less than 1 mg/L, or ± 0.2 mg/L for values greater than 1 mg/L
 - Dissolved oxygen if using CHEMets: ±0.1 mg/L for values less than 1 mg/L, or ±1 mg/L for values greater than 1 mg/L
 - Temperature: ±0.1 degree C
- 8. After field parameters have stabilized, disconnect the flow through cell and any tubing or hose used to route purge water to the ground. If the sampling port is located inside a well house, a 5-gallon bucket may be required to capture discharge water during sampling if a floor drain is not nearby.
- 9. Record unique well ID, sample date and time, and sampler's initials on each sample container, in the field notes, and on the Chain-of-Custody. Samples will be labeled in accordance with criteria described in Section 3.3. Bottles should not be filled until they are labeled.
- 10. Collect samples of water directly from the sampling port into laboratory-supplied containers for parameters listed in Table 1. The pump should be running when samples are collected. Do not use intermediate containers or vessels. Hands and clothing shall be clean when handling sampling equipment. Wear clean, disposable, latex gloves when filling bottles for analyses and change gloves between sampling locations. If it is necessary to set the bottle cap down during sampling, place it cap

side up on a clean sheet of plastic or clean plastic storage bag (e.g. sandwich bag). Collect samples in the following manner:

- Nitrate and nitrite: fill laboratory provided bottle to the top
- Ammonia and Total Kjedahl Nitrogen (TKN): fill laboratory provided bottle to the neck of the bottle, but *do not overfill*. Bottles for these analyses are provided by the lab containing preservative that should not be washed out by dumping or overfilling.



- 11. Collect QA/QC samples according to Appendix B in the manner described in Step 7.
- 12. Turn off sampling port.
- 13. Place sample bottles in a clean plastic bag and place the bag in a clean, insulated container (ice chest or cooler) containing frozen gel ice or wet ice to maintain sample temperatures at approximately 6 degrees Celsius, but not at or below, freezing. Double bag ice to prevent leakage during shipping. Use sufficient cooling materials to maintain sample temperature near 6 degrees Celsius during the entire time of transport to the lab.
- 14. Restore any objects at the wellhead that may have been disturbed during sampling. Obtain owner approval that conditions are satisfactory prior to departure. In winter, special procedures for start-up and shut-down will likely be required to protect equipment.
- 15. Maintain custody of samples from time of sampling to receipt at the laboratory. "Custody" means that samples remain:
 - In direct possession of a person who is recorded on the Chain-of-Custody form, or
 - Locked in secure vehicles or offices

Complete the Chain-of-Custody forms and any other pertinent sampling/shipping documentation to accompany the samples.

Ship or deliver samples to the selected Washington State accredited chemical laboratory, accompanied by Chain-of-Custody forms and any other pertinent shipping/sampling documentation. One set of Chain-of-Custody forms will be used per laboratory shipment.

In order to meet holding times, samples must be received by the lab less than 45 hours from the time they were collected.

3.3 MONITORING WELL SAMPLING

The following tasks will be performed at each water-table monitoring well to be sampled. An example Monitoring Well Sampling Field Form is presented in Appendix A.

- 1. Record date, time, unique well ID, appearance and condition of the wellhead, and weather conditions.
- 2. Measure and record static water level to the nearest 0.01 foot using a decontaminated electric well sounder. Well sounders shall be decontaminated by rinsing the length of the sounder that will be submerged in the well with distilled water prior to each use. Water level measuring points (top of PVC well casing) will be permanently marked on each well.
- 3. Install sampling pump.
 - If the depth to water is less than 25 feet, a peristaltic pump may be used to collect the sample. Wearing clean, disposable gloves, lower new, clean, ¹/₄ inch diameter

PE tubing or dedicated¹ ¼ inch diameter PE tubing into the well until the bottom of the tubing is below the water surface and within the well screen. Attach the top of the tubing to approximately 6 to 9 inches of silicone tubing and mount the silicone tubing in the peristaltic pump head. Attach approximately 2 feet of ¼ inch diameter PE tubing to the other end of the silicone tubing – this will be the sampling point. Confirm the pump rotation is set to lift water from the well.

- If the depth to water is greater than 25 feet, a portable or dedicated submersible pump should be used to collect the sample. Confirm with the distributor, manufacturer, or rental company that the pump has adequate lift for the anticipated depths to water. Wearing clean, disposable gloves, attach new, clean, PE tubing or dedicated PE tubing to the top of the pump motor and secure with a zip tie, hose clamp, or similar. Lower the pump until the intake is below the water surface and within the well screen. At the wellhead or ground surface, secure the electrical line of the pump so it does not slip during sampling. Attach the pump to the control box (if applicable), and power source.
- 4. If using a flow through cell, install the multi-parameter meter in the flow through cell and connect the pump discharge line to the inlet on the bottom of the cell. Connect a discharge line from outlet of the flow through cell of sufficient length to reach the discharge bucket.
- 5. Remove gloves and start the pump. Low-flow purge techniques will be used, with flow rates being less than 1.0 liters/minute (0.25 gallons per minute) to minimize drawdown and disturbance of sediment. Calculate flow rates using a stop-watch and calibrated vessel (e.g. kitchen measuring cup), adjust flow rates as necessary using the peristaltic pump speed dial, submersible pump control box speed dial, or a decontaminated PVC valve installed in the submersible pump discharge line. Discharge water into a 5-gallon bucket or similar that can be used to estimate purge volume. Filled buckets may be discharged to ground near the wellhead.
- 6. Record the make/model of water quality instrument(s) in the field notes. During purging, monitor the following field parameters at regular intervals (e.g. 2 to 5 minutes or every 0.5 gallons): temperature, pH, specific conductivity, dissolved oxygen, depth to water, estimated purge volume, and purge rate. Record the time and measurements in the field sheets. Also note on field sheets any purge water color or odor.
- 7. Continue purging until field parameters have stabilized according to:
 - pH: ± 0.1 standard units
 - Specific conductance: ±10.0 umhos/com for values less than 1,000 umhos/cm, or ±20 umhos/cm for values greater than 1,000 umhos/cm
 - Dissolved oxygen if using a probe (multi-parameter meter): ±0.05 mg/L for values less than 1 mg/L, or ±0.2 mg/L for values greater than 1 mg/L. If using CHEMets: ±0.1 mg/L for values less than 1 mg/L, or ±1 mg/L for values greater than 1 mg/L
 - Temperature: ±0.1 degree C

¹ "dedicated" devices are those permanently installed (left in the wells between sampling rounds).

- 8. Record unique well ID, sample date and time, and sampler's initials on each sample container, in the field notes, and on the Chain-of-Custody. Samples will be labeled in accordance with criteria described in Section 3.3. Bottles should not be filled until they are labeled.
- 9. Hands and clothing shall be clean when handing sampling equipment. Wear clean, disposable, latex gloves when filling bottles for analyses and change gloves between sampling locations. Wearing gloves, disconnect the pump discharge line from the flow through cell. Collect samples of water directly from the discharge line into laboratory-supplied containers for parameters listed in Table 1. Do not use intermediate containers or vessels. If it is necessary to set bottle caps down during sampling, place the caps side up on a clean sheet of plastic or clean plastic storage bag (e.g. sandwich bag). Collect samples in the following manner:
 - Nitrate and nitrite: fill laboratory provided bottle to the top
 - Ammonia and Total Kjedahl Nitrogen (TKN): fill laboratory provided bottle almost to the neck, but do not overfill (see photo in Section 3.1). Bottles for these analyses are provided by the lab containing preservative that should not be washed out by dumping or overfilling.
- 10. Collect QA/QC samples according to Appendix B in the manner described in Step 9.
- 11. Turn off the pump.
- 12. Bag sample bottles in a clean plastic bag and place the bag in a clean, insulated container (ice chest or cooler) containing frozen gel ice or wet ice to maintain sample temperatures at approximately 6 degrees Celsius, but not at or below, freezing. Double bag ice to prevent leakage during shipping. Use sufficient cooling materials to maintain sample temperature near 6 degrees Celsius during the entire time of transport to the lab.
- 13. Remove non-dedicated equipment (e.g. submersible pump) from the well². Dedicated peristaltic or submersible pump tubing may be stored in the well between sampling events provided the tubing is at least the length of the well casing (i.e. can be reached by hand if bottom of tubing rests on bottom of well). Alternately, dedicated pump tubing may be stored in labeled, clean, plastic bags. Secure, and lock the monitoring well.
- 14. Decontaminate non-dedicated submersible pumps, in-line flow valves, and water level sounders according to the following methods. Peristaltic pumps do not come in direct contact with purge or sampling water and therefore do not require decontamination:
 - Fill a clean bucket with sufficient distilled water to submerge the pump motor and intake and pour in approximately 1 ¼ ounces (or 2.5 tablespoons) per gallon of water of LiquinoxTM or similar liquid detergent.

² For certain types of submersible pumps (e.g. Grundfos RediFlo 2TM), it is often easiest and most effective to decontaminate the electrical line as the pump is being removed from the well, especially with a two-person sampling team. Soak heavy paper towel in a distilled water and LiquinoxTM (or similar) solution (See Step 14) and grasp the electrical line in the paper towel with the hand closest to the well. Soak another heavy paper towel in distilled water and grasp the electrical line in the paper towel with the hand farthest away from the wellhead. Have the second team member pull up the pump. Re-soak or replace paper towels as necessary.

- One at a time, scrub the outside of the pump motor, pump electrical line (if not decontaminated during removal), in-line flow valve, and water level sounder (full length placed in the well) in the detergent solution using a clean nylon brush. Pour the detergent solution through the in-line flow valve.
- With the pump intake submerged, turn the pump on to run detergent solution through the pump.
- Rinse the outside of the pump motor, pump electrical line (if not decontaminated during removal), in-line flow valve, and water level sounder thoroughly with distilled water.
- Fill a second clean bucket with sufficient distilled water to submerge the pump motor and intake. Turn the pump on to rinse distilled water through the pump.
- Place decontaminated field equipment in clean bags or tote boxes for transport between stations.
- 15. Maintain custody of samples from time of sampling to receipt at the laboratory. "Custody" means that samples remain:
 - In direct possession of a person who is recorded on the Chain-of-Custody form, or
 - Locked in secure vehicles or offices

Complete the appropriate Chain-of-Custody forms and any other pertinent sampling/shipping documentation to accompany the samples.

Ship or deliver samples to the selected Washington State accredited chemical laboratory, accompanied by Chain-of-Custody forms and any other pertinent shipping/sampling documentation. One set of Chain-of-Custody forms will be used per laboratory shipment.

In order to meet holding times, samples must be received by the lab less than 45 hours from the time they were collected.

3.4 SAMPLE LABELING SYSTEM

Sample bottles will be provided and preserved by the analytical lab(s) chosen for the project. All containers will be clearly labeled in the field with indelible ink, **prior to filling**. Each sample container will be identified with the following information:

- Project (e.g. "LYV GWMA")
- Client/Entity analytical invoice will be submitted to (e.g. "Yakima County Health Department")

- Well ID (or QA/QC nomenclature)
- Well Owner name or Water System name and well name (e.g. "Hedges" or "Sunnyside Well 10")
- Initials of sampler (e.g. "SPS")
- Date and time of sample collection using the 24 hour time system (e.g. "5/16/14 14:20")
- Comments regarding bottle preservation, field filtering

Example labels for one sample (3 bottles) are shown to the right. Note that these labels are presented as examples for the type of information to be included

Client: Yakima Health Dept. Project? Sample <u>2209/3/3003</u> Site <u>Headges</u> Date <u>5/16/14</u> Time <u>14:20</u> Sampler <u>SPS</u> Analysis <u>TKN</u> Comments: Preserved
Client: Yakime Health Dept · LV GWMA Sample <u>2009/3/3003</u> Site <u>Hedges</u> Date <u>5/14/14</u> Time <u>14:20</u> Sampler <u>SPS</u> Analysis <u>Ammonia</u> Comments: <i>Preserved</i>
Client: Yakima Health Dept. LYV GWMA Sample 220913 13003 Site Hedges Date 5/16/14_Time.14:20_Sampler_SPS Analysis_ <u>Nitrate, Nitrite</u> Comments:

only. The actual lab(s) used for the GWMA Groundwater Monitoring program may group analyses into bottles differently than presented.

3.5 SAMPLING SCHEDULE

Sampling schedule should be established following identification of the Groundwater Monitoring well network.

As described in the *Potential Groundwater Stations* report (PGG, 2013), results of approximately 1,000 nitrate and nitrate-related samples are estimated to be required to meet the objective of measuring basin-wide averages at a level of confidence that supports use of the data for future GWMA purposes. Therefore, the sampling frequency is dependent on the number of wells in the Groundwater Monitoring well network.

3.6 WELL NETWORK

The monitoring well network should be established following completion of the Field Verification survey currently being performed by the Yakima County Health Department.

The final Groundwater Monitoring Plan will identify network wells in a table, present the well locations in a figure(s), and provide background of how the network was established.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

The Quality Assurance/Quality Control program is presented in Appendix B and identifies data quality objectives, quality control checks, and data validation and usability.

5.0 REPORTING AND DATA MANAGEMENT

Reporting frequency should be established following identification of the Groundwater Monitoring well network and sampling schedule.

Reports will be prepared to summarize data, update trend and other statistical analysis as appropriate, estimate basin-wide average concentrations as appropriate, identify data gaps or redundancies in the network, and present recommendations for adjustments to the monitoring program.

Water quality data associated with this Groundwater Monitoring Plan will be uploaded to Ecology's Environmental Information Management (EIM) System.

6.0 REFERENCES

Pacific Groundwater Group, 2013. Potential Groundwater Monitoring Stations Yakima Groundwater Management Area. Consultant's report prepared for HDR, Inc., Yakima County, and Lower Yakima Valley Groundwater Advisory Committee. December 3, 2013.

Washington State Department of Ecology, n.d. Lab Search. https://fortress.wa.gov/ecy/laboratorysearch/Default.aspx. Web. February 10, 2014

Washington State Department of Ecology, n.d. Methods and Analytes table. <u>http://www.ecy.wa.gov/programs/eap/labs/lab-accreditation.html</u>. Web. September 4, 2013.



Table 1. Water Quality Parameters of Concern, Analytical Methods, and Project MCLs

Table 1a. Lab Analyzed Parameters

Parameter	Recommended Analytical Method	Alternative Analytical Methods	Preservative	Holding Time	Bottle Type	GWMA Project MCLs ²	PQL Goal ³
Ammonia-N	EPA 350.1	EPA 349.0 / USGS 1-3520-85 / SM4500-NH3 C, D, E, F, G, H, or I / ASTM D1426-08 or -98A / ASTM D 6919-03	H2SO4	28 days	Lab Provided	Not Established	0.3 mg/L or lower
Nitrate	EPA 353.2 ¹	EPA 300.0 / SM 4110 B / SM 4500-NO3 B, D, E, F, H, or I		48 hours	Lab Provided	10 mg/L	1 mg/L or lower
Nitrite	EPA 353.2 ¹	EPA 300.0 / SM 4500-NO2 B / SM 4110 B / SM 4500-NO3 F or I		48 hours	Lab Provided	1 mg/L	0.1 mg/L or lower
Sum of organic nitrogen + ammonia + ammonium (Total Kjeldahl Nitrogen, TKN)	SM 4500-Norg D	EPA 351.1 / EPA 351.2 / SM 4500-Norg B or C / ASTM D1426-93B	H2SO4	28 days	Lab Provided	Not Established	1 mg/L or lower

¹ Method may be used to determine nitrate+nitrite, or nitrate. Nitrate and nitrite (individually) are parameters of concern for this study, while nitrate+nitrite is not. No preservative is used when individually measuring nitrate or nitrite concentrations, and therefore the holding time is 48 hours. If H2SO4 preservative is used the holding time is extended to 28 days, but only nitrate+nitrite concentrations can be measured and not individual nitrate or nitrite concentrations.

² As presented in Groundwater Monitoring Quality Assurance/Quality Control Plan Lower Yakima Valley GWMA Initial Characterization.

³ Practical Quantitation Limits/Lab Reporting Limits for these methods are determined by individual labs. Practical Quantitation Limits/Lab Reporting Limits must be 10-percent of Project MCLs or lower for nitrate and nitrite. PQL Goals for Ammonia and TKN based on the maximum PQL among 6 accredited labs located in Eastern Washington based on June 27, 2014 survey

Analytical Methods consistent with Ecology's Methods and Analytes Table at: http://www.ecy.wa.gov/programs/eap/labs/lab-accreditation.html

Discrepancies between Preservation/Holding Time between this table and the Analytical Methods should be resolved in favor of the Analytical Method

Table 1b. Field Parameters

Parameter	Meter	Stabilization Criteria
рН	Water Quality Meter	±0.1 standard units
Specific Conductance	Water Quality Meter	±10 umhos/cm for values <1,000 umhos/cm; ±20 umhos/cm for values >1,000 umhos/cm
Temerature	Water Quality Meter	±0.1 degrees Celsius
Dissolved Oxygen	Water Quality Meter or CHEMets™	Water Quality Meter: ±0.05 mg/L for values <1mg/L; ±0.2 mg/L for values > 1mg/L CHEMets™: ±0.1 mg/L for values < 1 mg/L; ±1 mg/L for values > 1 mg/L

Table 2. Ecology Accredited Labs for GWMA Parameters of Concern*

			_		Accredited GWMA Parameters of Concern				
Analytical Lab Name	City	State	Phone	Accreditation No.	Ammonia	Nitrate	Nitrite	TKN	
AAA Laboratory	Cheney	WA	(509) 235-9390	C576-13	х	х	х	х	
ALS Environmental - Kelso	Kelso	WA	(360) 577-7222	C544-13a	х	Х	х	х	
AmTest Laboratories	Kirkland	WA	(425) 885-1664	C554-13	х	Х	х	х	
Analytical Resources, Incorporated	Tukwila	WA	(206) 695-6205	C558-13b	х	х	х	х	
Anatek Labs, Inc Spokane	Spokane	WA	(509) 838-3999	C585-13	х	х	х	х	
Aquatic Research, Inc.	Seattle	WA	(206) 632-2715	C550-13	х	х	х	х	
Archer Analytical	Richland	WA	(509) 375-6147	C872-13	х	х	х	х	
Avocet Environmental Testing	Bellingham	WA	(360) 734-9033	C602-13	х	х	х	х	
Benton-Franklin Health District Lab	Kennewick	WA	(509) 460-4206	H408-13	х	х	х	х	
Cascade Analytical, Inc Wenatchee	Wenatchee	WA	(509) 662-1888	C564-13	х	х	х	х	
Centric Analytical Labs, LLC	Port Orchard	WA	(509) 844-6597	C1003-13a	х	х	х	х	
Dragon Analytical Laboratory, Inc	Olympia	WA	(360) 866-0543	C890-13	х	х	х	х	
Edge Analytical, Incorporated	Burlington	WA	(800) 755-9295	C567-14a	х	х	х	х	
Everett Environmental Laboratory	Everett	WA	(425) 257-8230	M667-13	х	х	х	х	
Mukang Labs, Inc.	Pasco	WA	(509) 544-2159	C914-13	х	х	х	х	
Soiltest Farm Consultants, Inc. Laboratory	Moses Lake	WA	(509) 765-1622	C605-13	х	х	х	х	
Spectra Analytical, Inc.	Tacoma	WA	(253) 272-4850	C575-13a	х	х	х	х	
Tshimakain Creek Laboratories	Spokane	WA	(509) 928-3577	T975-13	х	х	х	х	
Twiss Analytical Laboratories, Inc.	Poulsbo	WA	(360) 779-5141	C594-13	х	х	х	х	
Valley Environmental Laboratory	Yakima	WA	(509) 575-3999	C862-13	х	х	х	х	
Water Management Laboratories, Inc.	Tacoma	WA	(253) 531-3121	C546-13	х	х	х	х	
Weyerhaeuser Analysis & Testing	Federal Way	WA	(253) 924-4294	C551-13	Х	х	х	х	
Anatek Labs, Inc Moscow	Moscow	ID	(208) 883-2839	C595-13a	х	x	х	x	
APPL, Incorporated	Clovis	CA	(559) 275-2175	C790-13	Х	х	х	х	
BSK Associates	Fresno	CA	(559) 497-2888 Ext.125	C997-13b	х	х	х	х	
CH2M Hill Applied Sciences Laboratory - Corvallis	Corvallis	OR	(541) 768-3111	C556-13	Х	х	х	х	
Environmental Science Corporation	Mt. Juliet	TN	(615) 758-5858	C847-13	х	х	х	х	
Eurofins Lancaster Laboratories, Inc.	Lancaster	PA	(717) 556-7327	C457-13	х	х	х	х	
<u>GEL Laboratories, LLC</u>	Charleston	SC	(843) 556-8171	C780-13	х	х	х	х	
Pace Analytical Services, Inc Billings	Billings	MT	(612) 607-1700	C993-13	х	х	х	х	
Pyxis Laboratories LLC	Portland	OR	(503) 254-1794	C924-13	х	х	х	х	
Specialty Analytical	Clackamas	OR	(503) 612-9007	C804-13	х	х	х	х	
SVL Analytical, Incorporated	Kellogg	ID	(208) 784-1258	C573-13	х	х	х	х	
TestAmerica Denver	Arvada	СО	303-736-0116	C583-13	х	х	х	х	
TestAmerica Nashville	Nashville	TN	(615) 301-5759	C789-13	Х	Х	Х	Х	

*As downloaded from Ecology's Lab Search Website February 10, 2014. https://fortress.wa.gov/ecy/laboratorysearch/Default.aspx

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APPENDIX A EXAMPLE FIELD SAMPLING AND INSTRUMENT CALIBRATION FORMS

Lower Yakima Valley Groundwater Management Area Supply Well Sampling Field Form

Date:				Weather:				
Sampler:								
Well ID:				Well Owner/System Name and Well Name:				
Wellhead	Condition:			<u> </u>				
Sampling	Point Descrip	otion:						
Time Spig Water Qu	ot Turned Or ality Meter(s):						
Time	Temp Circle:C/F	рН	Ec umhos/cm	Diss. Ox mg/L	Comments (odor, color, bubbles, etc.)			

Sample Date/Time:

Analytical Lab:

Number of Unpreserved Bottles Collected (Nitrate, Nitrite):

Number of Preserved Bottles Collected (Ammonia, TKN):

Lower Yakima Valley Groundwater Management Area Monitoring Well Sampling Field Form

Sampler:			
Well ID: Wellhead Condition:			
Well Diameter (circle):2 inch (gal/ft factor = 0.17)4 inch (gal/ft factor = 0.65)	4 inch (gal/ft factor = 0.65)		
Total Well Depth (TD) in feet below measuring point (ft bmp):			
Depth to Water (DTW) ft bmp:			
Height of Water (h) [calculate by TD-DTW] ft:			
One Casing Volume [calculate by h x gal/ft factor from Well Diameter] gal:			
Purge Volume [calculate by One Casing Volume x 3] gal:			
Pumping Method (circle): Peristaltic / Submersible (specify type):			
Water Quality Meter(s):			
Time Volume Temp Ec pH Diss. Ox DTW Rate Comment gallons Circle: C/E umbos/cm mg/L ft hmp mL/min			
Table continued on page 2 (circle): Yes / No			
Sample Date/Time·			

Number of Unpreserved Bottles Collected (Nitrate, Nitrite):

Number of Preserved Bottles Collected (Ammonia, TKN):

Monitoring Well Sampling Field Form Continued...

Well ID:	Wellhead Condition:

Time	Volume	Temp	Fc	рН	Diss. Ox	DTW	Rate	Comment
· ····c	gallons	Circle:C/F	uS/cm	P.1	mg/L	ft bmp	mL/min	connent

Lower Yakima Valley Groundwater Management Area Field Instrument Calibration Form

Date:

Start of Day	Time:		Field Staff:		
		Standard	Reading	Adjusted To	
	рН	4.00			
	рН	7.00			
	Ec (umhos/cm)	1413			
	Diss Ox	Aerated Water		NA (see text)	
Mid Day	Time:		Field Staff:		
		Standard	Reading	Adjusted To	
	рН	4.00			
	рН	7.00			
	Ec (umhos/cm)	1413			
	Diss Ox	Aerated Water		NA (see text)	
End of Day	Time:		Field Staff:		
		Standard	Reading		
	рН	4.00			
	рН	7.00			
	Ec (umhos/cm)	1413			
	Diss Ox	Aerated Water			

APPENDIX B GROUNDWATER MONITORING QUALITY ASSURANCE/QUALITY CONTROL PLAN LOWER YAKIMA VALLEY GWMA INITIAL CHARACTERIZATION GROUNDWATER MONITORING QUALITY ASSURANCE/QUALITY CONTROL PLAN LOWER YAKIMA VALLEY GWMA INITIAL CHARACTERIZATION

> September 16, 2013 Revised August 15, 2014

GROUNDWATER MONITORING QUALITY ASSURANCE/QUALITY CONTROL PLAN LOWER YAKIMA VALLEY GWMA INITIAL CHARACTERIZATION

Prepared for:

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QA/QC APPROVALS

This Groundwater Monitoring QA/QC Plan, developed September 16, 2013 for the Lower Yakima Valley Groundwater Management Area, has been reviewed and approved by the undersigned. Copies of the completed and signed QA/QC Plan shall be distributed to the undersigned and all field personnel.

Lower Yakima Valley Groundwater Management Committee	Date
Project Manager	Date
Analytical Lab Project Manager	Date
OC Coordinator	Date

This Groundwater Monitoring Quality Assurance/Quality Control Plan has been prepared as an appendix to the forthcoming Groundwater Monitoring Plan, which has an anticipated publication date of March 2014. References to the Groundwater Monitoring Plan within this appendix should be understood as information that will be available in the future.

Project Background, Project Objectives, Scope of Work, and Sampling Protocols will be detailed in the Groundwater Monitoring Plan and are not included herein.

This work was performed under HDR contract #CON0082545 and partially fulfills scope Item 1a. The QA/QC Plan was prepared in accordance with hydrogeologic practices generally accepted at this time in this area, for the exclusive use of the Lower Yakima Valley Groundwater Advisory Committee and HDR, for specific application to the Initial Characterization. No other warranty, express or implied, is made.

1.0 INTRODUCTION

This Quality Assurance/Quality Control (QA/QC) Plan has been developed as an appendix to the Groundwater Monitoring Plan for the Lower Yakima Valley Groundwater Management Area (GWMA) Initial Characterization. The QA/QC Plan has been prepared in general accord with U.S. Environmental Protection Agency (EPA) (EPA, 2002) and Washington State Department of Ecology (Ecology) (Ecology, 2004) guidelines and specifications. This document addresses:

- Data Quality Objectives for stations (groundwater quality sampling stations) and analytical data
- Quality Control Checks for field and laboratory
- Analytical methods
- Data Validation and Usability

While this QA/QC Plan is intended to be comprehensive, revisions and/or amendments may be required as the project evolves. Descriptions of the project background, project objectives, scope of work, and field protocols are provided in the Groundwater Monitoring Plan.

1.1 OBJECTIVE

The Initial Characterization will be developed from existing water quality data collected during previous investigations, and future water quality data that will be collected as described in the Groundwater Monitoring Plan. The Initial Characterization will be used by the Groundwater Advisory Committee (GWAC) to make administrative decisions and policy recommendations; therefore, the data inputs must be reliable and defensible. This QA/QC Plan defines the quality of data necessary for various uses within the Initial Characterization.

"Core data" as used in this project is the information that Pacific Groundwater Group recommended for inclusion in the project database related to groundwater quality samples (PGG, 2013). These data include analytical and field test results for parameters of concern (Section 1.2), station location, and well construction information.

QA/QC data for the project consists of information that documents the accuracy and precision of the analytical results. Each analytical batch should have associated QA/QC data, which may include results of method blanks, laboratory replicates, and field duplicates. QA/QC data, where available, will also be uploaded to the project database for the parameters of concern.

Data Quality Objectives (DQO) for the project are described in Section 2.0 of this QA/QC Plan. Station DQOs will be used to evaluate lateral and vertical distribution of the sampling network and to evaluate potential bias that could be introduced from treatment or wells with poor surface seals. Analytical DQOs will be used to evaluate representativeness, precision, and potential bias from sampling or lab artifacts. Stations

and analytical sets that do not meet DQOs may be qualified or considered unacceptable for some or all project needs.

1.2 PARAMETERS OF CONCERN AND PROJECT MCLS

As described in the Groundwater Monitoring Plan, the GWMA was formed in response to elevated nitrate concentrations in groundwater in Lower Yakima Valley. The boundaries of the GWMA are presented in Figure 1. The concentrations of nitrate detected in groundwater indicate impact by human activity and may pose significant risk to human health in localized areas. The GWMA was formed with the stated purpose of reducing nitrate concentrations in groundwater to below drinking water standards.

Based on previous investigations and the GWMA's purpose, the parameters of concern for this study are:

- Nitrate
 Ammonia-nitrogen
- Nitrite
 Sum of organic nitrogen + ammonia + ammonium (Total Kjeldahl Nitrogen)

These parameters are a subset of inorganic parameters that are referred to as conventionals. Recommended and alternative analytical methods and holding times (from sample collection to analysis) are summarized in Table 1. The analytical method list in Table 1 was derived from Ecology's *Methods and Analytes Table* on their environmental lab accreditation website (Ecology, n.d.). The recommended analytical methods meet the PQL requirements, are common analytical methods, and have frequently been used by PGG in characterization studies. Alternative analytical methods are listed so that multiple labs (which may use acceptable but different methods of analysis from the recommended methods) could be contracted to analyze the parameters of concern. If there are discrepancies regarding preservation or holding time between Table 1 and the analytical method, the analytical method shall be considered correct. Since nitrate and nitrite are being analyzed individually, rather than combined as nitrate+nitrite, the sample bottles will not have a sulfuric acid preservative. When sulfuric acid preservative is added to a sample, only nitrate+nitrite concentrations can be measured and not individual concentrations of nitrate or nitrite.

Method detection limits (MDLs) are the minimum concentration of an analyte that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero. Analytical methods may specify MDLs or may describe procedures for establishing MDLs. Practical Quantitation Limits (PQLs) or lab Reporting Limits are the minimum concentration of an analyte that can be reliably achieved during routine laboratory operating conditions within specified limits of precision and accuracy. PQLs and Reporting Limits are greater than MDLs and are statistically determined by individual labs. Because the analytical labs for this project have not been identified, PQLs and lab Reporting Limits cannot be specified in this QA/QC Plan. PQLs and lab Reporting Limits must be 10-percent or less of the GWMA Project Maximum Contaminant Levels (MCLs) defined below for nitrate and nitrite.

these parameters in Table 1 based on a June 27, 2014 survey of six accredited labs in eastern Washington.

Water quality standards or criteria established by regulatory agencies will be used to evaluate analytical results for the parameters of concern listed above. Standards applicable to the GWMA groundwater studies are EPA MCLs, Washington State Public Water Supply MCLs (WAC 246-290-310), and Washington State Groundwater Quality Criteria (WAC 173-200-050). Established standards for the GWMA parameters of concern are generally consistent between these regulations (Table 2). GWMA Project MCLs are based on the most stringent relevant regulatory water quality standards and are summarized in Table 2.

Water quality standards have not been established for ammonia-nitrogen or the sum of organic nitrogen + ammonia + ammonium under the regulations cited above; however, these analytical results may be useful for trend evaluation and for understanding nitrogen speciation.

2.0 DATA QUALITY OBJECTIVES

DQOs are qualitative and quantitative criteria established to limit uncertainty in analytical results. They are established to create analytical data sets that will support the study objectives. It is important to meet DQOs in order to produce analytical results that are considered defensible and reliable.

2.1 STATION DATA QUALITY OBJECTIVES

"Station Metadata" for this project refers to physical and access details about sampling stations, including the station location, owner and/or tenant name and contact information, well construction, and sampling point. Station DQOs will be used to:

- Understand the lateral distribution of the stations
- Understand what aquifer system (e.g. shallow or deep) the stations represent
- Understand potential bias in samples from surface contamination
- Understand potential bias in samples from treatment
- Identify stations for long-term monitoring consideration

A decision tree for evaluating Station Metadata against DQOs is presented in Figure 2. The DQOs may be used to evaluate those stations acceptable for Data Gap and Trend Analyses, and those acceptable for Long-Term Monitoring.

Data Gap and Trend Analyses DQOs. Station location and indications of completion depth and surface seals for wells are the DQOs for a station to be considered for Data Gap and Trend Analyses. Locations must be available by either coordinates in a known datum (preferred) or by a current parcel number. Station location information may be refined during field work. For wells, documented depth information must be available either for the open interval (preferred) or for the total depth of the well. Well depth

should be documented on a well log, video log, maintenance log, pump installation records, or similar means of documentation. An owner's recollection of total depth will not be considered valid documentation. An adequate surface seal should be documented in a well log. If no well log is available, field tests may be used to confirm the presence of seal material; however, field tests cannot confirm that the depth of the surface seal is adequate. Therefore, professional judgment shall be used to decide whether a well with a positive field test for the presence of a surface seal be advanced through the decision tree. A primary factor to consider is how critical the station is relative to other available stations in the area. Special consideration may be given to wells that do not meet the surface seal criterion in areas with limited stations; however, comparison of analytical results relative to project MCLs would not be valid.

Long-Term Monitoring Consideration DQOs. To be considered for Long-Term Monitoring, stations must meet the Data Gap and Trend Analyses DQOs plus long-term access to the station must be available. For well stations, the sampling port should be upstream of treatment. Long-term access and information about available sampling ports may be collected during field work. Special consideration may be given to wells that do not meet the sampling port relative to treatment criterion in areas with limited stations; however, comparison of analytical results relative to project MCLs would not be valid.

2.2 ANALYTICAL DATA QUALITY OBJECTIVES

QA/QC data associated with water quality samples can be used to assess the accuracy and precision of the analytical results. This QA/QC Plan stipulates the QA/QC data required for water quality samples, and the DQOs to evaluate the QA/QC data against. However, it is likely that some water quality data from previous investigations will not have available QA/QC data.

The availability and acceptability of QA/QC data will affect how sample results may be used in the GWMA Initial Characterization. A decision tree to assess usability of the analytical metadata is presented in Figure 3. If station location and depth information is available (Section 2.1), all existing analytical data will be considered in the evaluation of Data Gaps and Trends, regardless of whether associated QA/QC data are available. Water quality results with available QA/QC data that meet DQOs described in this section and water quality results associated with the Washington State Department of Health (DOH) compliance monitoring of public water systems will be considered in the evaluation of Data Gaps and Trends, and in addition will be used to establish Baseline Water Quality, evaluate Compliance with project MCLs, and establish Long-Term Monitoring Data. While QA/QC data associated with DOH compliance monitoring are not available, the data will be considered acceptable for the additional evaluations because the analytical labs are required to be accredited by Ecology; and samples are required to be collected and transported according to EPA or DOH approved methods (WAC 246-290-300 and WAC 246-291-300).

DQOs for analytical data are typically expressed in terms of accuracy, precision, representativeness, completeness, and comparability. Definitions of these terms follow.

Accuracy. Accuracy is how close an analytical result is to the true concentration in the sample. For conventional parameters, accuracy is analytically evaluated with spike samples.

A spike QA sample is prepared by adding a known concentration of an indicator parameter to an environmental sample. The indicator parameter should be the same or similar (for isotopically labeled compounds) as the target analyte. The spike should increase the concentration in the environmental sample by a predictable amount.

The analytical lab shall calculate and report the percent recovery (% R) of the target analyte in the spiked sample by:

$$\%R = \left(\frac{SSR - SR}{SA}\right) \times 100$$

Where:

SSR = measured value of analyte concentration in sample after addition of spike SR = measured value of analyte concentration in sample before addition of spike SA = value of spike added

The GWMA QA Reviewer (QA Reviewer) shall evaluate accuracy by comparing the %R to acceptable limits statistically determined by the laboratory (Section 4).

Precision. Precision measures the reproducibility of results and can be evaluated through field duplicate (collocated samples collected in the field that are analyzed independently) and lab replicate (aliquots prepared in the lab of the same sample that are analyzed independently).

Field duplicates will be collected on at least a 10 percent frequency (1 duplicate per 10 samples collected). At least one field duplicate shall be collected each event (Section 3.1). Lab replicates may be analyzed according to an individual lab's Standard Operating Procedure (SOP). Lab replicates are prepared in the lab by taking an aliquot of an environmental sample and treating that aliquot throughout the analytical method as though it were another sample.

Relative Percent Differences (RPD) values between field duplicates shall be calculated by the QA Reviewer and RPD values between lab replicates shall be calculated and reported by the lab. RPDs are calculated by:

$$RPD = \frac{|(D1 - D2)|}{\frac{D1 + D2}{2}} \times 100$$

Where:

D1 = measured concentration of duplicate or replicate 1 D2 = measured concentration of duplicate or replicate 2 The QA Reviewer shall evaluate precision by comparing the RPD to acceptable limits (Section 4). For this study, the acceptable RPD limits for field duplicates shall be 20 percent or \pm the lab reporting limit if the concentration of either the sample or duplicate is less than 5 x the lab reporting limit. The acceptable RPD limits for lab replicates shall be statistically established by the analytical lab.

Representativeness and Comparability. Representative samples accurately represent the environmental matrix being tested. Comparable samples are collected during different sampling events, but at the same station. For this study, representativeness and comparability shall be achieved by following the field sampling protocols and methods described in the Groundwater Monitoring Plan, using the same analytical methods, and to the degree possible, the same analytical lab.

As described in the Groundwater Monitoring Plan, the majority of water samples collected for this study will be collected directly into laboratory-provided bottles without the use of non-dedicated or non-disposable sampling devices such as bailers, portable pumps, dippers, or grab samplers. When non-dedicated or non-disposable sampling devices are used, representativeness and comparability will be evaluated using rinsate or decontamination blanks (Section 3.1). These blanks will be collected following decontamination of the sampling device, on at least a 10 percent frequency (1 blank per 10 samples collected with a non-dedicated or non-disposable sampling device) and a minimum of 1 blank will be collected per event where non-dedicated sampling devices are used.

Completeness. Completeness is the percentage of valid results obtained from a given sampling event. For this study, completeness is anticipated to be equal or better than 85 percent.

3.0 QUALITY CONTROL CHECKS

Quality control checks will be performed by project field staff and by the analytical lab as described below.

3.1 FIELD QUALITY CONTROL

Field quality control checks are summarized in Table 3.

Field Duplicates will be collected at a rate of at least 10 percent as described in Section 2.0. After collection of the original sample, a duplicate shall be collected by filling another set of laboratory-provided bottles using the same sampling procedure. Field duplicates shall be analyzed for each parameter of interest. Field duplicates will be labeled with a unique sample ID and collection date/time. Field sample forms shall document the stations where field duplicates were collected, the duplicate ID, and duplicate sample time.

Rinsate or decontamination blanks will be collected at a rate of at least 10 percent of samples collected per sampling team with non-disposable or non-dedicated equipment. After the non-dedicated equipment is decontaminated following procedures described in

the Groundwater Monitoring Plan, a rinsate or decontamination blank shall be collected by transferring commercially available distilled water from the sampling equipment to a set of laboratory-prepared bottles, or by pouring distilled water over the equipment and collecting the water that that rinses off in a set of laboratory-prepared bottles. The rinsate or decontamination blank shall be labeled with a unique sample ID and collection date/time. Field sample forms shall document the stations where field blanks were collected, the blank ID, and blank sample date/time.

Matrix Spike and Matrix Spike Duplicates (MS/MSD) will be analyzed per batch of samples. MS/MSDs prepared from samples collected for the GWMA project are preferred over MS/MSDs prepared from samples collected for another project that may be part of the same analytical batch. This may require additional volume to be collected in the field. The Field Sampling Manager or Lead should confer with the analytical lab about additional volume requirements when placing the bottle order. Sample bottles for MS/MSD analysis will be labeled with the station ID followed by "-MS/MSD" and field forms will document where the MS/MSD are collected.

3.2 LABORATORY QUALITY CONTROL

Analytical services for this study will be provided by labs accredited by Ecology for drinking water or non-potable water analyses of the parameters of concern (there are currently no drinking water accredited labs for analyses of ammonia or TKN, there are non-potable water accredited labs for these parameters). Prior to mobilization to the field, the lab will provide proof of Ecology accreditation for analytical methods and matrices related to this QA/QC Plan. Labs routinely perform performance checks and each analytical method requires specific QA/QC protocols that must be complied with by the lab. No additional audits will be performed on the analytical labs for this study.

The analytical lab will follow their written QA/QC Plan and Standard Operating Procedures (SOP) to assure data quality. Lab QC samples will be analyzed in accordance with the lab QA/QC Plan, SOP, and analytical method and may include the following:

- Method blanks are used to assess contamination that may be introduced in the lab during sample preparation. Method blanks are prepared, extracted, digested, and analyzed in the same manner as field samples. Analytical results will be included in lab reports.
- Laboratory control samples (LCS) are used to evaluate the performance of the total analytical system, including all preparation and analysis steps. They contain known concentrations of the analytes of interest and the percent recovery reflects the accuracy of the analysis. Analytical results will be included in lab reports.

Lab QA/QC also typically includes instrument-related calibration blanks and performance checks. Instrument-related QA/QC results will not be included in lab reports, but will be made available on request if other QA/QC results are considered unacceptable.

4.0 DATA VALIDATION AND USEABILITY

Data validation will be performed by the lab in accordance with their QA/QC plan and SOP prior to the release of the analytical results. The lab shall document their data validation in a case narrative, identifying any QA/QC recoveries that were outside the lab's acceptance criteria, and potentially flagging or reanalyzing unacceptable results.

The QC Reviewer will review field notes for compliance with sampling protocols described in the Groundwater Monitoring Plan and will validate the analytical data in accordance with the QA/QC requirements specified in this QA/QC Plan and the analytical methods. The analytical reports shall be checked for completeness that the data requested has been delivered. They shall also be checked for compliance of the analytical QA/QC results with acceptance limits. Data validation will also include review of the method blanks, holding times, and lab reporting limits.

DQOs or acceptance limits for Percent Recoveries (%R) of spike samples, including matrix spikes, shall be established statistically by the lab and provided in the lab reports. In the event that statistical acceptance limits are not available, the following limits from the Quality Assurance Project Plans for the Yakima Basin Nitrate Study Phase 3 (U.S. EPA, 2010b) and Lower Yakima Valley Dairy Investigation (SAIC, 2012) shall be applied:

- Accuracy (percent recovery of spikes including laboratory control samples and matrix spikes): 80-120 percent
- Precision (lab replicate and matrix spike duplicate): ± 20 percent

For this study, the acceptable RPD limits for field duplicates shall be 20 percent or \pm the lab reporting limit if the concentration of either the sample or duplicate is less than 5 x the lab reporting limit.

Data associated with QA/QC results that fall outside acceptance limits may be qualified or rejected. The EPA Contract Laboratory Program National Functional Guidelines for Inorganic Superfund Data Review (EPA 2010a) generally do not extend to conventional parameters; however, the guidelines may be referred to for qualification guidance. Findings and conclusions of the Data Validation will be summarized in a narrative by the QC Reviewer.

As presented in Figure 3 and described in Section 2.2, all existing analytical data will be considered in the evaluation of Data Gaps and Trends, regardless of whether associated QA/QC data are available or whether associated QA/QC data meet Analytical DQOs (acceptance limits) described in this Plan. Analytical results with QA/QC data that meet DQOs and analytical data associated with DOH compliance monitoring of public water systems will be considered to meet project needs to be valid for: Data Gaps and Trend analyses, establishing Background Water Quality, evaluating Compliance with project MCLs, and establishing Long-Term Monitoring Data.

5.0 REFERENCES

- Pacific Groundwater Group, 2013. Core Data Recommendations. Consultant's technical memorandum prepared for Yakima County and HDR. July 29, 2013.
- SAIC. 2012. Quality Assurance Project Plan Lower Yakima Valley Dairy Investigation Yakima County, Washington. Consultant's plan prepared for U.S. Environmental Protection Agency, Region 10. December 2012.
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- Washington State Department of Ecology, 2004. Guidelines for Preparing Quality Assurance Project Plans for Environmental Studies. Publication No. 04-03-030. Revision of Publication No. 01-03-003. July 2004.
- Washington State Department of Ecology, n.d. Methods and Analytes Table. <u>http://www.ecy.wa.gov/programs/eap/labs/lab-accreditation.html. Web. September 4</u>, 2013.

Table 1. Water Quality Parameters of Concern and Analytical Methods

Parameter	Recommended Analytical Method	Alternative Analytical Methods	Preservative	Holding Time	Bottle Type	PQL/Lab Reporting Limit Goals ²
Ammonia-N	EPA 350.1	EPA 349.0 / USGS 1-3520-85 / SM4500-NH3 C, D, E, F, G, H, or I / ASTM D1426-08 or -98A / ASTM D 6919-03	H2SO4	28 days	Lab Provided	PQL Goal 0.3 mg/L or lower
Nitrate	EPA 353.2 ¹	EPA 300.0 / SM 4110 B-00 / SM 4500-NO3 B, D, E, F, H, or I		48 hours	Lab Provided	PQL must be 10-percent or less of GWMA MCLs (Table 2), or 1 mg/L
Nitrite	EPA 353.2 ¹	EPA 300.0 / SM 4500-NO2 B / SM 4110 B / SM 4500-NO3 F or I		48 hours	Lab Provided	PQL must be 10-percent or less of GWMA MCLs (Table 2), or 0.1 mg/L
Sum of organic nitrogen + ammonia + ammonium (Total Kjeldahl Nitrogen, TKN)	SM 4500-Norg D	EPA 351.1 / EPA 351.2 / SM 4500-Norg B or C / ASTM D1426-93B	H2SO4	28 days	Lab Provided	PQL Goal 1 mg/L or lower

¹ Method may be used to determine nitrate+nitrite, or nitrate. Nitrate and nitrite (individually) are parameters of concern for this study, while nitrate+nitrite is not. No preservative is used whe individually measuring nitrate or nitrite concentrations, and therefore the holding time is 48 hours. If H2SO4 preservative is used the holding time is extended to 28 days, but only nitrate+nitrite concentrations can be measured and not individual nitrate or nitrite concentrations.

² Practical Quantitation Limits/Lab Reporting Limits for these methods are determined by individual labs and therefore are not specified in this QA/QC Plan. Practical Quantitation Limits/Lab Reporting Limits must be 10-percent of Project MCLs or lower for nitrate and nitrite. PQL Goals for ammonia and TKN are based on a June 27, 2014 survey of six accredited labs located in eastern Washington.

Analytical Methods consistent with Ecology's Methods and Analytes Table at: http://www.ecy.wa.gov/programs/eap/labs/lab-accreditation.html

Discrepancies between Preservation/Holding Time between this table and the Analytical Methods should be resolved in favor of the Analytical Method

	Relevant Re	GWMA			
Parameter	EPA MCLs	WA Public Water Supply MCLs	WA Groundwater Quality Criteria	Project MCLs	
Ammonia-N	Not Established	Not Established	Not Established	Not Established	
Nitrate (as N)	10 mg/L	10 mg/L	10 mg/L	10 mg/L	
Nitrite (as N)	1 mg/L	1 mg/L	Not Established	1 mg/L	
Sum of organic nitrogen + ammonia + ammonium (Total Kjeldahl Nitrogen (TKN))	Not Established	Not Established	Not Established	Not Established	

Table 2. Relevant Regulatory Water Quality Standards and GWMA Project MCLs

EPA MCLs established by Safe Drinking Water Act (SDWA)

WA Public Water Supply MCLs established by WAC 246-290-310

WA Groundwater Quality Criteria established by WAC 173-200-040

Practical Quantitation Limits/Lab Reporting Limits for these methods are determined by individual labs and are therefore not specified in this QA/QC Plan. Practical Quantitation Limits/Lab Reporting Limits must be 10-percent of Project MCLs or lower.

Type of Quality Control Check	Minimum Frequency	Bottle ID	Process
Field Duplicates	1 per 10 samples collected	Station ID + 200	After collection of the original sample, fill a second set of laboratory-provided bottles using the same sampling procedure. Label the duplicate uniquely and analyze for all sampling event parameters.
Rinsate/ Decontamination Blank	1 per 10 samples per team collected with non- disposable or non- dedicated equipment	Station ID + 100	Decontaminate the non-dedicated/non- disposable equipment following procedures described in the Work Plan. Transfer commercially available distilled water from the sampling equipment to a set of laboratory-prepared bottles, or pour DI water over the equipment and collect the water that rinses off in a set of lab-prepared bottles. Label the blank uniquely and analyze for all sampling event parameters.
MS/MSD	1 per event	Station ID + "-MS/MSD"	After collection of the original sample, fill a second and third set of laboratory- provided bottles using the same sampling procedure. Label the bottles with the addition of "-MS/MSD" and analyze for all sampling event parameters.

Table 3. Field Quality Control Summary

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