



Benton Conservation District



Quality Assurance Project Plan

Benton County Groundwater Nitrate Monitoring Study

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September 2015

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1.0 Abstract

Nitrate groundwater contamination is a potential public health issue in Benton County. An understanding of the potential contaminant sources and pathways are not well characterized or understood for the county's groundwater supply. Before an effective and targeted management program can be built, the magnitude and extent of nitrate contamination within the county must first be characterized. This project, to be implemented by the Benton Conservation District, will help build that foundation through the targeted and systematic collection of new sampling data from approximately two-hundred groundwater wells. The new data are to be collected seasonally over the course of the two-year study to help identify the influence of potential nitrate sources or nitrate dilution sources (such as irrigation water) and seasonal changes to the groundwater nitrate contaminant levels.

This Quality Assurance Project Plan (QAPP) governs the methods, study design, and data quality procedures for the *Benton County Groundwater Nitrate Monitoring Study*. The groundwater nitrate monitoring study is part of sub-task 4 under the larger FY2016 Water Quality Financial Assistance Program agreement: WQC-2015-BentCD-00102 - *Groundwater Nitrate Characterization, Monitoring and Stakeholder Engagement*. The results from this nitrate monitoring will feed into the larger grant effort aimed at developing a stakeholder group, public health campaign, and nitrate groundwater quality improvement. The public health campaign will alert residents to the vulnerability of their groundwater supply and inform them as to how they can be involved in groundwater protection.

2.0 Background

2.1 Study area

The study area for this project is Benton County, Washington, exclusive of the Hanford Site, which encompasses 857,309 acres or 1,340 square miles. It includes portions of Water Resource Inventory Areas (WRIA) 31 (Rock/Glade), 37 (Lower Yakima), and 40 (Alkali Squilchuck) in south central Washington State. The Rock/Glade WRIA is bordered to the north by the Horse Heaven Hills, a broad east-west ridge, and to the south and east by the Columbia River; the City of Kennewick is included in the Rock/Glade WRIA. The Lower Yakima WRIA is bordered to the south by the Horse Heaven Hills and the North/East by the USDOE Hanford Site. The Alkali/Squilchuck WRIA encompasses the USDOE Hanford site and the City of Richland. Figure 1 shows the study area and WRIA's within Benton County.

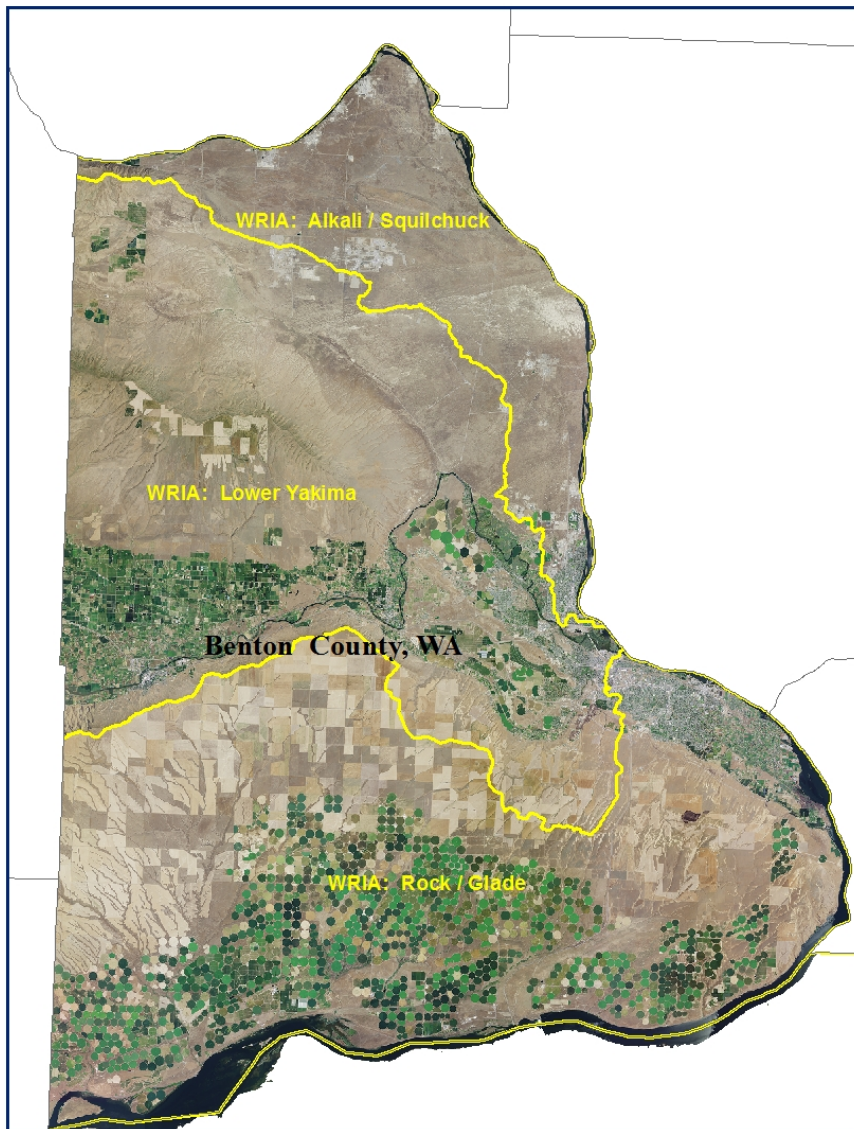


Figure 1. Map of Study Area (Benton County, WA) and WRIA units.

2.2 Study logistical problems

Candidate sampling wells will be selected based on several factors including: locations that characterize extent and magnitude of nitrate distributions in Benton County; wells with a previous history of sampling; wells that are open to different hydro-stratigraphic units and well accessibility. The primary logistical problems for the project will be accessibility of the wells for nitrate sampling collection. Well access may be limited either because of physical constraints or landowner willingness. Sampling of privately owned wells requires landowner permission. Some candidate wells may not be sampled if landowner consent is not provided. If a selected candidate well is not available for sampling, the project hydrogeologist will select a suitable alternate well for sampling.

Scheduling conflicts, bad weather, logistics with sample delivery, or vehicle problems may interfere with the outlined sampling schedule. Any circumstances that interfere with scheduled data collection and quality will be noted and discussed in the final report.

2.3 History/Setting of study area

2.3.1 Physical Setting

The Rock/Glade WRIA encompasses John Day Dam to the west and Kennewick, WA to the east. This watershed is divided into four sub basins: Rock Creek, Wood/Alter Creeks, Glade-Fourmile Creeks, and Kennewick. Only Glade-Fourmile Creeks and Kennewick sub basins are included within the boundaries of Benton County. The maximum elevation of the Glade-Fourmile Creeks sub basin is 3,596 feet along the ridge of the Horse Heaven Hills. The minimum elevation is 266 feet along the Columbia River. The Glade-Fourmile Creeks sub-basin is generally characterized by elevated plateaus, gentle slopes, but locally dissected by deep canyons. Under normal precipitation conditions, this results in relatively low stream velocities and erosion potential. The Kennewick sub basin has a maximum elevation of 2,198 feet, along the ridge of the Horse Heaven Hills and a minimum elevation of 341 feet along to Columbia River. The slightly higher slopes on the southern boundary of the Kennewick sub-basin are a result of the change in elevation over a smaller footprint area. The slightly higher slopes lead to moderate incised canyons draining the watershed from south to north.

The Lower Yakima WRIA spans east to west from the crest of the Cascade Range to the Columbia River. Approximately half of Benton County, north of the Horse Heaven Hills ridgeline, lies within the lower reaches of the Lower Yakima WRIA. In the southern portion of the Lower Yakima WRIA, within Benton County boundary, the mainstem Yakima River is joined by three tributary wasteways: Spring Creek Wasteway, Snipes Creek Wasteway, and Coral Canyon Creek Wasteway. These wasteways drain off the Rattlesnake Hills and Rattlesnake Mountain from north to south across moderate slopes. In the northern portion of the Lower Yakima WRIA, within the Benton County boundary, drainage is a result of a moderate slope from south to north off the Rattle Snake Hills and Rattlesnake Mountain. The drainage combines into the ephemeral Cold Creek Wasteway. The Lower Yakima WRIA within the Benton County has a maximum elevation of approximately 3,520 feet on Rattlesnake mountain and a minimum elevation of approximately 340 ft at the Columbia River. Moderate to gentle slopes results in relative low stream velocities and erosion potential from tributaries under normal precipitation conditions.

The Alkali/Squilchuck WRIA spans the west side of the Columbia River from Wenatchee to Richland. The southern extent of the Alkali/Squilchuck WRIA encompasses the entire USDOE Hanford Site and the City of Richland. The Alkali-Squilchuck WRIA within the Benton County boundary is a flat floodplain remnant of the Missoula floods. There is relatively little to no slope that results to low erosion potential.

2.3.2 Climate

Benton County climate is influenced by marine air masses traveling eastward over the Cascades and along the Columbia River, as well as by continental air masses typically travelling southward from Canada. Within the Benton County boundary mean annual precipitation is less than 8 inches per year. The majority of precipitation occurs between October and April, with some precipitation occurring as snow, particularly at higher elevations in the Horse Heaven Hills.

2.3.3 Geology and Structural Geology

The Columbia River Basalt Group (CRBG), interbedded sediment of the Ellensburg Formation, and the alluvial sediments commonly referred to as Quaternary loess, Quaternary alluvium, the Hanford formation, and the Ringold Formation all which underlay Benton County.

The CRBG consist of a thick sequence of more than 300 continental tholeiitic flood-basalt flows that were erupted over an 11 million year period from about 17 to 6 Ma. These flood-basalt flows cover an area over 200,000 km² in Washington, Oregon, and western Idaho. The source for most of the flows was a series of north-northwest-trending linear fissure systems located in eastern Washington, eastern Oregon, and western Idaho. Detailed study and mapping of the Columbia River flood-basalts has allowed for the establishment of stratigraphic units that can be reliably identified and correlated on a regional basis. The CRBG has been divided into six formal formations (from oldest to youngest), the Imnaha, Grande Ronde, Prineville, Picture Gorge, Wanapum, and Saddle Mountains Basalts. For this assessment units of the Saddle Mountains Basalt, and inter-bedded Ellensburg sediments, are of prime importance. Most of the geologic information available for the area of interest has been obtained by surface geologic mapping that was compiled by Reidel and Fecht (1994).

In Benton County, the major sedimentary units of interest to this project include Ellensburg Formation interbeds within the CRBG, the Ringold Formation and associated caliches overlying the CRBG, Hanford formation cataclysmic flood deposits present at the surface throughout the Yakima River valley and Columbia River valley, and Quaternary loess mantling the Horse Heaven Hills and Rattlesnake Hills.

The Columbia Plateau region can be general subdivided into the Yakima Fold Belt, Palouse Slope, Blue Mountains, and Clearwater/Weiser Embayment sub-provinces. The Yakima Fold Belt (YFB) includes the western and central parts of the Columbia Basin (including Benton County) and is characterized by a series of major anticlinal ridges and synclinal valleys. The anticlines and synclines are typically segmented by cross-cutting faults and folds. Structural relief is typically less than 600 m but varies along the length of the fold. The Olympic-Wallowa lineament (OWL) is a major northwest-trending topographic feature in Washington and Oregon that cross-cuts the Columbia Basin and Benton County, where it is defined by the hills overlooking the south side of Kennewick.

2.3.4 Hydrogeology

In the Columbia Plateau and western Oregon and Washington, groundwater in the CRBG generally occurs as a series of aquifers hosted by the upper three CRBG formations (Grande Ronde, Wanapum, and Saddle Mountains) and the interstratified Ellensburg Formation sediments. CRBG aquifers have been characterized as generally semi-confined to confined. The major water-bearing and transmitting zones (aquifers) within the CRBG are variously identified as occurring in sedimentary interbeds, between adjacent basalt flows (interflow zone), and in basalt flow tops.

Groundwater flow direction and rates within CRBG aquifers depend on the presence and extent of dense, low permeability basalt flow interiors and rubbly, vesicular, and permeable flow tops, bottoms, and sedimentary interbeds (collectively referred to as interflow zones). Groundwater within CRBG aquifers appears to be generally separated from one another by very low permeability, dense basalt flow interiors. Some groundwater flow may occur locally around the flow pinch-outs, through vertically oriented and interconnected joints and fractures, and through faults. However, overall vertical groundwater flow rate through the basalt interiors between interflow zones is expected to be orders of magnitude lower than the horizontal flow through the interflow zones because of the very low permeability of flow interiors.

Faults have been found to impact the CRBG groundwater system in a number of ways. They can form barriers to the lateral and vertical movement of groundwater; a series of faults can create hydrologically isolated areas. Faults can provide a vertical pathway (of varying length) for groundwater movement allowing otherwise confined CRBG aquifers to be in direct hydraulic communication. They can expose interflow zones creating local opportunities for aquifer recharge and/or discharge. The ability of faults to affect CRBG groundwater systems in a variety of ways reflects the potential for both lateral and vertical heterogeneities in the physical characteristics of fault zones.

Folds also can affect the occurrence and movement of groundwater through CRBG aquifers. In many cases, folds have been identified as groundwater barriers or impediments that either block or restrict lateral groundwater movement through the CRBG aquifer system. Because most of the folds in this region have genetically related faults, it is possible that the observed effects on groundwater are by a combination of the folds and faults.

2.3.5 Land use, habitat, and built environment

Agriculture dominates the Glade/Fourmile Creeks and Kennewick sub basins of the Rock/Glade WRIA, and the Lower Yakima WRIA within the Benton County boundary. Irrigated land dominates the low-elevation southern half of the Glade/Fourmile Creeks sub basin and the Yakima River valley. Alternating areas mapped as small grain and fallow land encompass much of the northern half and far eastern portion of the Glade/Fourmile Creeks sub basin. Developed land of the metropolitan Kennewick area occupies the northern half of the Kennewick sub basin. The southern half of the Kennewick sub basin is comprised of irrigated and dryland farming.

2.4 Contaminants of concern

Nutrient loading to groundwater and surface waters in the form of nitrates comes primarily from diffuse sources such as runoff and leaching from fertilizer application, animal waste, urban runoff, vegetation decay, and septic system effluent (Wise et al., 2009). Groundwater

contaminated with nitrates has the potential to feed into the county's surface waterways. Higher levels of nitrates in surface waters can lead to excessive plant and algal growth leading to potential eutrophication of the surface waters. Highly eutrophic systems cause decreased levels of dissolved oxygen concentrations, thus creating unfavorable conditions for aquatic life.

Nutrient pathways into the groundwater are complex and are influenced by land use characteristics, soil properties, vegetation cover, seasons and precipitation, and irrigation application and timing. Nitrate loadings also depend on a complex system of biotic and abiotic processes that include nitrogen fixation by bacteria and adsorption and absorption of the nutrients by the soil matrix (Wise et al., 2009).

Groundwater nitrates can become a public health concern if excess levels are found in drinking water supply wells. There is rising concern regarding the potential for high nitrate levels in drinking water within Benton County from non-point sources. Documenting contaminated wells and elevated nitrate concentrations are imperative for public health protection and safety.

Nitrogen sources for domestic wells may result from manure, chemical fertilizers, on-site sewage systems, and biosolids, to name a few. An increase in the use of nitrogen for agricultural practices as well as from increased livestock densities over the last several decades have left a legacy of nitrates in the groundwater. Over 20,000 residents, approximately 11% of Benton County's population, live in rural areas. Rural drinking water wells are unregulated and often not tested. Nitrate is classified as an acute contaminate, meaning that even one exposure can affect a person's health (Yakima County, 2011). Groundwater flow is slow and nitrate concentrations in groundwater can take a long time to abate, even when sources are controlled (Puckett, 2011). As such, groundwater contamination can happen slowly over decades and remediation can take even longer.

Nitrates are colorless, odorless, and tasteless, so the only method of detection is chemical testing. Domestic wells in Benton County have tested for nitrate levels that exceed the State groundwater standard of 10 mg/L. Well testing can serve many functions including: prioritization of areas to implement agricultural Best Management Practices (BMP's) for nitrate loading reduction, alerting residents of the health risks associated with increased nitrate levels, and provide data to help characterize groundwater nitrate contamination in Benton County.

This project is in alignment with the Ecology's Washington Nitrate Prioritization Project (Morgan, 2014) in which Benton County is identified by USGS mapping as having areas with predicted levels of groundwater nitrates in excess of 10 mg/L. In Benton County, a foundation to understand the specific sources and pathways of nitrate contamination is needed before an effective and targeted groundwater quality management effort can be built. This project will lay the groundwork for future targeted remediation and protection efforts of drinking water and groundwater within Benton County.

2.5 Previous studies

2.5.1 Surface Hydrology and Water Quality

Ecology (Davis, 1993) sampled surface water at the mouth of Glade Creek as part of the Washington State Pesticide Monitoring Program (WSPMP). Nitrate was detected in that sample at 34.5 mg/L and a suite of pesticides were detected at trace concentrations (less than 0.0004

mg/L). Ecology (Garrigues, 1996) completed a groundwater and surface water quality characterization, focusing on nitrate, for the Glade Creek drainage. The study involved sampling of three surface water locations in Glade Creek – one at the mouth and one each on the East Branch Glade Creek and Upper Glade Creek (mainstem) just upstream from their confluence. The Glade Creek sampling location at the mouth was the same as that sampled in 1993 during the WSPMP. Samples were collected from the three locations in May 1995; the location at the mouth was sampled again in September 1995. In May, nitrate concentrations were higher in the downstream sample compared to the upstream sample, 11 to 13 mg/L at the two upstream locations and 36 mg/L at the mouth. In September 1995, sampling again at the stream mouth, nitrate was detected at 40 mg/L. The study concluded that nitrate contamination is widespread in Glade Creek surface water. More recently, Ecology monitored Glade Creek at Highway 14 from 2011 thru 2012 (Ecology 2012 and Hallock and Von Prause 2013). Glade creek samples collected monthly between October of 2011 and September of 2012 contained elevated nitrate/nitrites levels ranging from 48 – 53 mg/L.

In the Lower Yakima WRIA during the fall of 2002, Ecology rated surface water quality conditions of the Snipes Creek, Spring Creek, and Corral Canyon Creek tributaries. In Snipes Creek, tributary pesticides rated fair, sediment rated fair, dissolved oxygen rated good, temperature rated fair, fecal coliform rated fair, and pH rated fair. In Spring Creek, pesticides rated fair, sediment rated poor, dissolved oxygen rated good, temperature rated fair, fecal coliform rated poor, and pH rated fair. In Corral Canyon Creek, pesticides rated fair, sediment rated fair, dissolved oxygen rated fair, fecal coliform rated fair, and pH rated fair. All three tributaries rated good for the 303d list. Additionally, Snipes Creek Wasteway, near the confluence with the Yakima River, was measured by Ecology in 2011 (Ecology 2011 and Hallock 2011). Nitrates and nitrites were detected in the surface water ranging between 0.3 mg/L to 3.5 mg/L. Samples also had elevated levels of fecal coliform bacteria in January and February and temperatures exceeded water quality criteria for the summer months (July through early September) with pH levels elevated in the winter and spring.

2.5.2 Groundwater Studies

Nitrate in Benton County (exclusive of the Hanford Site) groundwater has been identified as an issue in various reports, each focusing on a portion of the County. Basic findings relating to groundwater nitrate in these reports include:

- Ebbert et al. (1993), which showed that in the mid 1980's approximately 10 percent of the wells they sampled in the Kennewick and Finley areas of Benton County had nitrate concentrations exceeding the maximum contaminant level (mcl) of 10 mg/L.
- Watershed Management Plan (2003), focusing on the entire Yakima River valley, although not dealing extensively with groundwater quality issues, noted the presence of nitrate in at least some wells in the region, indicating that groundwater quality is at least locally impaired by elevated nitrate in portions of the basin.
- Aspect Consulting (2004), which focused on the Horse Heaven Hills (Glade/Fourmile Creeks subbasin) and Kennewick portions of the County, summarized Department of Health data for public water systems that showed nitrate concentrations exceeding 10 mg/L (at least periodically) in 10 public water systems, having wells in both the alluvial and basalt aquifer systems.

- Jones et al. (2006), for the lower Yakima River valley portion of Benton County, showed the presence of wells containing elevated nitrate concentrations above 20 mg/L.
- Ecology (2010), which focused primarily on the Yakima County portion of the Yakima River valley also shows elevated nitrate concentrations (above 10 mg/L) in wells immediately up gradient of Benton County in the Yakima River valley.

None of these reports synthesize groundwater quality for all of Benton County into a single database, nor do they provide a comprehensive evaluation of the cause and extent of groundwater nitrate conditions in the County. Nevertheless, taken together, these reports show that nitrate concentrations above the MCL of 10 mg/L occurs in portions of the County.

2.6 Regulatory criteria

The WAC 173-200-040 provides a groundwater criterion for nitrate as nitrogen (NO₃-N) of 10 mg/l. This Maximum Contaminant Level is based on standards set by the Environmental Protection Agency (under the Safe Water Drinking Act) for the safety of drinking water. This standard was set to prevent methemoglobinemia (Morgan, 2014).

The impacts of drinking high nitrates (> 10 mg/L) on public health are well documented. Methemoglobinemia, also known as “blue baby syndrome, occurs when high levels of nitrates reduce the capacity for red blood cells to carry oxygen. Populations at high risk are infants, pregnant women, individuals with a hereditary lack of methemoglobin reductase, and the elderly. Although treatable, methemoglobinemia can be lethal and the best solution is avoidance of high nitrates.

The Washington State Department of Health (WDOH) requires more frequent sampling when *public* drinking water supply samples are over 5 mg/L. Compliance orders to systems are issued by the WDOH when samples are over 10 mg/L and public water systems must be remediated. Residents with privately owned wells are not regulated in the same manner as the public water supply system and are not required to sample their wells. As such, owners may not be aware of contaminated drinking water and when their source of drinking water is contaminated, options for alternative sources or remediation may be costly (Morgan 2014). Well testing through the *Benton County’s Nitrate Groundwater Monitoring Study* can serve two functions: to alert residents of health risks and to provide data to characterize groundwater nitrate contamination in Benton County.

3.0 Project Description

This QAPP covers one aspect of a larger groundwater project undertaken by BCD as detailed in the FY2016 Water Quality Financial Assistance Program agreement: WQC-2015-BentCD-00102. The *Benton County Groundwater Nitrate Monitoring Study* that is governed by this QAPP falls under *Task 4: Well Sample Data Collection and Groundwater Nitrate Monitoring*. The full project involves the formation of a Stakeholder Committee, development of a Benton County Groundwater Community Action Plan, and public health and education outreach. Recommendations drawn from the collected nitrate data under this QAPP will be fed into the larger project and used for the long-term goal of reducing nitrate threats to groundwater through the development of a Stakeholder Group and community-based action plan.

3.1 Project goal

The project goal is to develop an essential foundation for groundwater quality restoration in Benton County with regards to elevated nitrates.

The only parameter and contaminant sampled will be nitrate. Samples will be analyzed for nitrate in a certified laboratory at the Benton Franklin Health District. This project is part of a foundational program for Benton County implemented by BCD. The program was initiated due to limited data and resources available for groundwater in Benton County. This project is a first step designed to establish a framework for identification of problematic groundwater areas in regards to elevated nitrates.

Data collected from the QAPP project monitoring will be used in the creation of a database as well as GIS mapping of contamination. The data analysis and GIS Mapping are grant deliverables that are not part of the purview of this QAPP. Ultimately, collected project data will be used to:

- Help provide an understanding of groundwater nitrate concentrations and distributions within Benton County.
- Inform a newly formed Stakeholder Group tasked with establishing a Benton County Groundwater Community Action Plan.

The project goal at completion of the monitoring effort is to have obtained useful and scientifically rigorous nitrate data that are representative of the groundwater concentrations within the county and can be used in the completion of the BCD grant deliverable tasks 2, 3, and 5. The data will be suitable for public distribution to help landowners make knowledgeable decisions for aiding in groundwater protection and drinking water safety.

3.2 Project objectives

The technical objectives of the project include:

- Selection and implementation of a groundwater-monitoring network comprised of 200 privately owned wells. The wells are to be determined using the procedure outlined below. The consulting project hydrogeologist will perform steps 1 through 4 using existing records. Subsequently, BCD staff will perform steps 5 and 6 during field verification of candidate well suitability.

Well Selection Criteria

1. When possible (based on criteria listed below), use wells with previous nitrate sampling and data history regardless of the sampled nitrate levels results (i.e., high, low, non-detect, etc.).
 2. Select candidate wells to fill spatial gaps identified by statistical analysis and visual /spatial review of existing nitrate sampled wells.
 3. Determine if a candidate well has a well construction log that can be used to aid in the identification of hydro-stratigraphic unit that the candidate well is open to. If the well has a construction log, it is available for further evaluation as a potential candidate. If a construction log is not available then it will be dropped from further consideration.
 4. Determine if a well fills hydro-stratigraphic coverage gaps (depth gaps), selecting, where possible, wells that are open to different hydro-stratigraphic unit groupings in an effort to evaluate the vertical/subsurface distribution of nitrates. The hydro-stratigraphic unit groupings are as follows:
 - a. Alluvial.
 - b. Alluvial/shallow basalt (Saddle Mountains).
 - c. Shallow/intermediate basalt (Saddle Mountains and Wanapum).
 - d. Intermediate/deep basalt (Wanapum and Grande Ronde).Hydro-stratigraphic unit coverage gaps are identified by visual examination of mapped candidate wells and statistical analysis of existing nitrate data sampling. The majority of candidate wells will be in the alluvial and alluvial/shallow basalt groupings.
 5. The well must be a current in-active use well
 6. A field visit will be performed of each candidate well location to determine the following:
 - a. The well location is where indicated in the available data records and appears to physically match the descriptions in the records, predominantly the Ecology well log database
 - b. The landowner grants permission to access and sample the candidate well
 - c. The well is physically accessible to sampling
- Investigation of seasonal effects on groundwater nitrate concentrations through the biannual sampling of each of the 200 privately owned wells. Samples will be collected in the fall and spring yielding 400 samples collected per year.
 - Spring sampling of well water is important as it captures concentrations prior to the initiation of the local irrigation season.
 - Fall sampling of well water is important as it captures concentrations prior to the termination of the irrigation season.
 - Investigation of yearly trends. Water samples will be collected for two consecutive sampling years from each of the 200 domestic wells starting in 2015 and analyzed for nitrate. This will yield a total of 400 samples per year (as samples are collected biannually). As such, the project will collect and analyze 800 water samples for nitrate contamination prior to project completion.

- Collection of accurate GPS units for each well location for data management and GIS applications.
- Storage and tracking of nitrate analytical data into Ecology’s Environmental Information Management (EIM) system to maintain a nitrate database for Benton County.
- Well sampling results will be added to the groundwater monitoring report to be shared with participating landowners, the public, and the Benton County Groundwater Stakeholder Committee. The report will include:
 - Maps of the study area showing sample sites, contaminant concentrations, and distribution.
 - Discussion of water quality results.
 - Significant or potentially significant findings.

3.3 Information needed and sources

A licensed and qualified hydrogeologist is conducting an analysis to assist in the identification of candidate wells and synthesis of any previous data. These analyses will aid in the development of the project nitrate monitoring study. The certified hydrogeologist will:

- Collect and compile existing Benton County data on groundwater nitrate, drinking water wells, well depth, well construction, soils, and other related data. Sources include Washington Department of Health, US Geological Survey, and Washington Department of Ecology.
- Conduct an initial study to examine the nature and extent of nitrate concentrations in Benton County and identify/rank any nitrate “hot spots” as appropriate.
- Evaluate existing data for gaps that could be filled with strategic and county wide well sampling.
- Prioritize data gaps for targeted data collection (well sampling) and identify residential properties in locations that would best fill those data gaps.

Once the project hydrogeologist has gathered the necessary information, then the nitrate monitoring portion of the project will gather nitrate data from 200 privately owned wells within Benton County to characterize nitrate levels and distribution.

3.4 Target population

The project will track nitrate concentrations in the spring and fall from privately owned wells within Benton County. The target population will be the nitrate data gathered at each well location monitored over the 2-year project implementation.

Measurements of the target population are intended to be representative of the nitrate distributions and concentrations for Benton County. Candidate well sampling sites will be chosen so that representative samples are obtained for the target population.

3.5 Study boundaries

The study boundaries are the Benton County lines within Washington. The Water Resource Inventory Areas (WRIA) that fall within Benton County are:

- WRIA 31 (Rock/Glade)
- WRIA 37 (Lower Yakima)
- WRIA 40 (Alkali Squilchuck)

3.6 Tasks required

BCD staff will coordinate with the project hydrologists for determination of the 200 well locations. A map of the potential sampling locations will be created by the project hydrologist prior to the start of the nitrate collection and sampling. Permission from private landowners will be obtained by BCD staff.

BCD staff will collect the well water samples and take GPS coordinates of each well site. BCD staff will also be responsible for following the collection procedures outlined in this QAPP, maintaining equipment supplies (per Appendix A), filling out the field log, chain of custody, sample tracking form, and Ecology Tags which are included as Appendices B-E. The water samples will be submitted by BCD staff to the Benton-Franklin Health District laboratory, an Ecology accredited laboratory. The samples will be analyzed by the nitrate ion selective method according to the SOP included as Appendix F.

The selected hydrogeologist consultants will analyze the data and map the resulting nitrate trends. Following analysis of the nitrate concentrations, the results and appropriate recommendations will be provided to the residents, the public and the newly formed Stakeholder Group.

3.7 Practical constraints

The candidate sampling wells to be used for monitoring will be selected by the project hydrogeologist and verified by BCD staff. Candidate wells will be selected based on numerous factors as described above in Section 3.2 Project Objectives.

The practical constraints on the project will be accessibility of the wells for sampling. Access may be limited to the selected wells either because of physical constraints or landowner willingness, as sampling of domestic wells will require landowner permission. If a candidate well is not available for sampling, the project hydrogeologist will select suitable alternate wells for sampling.

3.8 Systematic planning process

Preparation of the QAPP provides the systematic planning process for the BCD Nitrate Monitoring Study. Development of this QAPP utilizes the Performance and Acceptance Criteria (PAC) process as the systematic planning process as will be discussed further under 5.0 Quality Objectives.

4.0 Organization and Schedule

4.1 Key individuals and their responsibilities

- District Manager / Project Manager (Mark Nielson) – Overall project management.
- Water Quality Specialist and QA/QC Officer (Marcella Appel) - Develop QAPP, oversee sampling, conduct QA/QC, data analysis, and GIS mapping.
- GSI Water Solutions, Inc. (Dr. Kevin Lindsey et. al.) – Project hydrogeologist conducting initial groundwater monitoring, sampling design, QAPP review, and data analysis.
- Samplers (Marc Miller and Erin Hightower) – Obtain permission from private well owners to use their wells for sampling purposes and then collect and preserve water samples and deliver them to the laboratory.
- Laboratory (Benton-Franklin Health District) – Analyze water samples for NO₃-N.
- Private Well Owners – Allow access and sampling of wells twice per year for two years.

4.2 Special training and certifications

The Benton-Franklin Health District laboratory is accredited through Ecology to analyze nitrate-nitrogen in water using the ion specific electrode method. Samplers will be trained to conduct field collection as well as to adhere to this QAPP including all documentation requirements and QA samples to be collected. No other special training or certifications are required.

4.3 Organizational chart

The chain of communication is listed in Figure 2.

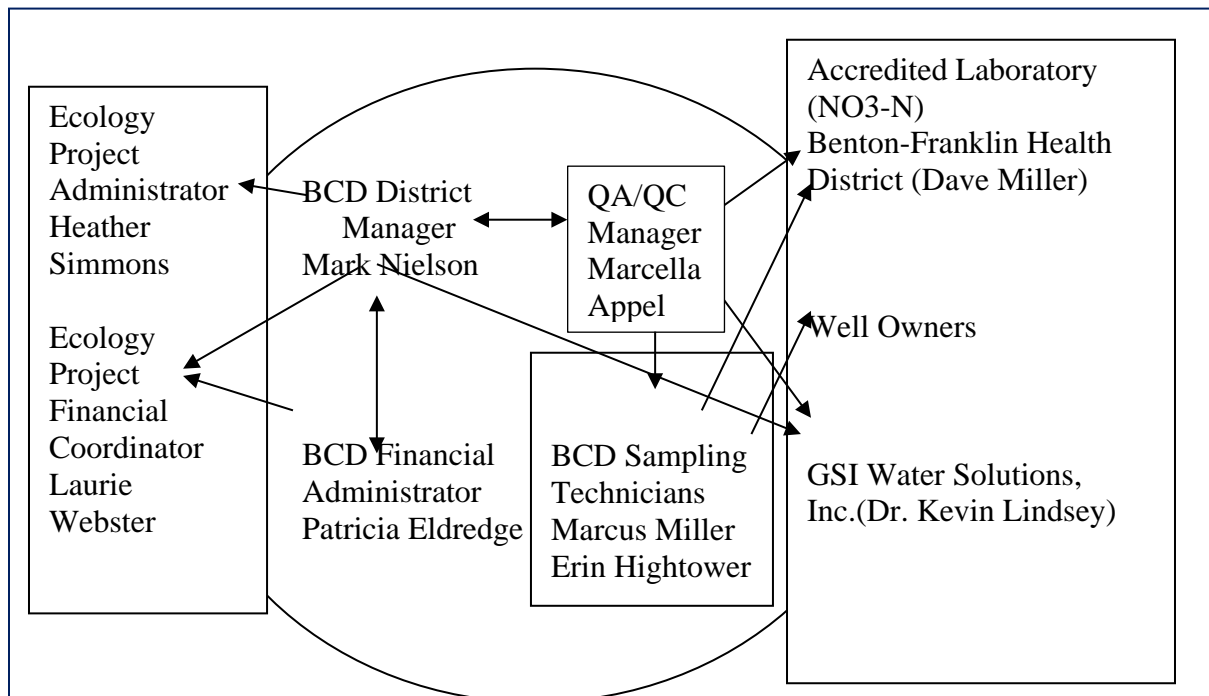


Figure 2. Example chain of communication between CD, partners, and Ecology.

4.4 Project schedule

The monitoring phase of the project will begin May 31, 2015 and will end in the fall of 2017.

Table 1. Project schedule.

Activity	Estimated Completion Date
Develop QAPP	May 31, 2015
QAPP Reviewed and Approved by Ecology	July 15, 2015
Existing Data Review and Data Gaps Identified	July 31, 2015
Wells Selected for Monitoring Network	July 31, 2015
Well Sampling (Sample same wells 2 times per year for 2 years)	Spring of 2017 or Fall of 2017
Laboratory Analysis	Occurs concurrent with sampling periods
Data report and GIS mapping (Year 1 data included in overall groundwater monitoring report, Year 2 data provided as an addendum to monitoring report).	July 2016

4.5 Limitations on schedule

The goal is to begin sampling during the Fall (mid-September to mid-October) of 2015.

However, this schedule may have to be pushed out to the Spring of 2016. Factors that limit the preferred schedule include final approval of this QAPP by Ecology and private landowner permission for the wells selected.

4.6 Budget and funding

This project is funded with the FY2016 Water Quality Financial Assistance Program agreement: WQC-2015-BentCD-00102, with match being provided by BCD, Benton-Franklin Health District, and Benton County (Table 2).

Table 2. Benton County Groundwater Project Budget Agreement.

								Total		Ecology
Project Activity	Cost per unit	Cost Descr.	Unit	Unit Descr.	Occurrences	Occr descr	# years	Cost	Match	Eligible cost
Sample analysis - health risk referrals	\$25	per sample	200	wells	1	samples per well	2	\$10,000	(\$2,500)	\$7,500
Sample collection - health risk referrals	\$30	per hour	256	hours			2	\$15,360	\$0	\$15,360
Sample analysis - characterization data	\$25	per sample	200	wells	2	samples per well	2	\$20,000	(\$5,000)	\$15,000
Sample collection - characterization data	\$30	per sample	256	hours	2	samples per well	2	\$30,720	\$0	\$30,720
Mileage - sample collection	\$0.57	per mile	120	miles per day	180	days		\$12,204	\$0	\$12,204
Postage - mail results to residents	\$0.46	per letter	1,200	letters				\$552	\$0	\$552
Water Resource Specialist - Develop QAPP, oversee sampling, conduct QA/QC, data analysis, and GIS mapping	\$35.00	per hour	40.75	hours per month	36	# of months		\$51,345	(\$25,500)	\$25,845
Contract Hydrogeologist - Initial characterization, sampling design, review QAPP, and data analysis								\$34,400	\$0	\$34,400
Total Cost								\$174,581	(\$33,000)	\$141,581

5.0 Quality Objectives

5.1 Decision Quality Objectives

The *Benton County Groundwater Nitrate Monitoring Study* utilizes the Performance and Acceptance Criteria (PAC) systematic planning process. The PAC process will be used because decision-making is not the primary focus or intended outcome for the data set. This data set will be used for informational and descriptive purposes only. This is a baseline study to gather data for which to build upon and develop future groundwater studies within Benton County. Data collected during this project will be used as a record for which to compare against future studies in the county.

The quality objectives for this study are:

- Collect samples from private drinking wells that are *representative* of Benton County's groundwater nitrate concentrations. Sampling locations will be chosen as outlined in Section 3.2 above. The well sampling locations were selected to be representative of various groundwater depths/aquifers in Benton County as well as represent the various geographic locations within Benton County.
- *Minimize bias* introduced into the samples collected at each site by using standard sampling and analytical procedures from point of collection through laboratory sample analysis. Bias may be introduced into the sample design in that some wells with a previous history of nitrate sampling (regardless of whether they had a presence or absence of detected nitrates) will be prioritized for monitoring due to accessibility for sampling access.
- *Obtain analytical results that minimize uncertainty* and may be used to determine current concentrations and distribution of nitrate concentrations within private Benton County groundwater sources.

5.2 Measurement Quality Objectives

The laboratory measurement quality objectives are listed in Table 3. These goals are based on performance characteristics of measurements done by the Benton Franklin Health Department Laboratory and outlined in the SOP provided as Appendix F.

Table 3. Laboratory Measurement Quality Objectives

Parameter	LCS	Duplicate Samples	Matrix Spikes	Matrix Spike-Duplicates	MDL*
	% Recovery Limits	RPD	% Recovery Limits	RPD	mg/L
Nitrate - N	80–120%	20%	75-125%	20%	0.02 mg/L

LCS: Laboratory Control Standard

RPD: Relative Percent Difference

MDL: Method Detection Levels

* Per the laboratory Standard Operation Procedure (Appendix F), the sensitivity is defined by the MDL

Objectives for precision, bias and sensitivity are summarized below. These Measurement Quality Objectives have been established to ensure the *Benton County Nitrate Monitoring Study* meets its overall objectives as described within the Project Description section.

5.2.1 Targets for Precision, Bias, and Sensitivity

Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Field precision for water samples will be measured by collecting duplicate samples and blind replicate samples as described in the Quality Control section. These samples will be submitted to the Benton Franklin Health District laboratory for analysis. Field precision will be evaluated by the relative percent difference (RPD) between the well sample results and the duplicate or replicate sample results from the sample well. An RPD of 20% will be acceptable for this project. If RPD's regularly fall outside of this range, BCD will evaluate the sampling methods to determine a course of action to obtain the desired data quality. Any changes in the procedure will be submitted for approval to Ecology. The RPD will be calculated with the following formula:

$$RPD = \frac{ABS (R1 - R2)}{(R1 + R2)/2}$$

ABS = Absolute Value

R1 = Recovery for duplicate 1

R2 = Recovery for duplicate 2

Laboratory precision for water samples will be measured using Standard Operation Procedure (SOP) *Nitrates by Ion Selective Electrode (Method 4500-NO3-D)* implemented by the Benton Franklin Health District laboratory. The SOP is adequate for this project and is included as Appendix F. Precision calculations as well as the results of the internal laboratory QA samples will be reported to the BCD manager.

Bias

Bias may be present in the selected sample design as the candidate wells are to be chosen based on the criteria outline in Section 3.2, including selection of previously sampled wells. These sampled wells may or may not have a history of detected levels of nitrates. This is a baseline study to gather nitrate-monitoring data to build upon for future studies and work within the county.

Bias in the samples is the difference between the population mean and the true value. To measure bias, Performance Evaluation (PE) samples (i.e., water with known nitrate concentrations) will be purchased from an independent source and submitted blind to the Benton Franklin Health District. Four concentrations of PE samples will be used. PE sample concentrations will be 1.0, 10.0, 35.0, and 100.0 mg/l nitrate. These concentrations were selected to span the range of expected values of the well sampling results. Benton Franklin Health District will receive samples from all four concentrations at least four times during the project time period. The percent recovery between the known value and the report value will be calculated with the following formula:

$$\text{Percent Recovery} = \frac{\text{Measured Concentration} \times 100}{\text{Actual Concentration}}$$

A recovery value of 75 – 125% will be acceptable for this project. If the percent recovery regularly falls outside this range, BCD will take corrective action that will include contacting Benton Franklin Health District to resolve the unacceptable recovery.

Laboratory bias will be measured using the *Standard Operation Procedure for Nitrates by Ion Selective Electrode (Method 4500-NO₃-D)* as implemented by the Benton Franklin Health District. The Benton Franklin Health District's SOP is adequate for this project and is included as Appendix F. Results of the internal Quality Assurance (QA) samples will be reported to the BCD manager.

Sensitivity

Sensitivity is a measure of the capability of a method to detect a substance. Benton Franklin Health District will be implementing the *Standard Operation Procedure for Nitrates by Ion Selective Electrodes (Method 4500-NO₃-D)*, provided as Appendix F. *Per the SOP, the sensitivity for this project is defined by the SOP's Method Detection Level (MDL).* The project MDL is estimated to be 0.02 mg/l as outlined by the SOP. Benton Franklin Health District will perform a check of the MDL on an annual basis using a 0.2 mg/l nitrate standard. Benton County Health District will report down to 0.5 mg/l nitrate for analyzed samples. Anything below 0.5 mg/l will be reported as < 0.5 mg/l.

5.2.2 Targets for Sampling Design Comparability, Representativeness, and Completeness

Comparability

Comparability is the degree to which data can be compared directly to similar studies. Using standardized sampling analytical methods and units of report with comparable sensitivity helps ensure comparability. Results from this study should be comparable to results of previous nitrate studies as well as studies performed in neighboring counties as the test methods and sampling procedures by BCD sampling teams will be the same as were used for previous Ecology nitrate studies. This plan also strives to ensure that all field sampling and data analysis are consistent over the course of the groundwater-monitoring program.

Representativeness

Representativeness is the degree to which data from the project accurately represent a particular characteristic of the environmental matrix that is being tested. The 200 wells to be sampled during this project will be selected by the hydrogeological consultant and will be chosen as best as possible to represent various ground water nitrate conditions within Benton County. This is a baseline-monitoring project and as such, the goal is to collect initial nitrate data on which future projects and studies can be built. The project hydrogeologist, according to the criteria outlined in Section 3.2, will select the candidate wells. When possible, wells with a previous data history will be chosen. These wells may have high, low, or non-detect values of nitrates. Using previously sampled wells may decrease some of the representativeness in the sample design. Candidate wells will be identified that fill spatial gaps based on statistical analysis and visual/spatial review of existing well sites. Where possible, wells open to different hydro-stratigraphic unit groupings (e.g., alluvial, alluvial/shallow basalt, shallow/intermediate/basalt and intermediate/deep basalt) will be selected. Hydro-stratigraphic unit coverage gaps will be

identified by visual examination of mapped candidate wells and statistical analysis of existing nitrate data sampling.

Samples will be collected over a 4 week period during the spring and the fall at all of the 200 pre-selected well sites. These samples will investigate the variability of nitrate concentrations with the flux of the water changes resulting from the irrigation season. While four samples will not adequately represent and capture all of the seasonal variability, it will provide baseline data for future projects and development of groundwater sampling studies in Benton County. The samples will capture flows prior to irrigation and at the end of the irrigation season to give an idea of any potential changes in nitrate concentrations as a result of groundwater flow changes. In addition to seasonal variation, sampling will take place in two consecutive years. This will help capture yearly variations. A total of 800 samples (200 wells x 2 years x 2 seasons) will be collected and analyzed during the course of the project.

Representativeness of the water samples collected is ensured by adherence to the field sampling protocols and standard laboratory protocols detailed in this document.

Completeness

Completeness is the percentage of valid results obtained compared to the total number of samples taken for a parameter. A complete or valid result will include full completion of the Field Log and laboratory analysis report. Benton Conservation District expects 95% completeness.

$$\% \text{ Completeness} = \frac{\# \text{ of valid results}}{\# \text{ of possible results}} \times 100$$

Another definition of completeness for this project will be based on the percentage of wells sampled of the total number of targeted wells. The completeness goal for the project is 100%, but some wells may not be suitable to sampling due to owner refusal, inaccessibility, or location issues. As such, Benton Conservation District expects at least 150 wells to be sampled providing a 75% completeness to be considered acceptable for this project.

6.0 Sampling Process Design (Experimental Design)

This document governs the development of a well sampling program as part of the FY2016 Water Quality Financial Assistance Program agreement: WQC 2015 BentCD 00102 - *Task 4: Well Sample Data Collection and Groundwater Nitrate Monitoring*. The study design will collect sample data from across Benton County utilizing this QAPP to facilitate scientifically rigorous well water testing for nitrate.

6.1 Study design

6.1.1 Sampling locations

All wells within the sampling network will be selected during the fall of 2015 with collection of field samples beginning fall of 2015. The candidate well selection will be performed by the licensed project hydrogeologist selected for the project through BCD's established Request for Proposals (RFP) process. Sample locations are not finalized, as they are a product of the data analysis and synthesis task being conducted by the hydrologist. A map of the potential candidate well locations is provided in Figure 3.

The methodology for selecting groundwater wells and finalization of well sampling locations is as follows:

Well Selection Criteria

1. When possible (based on criteria listed below), use wells with previous nitrate sampling and data history regardless of the sampled nitrate levels results (i.e., high, low, non-detect, etc.).
2. Select candidate wells to fill spatial gaps identified by statistical analysis and visual /spatial review of existing nitrate sampled wells.
3. Determine if a candidate well has a well construction log that can be used to aid in the identification of hydro-stratigraphic unit that the candidate well is open to. If the well has a construction log, it is available for further evaluation as a potential candidate. If a construction log is not available then it will be dropped from further consideration.
4. Determine if a well fills hydro-stratigraphic coverage gaps (depth gaps), selecting, where possible, wells that are open to different hydro-stratigraphic unit groupings in an effort to evaluate the vertical/subsurface distribution of nitrates. The hydro-stratigraphic unit groupings are as follows:
 - a. Alluvial.
 - b. Alluvial/shallow basalt (Saddle Mountains).
 - c. Shallow/intermediate basalt (Saddle Mountains and Wanapum).
 - d. Intermediate/deep basalt (Wanapum and Grande Ronde).

Hydro-stratigraphic unit coverage gaps are identified by visual examination of mapped candidate wells and statistical analysis of existing nitrate data sampling. The majority of candidate wells will be in the alluvial and alluvial/shallow basalt groupings.

5. The well must be a current in-active use well
6. A field visit will be performed of each candidate well location to determine the following:

- d. The well location is where indicated in the available data records and appears to physically match the descriptions in the records, predominantly the Ecology well log database
- e. The landowner grants permission to access and sample the candidate well
- f. The well is physically accessible to sampling

The consulting project hydrogeologist using existing records will perform steps 1 through 4. Subsequently, BCD staff will perform steps 5 and 6 during field verification of candidate well suitability (e.g., ease of access and landowner willingness). The owners of candidate wells will be contacted by a letter, phone call, and onsite visits to discuss their willingness to participate in the project. If a candidate well does not meet the field criterion, the BCD District Manager will be notified and it will be removed from the candidate sampling well list. A suitable alternative well will be provided in its place.

6.1.2 Sampling frequency

The nitrate sampling effort will begin in the fall of 2015. Discrete water samples from the 200 wells will be collected twice a year for two years. Well water samples to be analyzed for nitrate will be collected from each well, once in the spring and once in the fall. The spring sampling window will be defined as a four consecutive week period falling between March 15 – May 1 and the fall sampling window will be defined as a four consecutive week period falling in October 1 – November 15. This sampling effort will yield a total of 400 groundwater samples collected per year and 800 samples in total. It is recognized that there is inherent variability within the 4-week sampling window but the purpose and goal of this sampling is to gather baseline-monitoring data and to ascertain if there are differences in nitrate levels at the sampled locations between spring and fall when groundwater levels fluctuate with irrigation.

Additionally, landowners can request well testing through the Benton Franklin Health Department at any point during the year. The testing of these wells will be conducted by the BCD and wells will be sampled and analyzed in accordance with this QAPP.

6.1.3 Parameters to be determined

In the field, the only parameter to be determined is the GPS coordinates of each the well. Well water samples will be collected in the field per the outlined in Section 8.0 Sampling Procedures. The well samples will be tested by the Benton Franklin Health district. The only laboratory parameter tested will be nitrate.

6.1.4 Field measurements

No measurements will be made in the field other than the GPS coordinate locations.

6.2 Maps or diagram

A map of the potential candidate wells is provided in Figure 3. These locations are subject to change based on well access and well suitability.

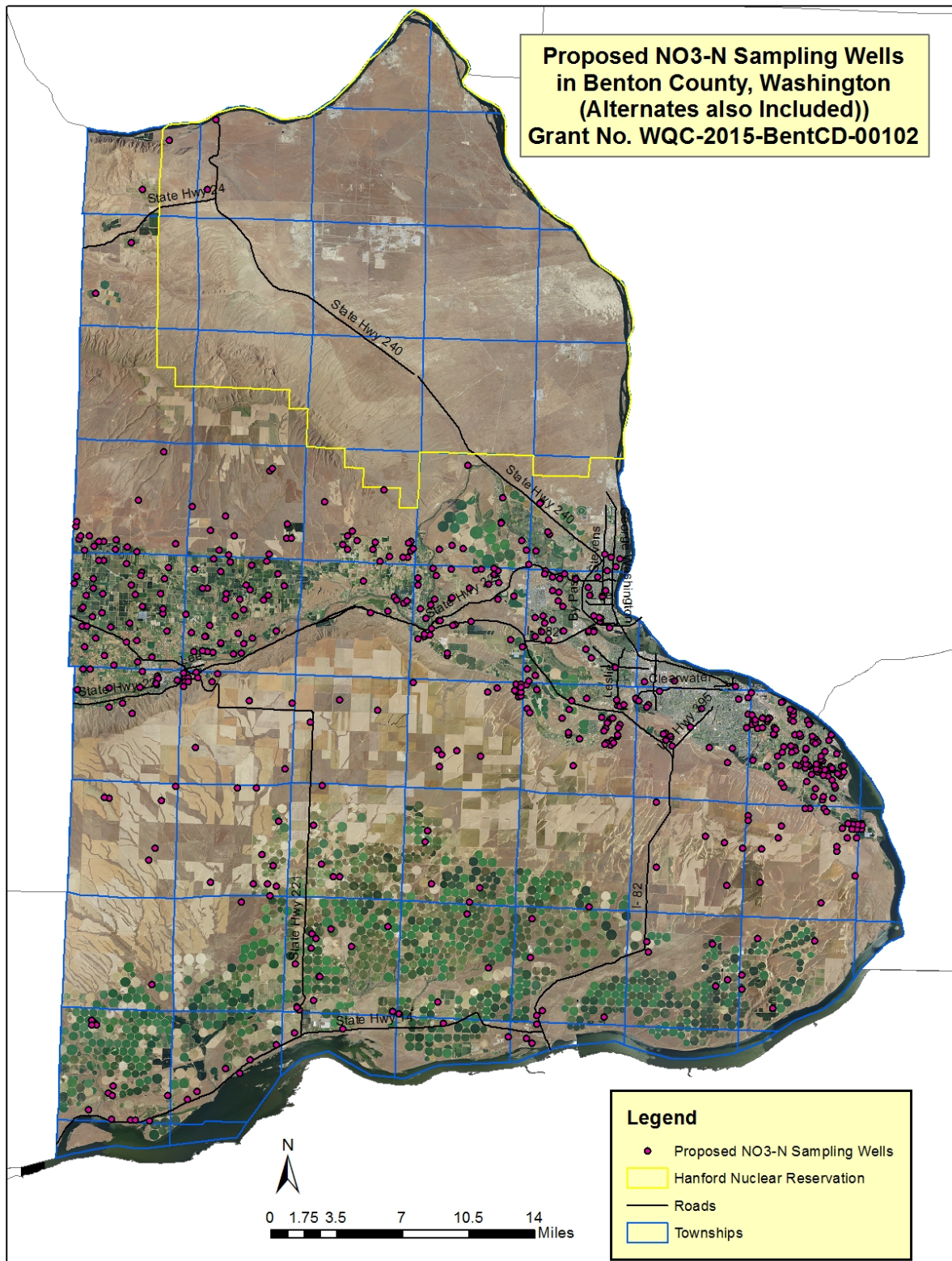


Figure 3. Map of Proposed Sampling Wells within Benton County, WA.

6.3 Assumptions underlying design

The primary assumptions underlying the proposed design are that the landowners are interested and willing to be part of the sampling study, which the selected seasonal sampling windows will adequately capture changes in nitrate concentrations with irrigation changes, and that the selected wells will provide adequate information regarding nitrate concentrations on a depth and area basis. Furthermore, it is assumed that 800 samples will be sufficient for an initial identification and monitoring of nitrate concentrations within Benton County for use in developing a Nitrate Management Plan. The hydrogeologist will select candidate wells that best represent the county, however, participation is based on landowner willingness and, as such, the distribution and location of the monitoring sites will be dependent on landowner participation.

6.4 Relation to objectives and site characteristics

The proposed frequency of measurements and the number of wells to be sampled is intended to capture baseline monitoring for nitrate concentrations within Benton County. The seasonal sampling is intended to illustrate fluctuations that may occur as a result of irrigation changes and timing to Benton County's groundwater sources. The candidate well locations will be selected so that they are distributed across the county with coverage accounting for variability in hydro-stratigraphic gaps (depth gaps) in an effort to evaluate the vertical/subsurface distribution of nitrate. Candidate wells will also be selected to fill spatial gaps as identified by statistical analysis and visual /spatial review of the selected existing nitrate sampled wells. Accessibility to the sites may change during the study either due to physical access limitations, landowner participation, or inclement weather. If less than 75% of the sites are accessible, then the sample design will be reassessed.

6.5 Characteristics of existing data

The licensed project hydrogeologist is compiling existing Benton County data on groundwater nitrate, drinking water wells, well depth, well construction, soils, and other related data. These data will be compiled from various sources from Washington Department of Health, US Geological Survey, and Ecology. The hydrogeologist will evaluate the existing nitrate data for trends and gaps that could be filled with strategic and county wide well sampling. The analysis of existing data will support the development of the sampling well locations. The synthesis of existing data will be included within the final project report deliverable. Analysis of existing data is a separate task deliverable under the FY2016 Water Quality Financial Assistance Program agreement: WQC 2015 BentCD 00102. The analysis of existing data is not governed as part of this QAPP.

7.0 Sampling Procedures

7.1 Field measurement and sampling SOP

Pre-Field Activities

Prior to working in the field, the field samplers will:

- Coordinate the process of contacting well owners and mail out the pre-sampling letters to owners notifying them of the upcoming sampling of their well.

Contact well owners sufficiently in advance of sampling to allow multiple attempts at contacting the owner for permission to sample and access their wells and arrange to meet with them or their representative onsite.

- Review the field supply list and coordinate securing any necessary supplies for the sampling events.
- Check availability of sampling supplies and field forms. A list of needed supplies is enclosed as Appendix A. Blank field forms are attached to this document.
- Identify field QA samples to be collected as described in the Field Quality Control Section of this document.
- Table 4 also describes sampling frequencies for QA samples.
- Check proper operation of the Global Position System (GPS) units.

Field Activities

The following activities will be completed following arrival at the well site.

Meet Well Owner

Field samplers will meet with well/property owners or representatives, if available, and offer standard information on the BC sampling project and mission.

Well Coordinates/Field Verification

Accurately identifying well locations is a critical component of field activities and the project. To prevent erroneous recordings of well locations the location of wells, or sampling ports if the sample cannot be collected from the well head, will be re-coded in the field as follows:

- Field samplers while at the well site will record latitude and longitude values using GPS units to within 30 seconds (1/4 to 1/2 mi).
- The latitude and longitude data will be read and recorded in degrees, minutes, and seconds. Operation of the field GPS unit will be provided during the field training session (as described in the Field Sampler Training Section of this document).

7.1.1 Water measurement and sample collection

Pre-Sample Collection Methods

For water sampling, the BCD field samplers will conduct the following steps:

- Fill out sample labels in triplicate with sample IDs. If collecting a QA sample, use the same 4 digit numerical identifier as the well sample followed by the proper QA sample type designation.
- Affix one label to back of Ecology Sample tag. An example of the Ecology tag is provided in Appendix E.
- Attach tag and a second label to bottle, also mark bottle with sample ID.
- Affix the third label where indicated in the Field Log.

Water Sample Collection Methods

Well Purging

Samplers will inquire about well pumping schedule and duration from the owner. A minimum continuous purge time of 10 minutes is required and the field technician will not collect samples until they hear the pump running to be sure the sample is not collected from the tank. If the well is not pumping at the time of sampling pump the well for at least 10 minutes. The well and the water line between the well and the sampling point all need to be purged for 10 minutes.

Information regarding purge time will be recorded on the Field Log. It should be noted that the wells to be sampled are “active in-use” wells (not stagnant, or operating wells) that will be undergo constant routine pumping during the day to supply water for irrigation, domestic, and other uses. Therefore, a 10-minute purge time is expected to provide a sufficient “safety factor” to collect a representative sample. Field Samplers need to look for wells that pump to a storage tank or cistern. If a sampling well has a tank/cistern, the sample will be collected between the well and the storage device.

Water Sample Collection Procedures

Field Samplers will:

- Collect samples from the first available port closest to the well-head. In some cases the first port in line may be at the well-head, at others further hydraulically downstream (e.g., at the surge tank). Note that the Representativeness of the samples may crucially be dependent on the port location. For example, if a garden hose is attached to the first port, take the sample from the faucet prior to the hose and not the hose itself. Furthermore, samples should be collected prior to the water passing through a water treatment unit that may remove nitrate. Treatment units using reverse osmosis, ion exchange, steam distillation, or electrodialysis may remove nitrate and therefore the analysis results may not be representative of actual ground water conditions. The sampler shall describe on the Field Log the location of the sampling point relative to any treatment units or other in-line hydraulic components such as surge/pressure tanks or cisterns.

Collect samples in a clean 125 mL polyethylene bottle by holding the bottle directly under the faucet. Fill the container to the shoulder, approximately ½ inch below rim and close tightly.

- Enter samples onto the Chain of Custody (COC) form immediately after sample collection.

QA/QC Collection Procedures

Field Samplers will:

- Collect necessary QA/QC samples per scheduled outline within the QAPP.
- When collecting Performance Evaluation (PE) samples pour the nitrate stock standard solutions of 1.0, 10.0, 35.0, and 100.0 mg/l nitrate into 4 separate polyethylene sampling bottles. Seal, label and fill out the COC form for the PE samples and place on ice for delivery with collected water samples.
- Field Blank (FB) samples will be collected by pouring de-ionized water into a polyethylene bottle while in the field. The de-ionized water will be obtained from the Benton Franklin Health District laboratory prior to the sampling event. Seal, label and fill out the COC form for the FB samples and place on ice for deliver with the collected water samples.

Post-Sample Collection Methods

After sample collection is complete, the BCD Field Samplers will complete the following:

- Place samples, QA/QC samples, and the COC in individual Ziploc™ bags and place in the cooler. All samples will be placed in coolers with sufficient ice to maintain the temperature of the samples around 4 °C.
- At the end of the sampling trip, complete the laboratory COC form. A copy of the Department of Ecology's COC is enclosed as Appendix C. Fill the form as required and supply the information marked with an "X" or as otherwise indicated.

The sampling team will transport the samples to the Benton Franklin Health District's accredited laboratory within 24 hours of collection. Water samples and QA samples will only be collected in the field after 12 pm on Monday and prior to 3 pm on Thursday. This ensures that the laboratory will have sufficient time to analyze the samples within the 48 hour holding time as outlined by the *Standard Operation Procedure for Nitrates by Ion Selective Electrodes (Method 4500-NO3-D)*.

7.2 Containers, preservation, and holding times

The samples to be collected include water samples and field QA samples to be analyzed by the Benton Franklin Health Department laboratory. Sample types, designations, and collection frequencies are listed in

Table 4.

Samples will be placed in bottles obtained by BCD for the sampling project. Bottle materials, preservation, and holding times for the laboratory nitrate method are listed below:

- Containers: 125 mL wide mouth polyethylene bottles
- Preservation: Kept on ice, or refrigerated at 4°C
- Holding Time: 48 hours

7.3 Equipment decontamination

Equipment decontamination is not necessary as the collected samples are from drinking water sources. Additionally, no in-field preservatives or additives are required for the ion selective electrode method utilized.

7.4 Sample identification

Sample Identifications (IDs) will be comprised of two-character sample type designations (Table 4) and four digit numerical identifiers. The sample IDs will read as follows: BCxxxxZZ, in which BC is Benton County, xxxx is the four-digit identifier starting with 0001, and ZZ is the sample type designation.

7.6 Chain-of-custody

A COC will be used to maintain a tracking record for the environmental samples. The COC provided by the Department of Ecology will be used for this project. A sample is included as Appendix C.

The COC will be filled out by the field sampler in accordance with their field sampler training and reviewed for completeness at the end of sampling. The COC will be included in a ZiplocTM bag with the water samples upon sample completion and delivered to the laboratory.

Table 4. Sample Type, Designation, Collection Frequency.

Sample Type	Sample Type Designation (ZZ)	Collection Frequency
Well Water Samples	WW	1/well/Event*
Well Duplicate Samples	WD	1/Sampler/week
Field Blank Samples	FB	1/Sampler/Week
Performance Evaluation Samples	PE	4/Week for 4 weeks/Event*
Trip Blank Samples	TB	1/Event*

**Event is defined as once during the biannual sampling (Fall and Spring) and will consist of 4 consecutive sampling weeks. Two samplers will be in the field during an Event.*

7.7 Field log requirements

The Field Samplers, in accordance with their Field Sampler training and this QAPP, will maintain a field log page for each sampling trip. A sample field log page is included as Appendix B. The field log page will record and include:

- Name and location of well site.

- Name of Field Sampler.
- Date and Time of sampling event.
- GIS coordinates (latitude and longitude) of the well location.
- Sample numbers and description of sample type to be collected (e.g., water sample, QA samples).
- Well purging conditions.
- Any changes or deviations made from the QAPP.
- Unusual circumstances that might affect interpretation of results.

In the field, Field Samplers will check for accuracy in the latitude/longitude GIS coordinate entries between previously collected location data and the current reading. *It is extremely important that accuracy and consistency are maintained by the Field Sampler when filling out the sample ID between the field log, the bottle label, and the COC.*

7.8 Sample tracking form/checklist

This form is a checklist to review that field data verification and other steps have been completed prior to the delivery of samples to the Benton Franklin Health District laboratory. It is included as Appendix D. Sampling Tracking Form. Following review of the forms, the samples will be delivered to:

Benton Franklin Health District Laboratory
7102 W Okanogan Place
Kennewick, WA 99336
Phone: (509) 460-4200

7.9 Sampler training and safety

7.9.1 Field sampler training

The BCD Field Samplers, who will be trained in the appropriate field measurement and collection standard operating procedures, will collect the field samples. All BCD Field Samplers will be required to attend a training session prior to the initiation of the well sampling activities. The training will include review of the QAPP as well as detailed instruction on sample collection, labeling, handling, transport, shipping and completion of all necessary forms. The training will also cover proper use of GPS equipment as well as safety issues that may be encountered during sampling. Samplers will also receive training on sample data tracking, logistics of securing and distributing supplies and the administrative requirements necessary for project implementation. The BCD District Manager who is experienced with both sample collection procedures and the administrative requirements of this program will provide the staff training.

7.9.2 Field sampling safety

Samplers should enter all well houses with caution. Samplers should be aware that some well houses may contain spiders, wasps and hornets, mice and rats, and snakes. If a sampler is uncomfortable entering the well house they should contact the well owner or BCD District Manager to remedy the condition such that the well can be safely sampled.

8.0 Measurement Methods

8.1 Laboratory procedures table

The primary purpose of this project is to determine representative nitrate concentrations of groundwater. To minimize bias (systematic error) standard sample collection procedures will be used that minimize potential changes to sample chemistry during each sampling event. Samples will be preserved, handled, and stored using accepted procedures for maintaining sample integrity prior to analysis.

No field sample measurements will be made for this project. The laboratory measurement methods will be performed by the Benton Franklin Health Department, a listed Ecology accredited laboratory. **Table 5** provides the Laboratory Measurement Methods for the nitrate analysis. The Ion-selective electrode method for analysis of nitrate is an accepted routine analytical method for testing nitrate concentrations in groundwater. The full sample preparation method is provided in Appendix F.

The parameters, test methods, and the expected range of results for the project are listed in **Table 5**.

Table 5. Laboratory Measurement Methods.

Analyte	Sample Matrix	Samples [Number/Arrival Date]	Expected Range of Results	Reporting Limit (Method of Detection)*	Analytical (Instrumental) Method	Sample Preparation
Nitrate	Water	800	0.5 – 70 mg/L	< 0.5 mg/L	SM 4500-NO3 D-00*	Addition of Interference suppressor buffer*

*The Analytical Method and Sample preparation method are provided as Appendix F: *Nitrates by Ion Selective Electrode (Method 4500-NO3-D)*. Per the laboratory Standard Operation Procedure (Appendix F) the sensitivity is defined by the MDL

8.2 Sample preparation method

There is no in-field sample preparation method. The laboratory sample preparation method is outlined in the laboratory SOP provided as Appendix F.

8.3 Special method requirements

There are no special method requirements for the method of analysis being utilized.

8.4 Field procedures table

Field procedures are outlined in Table 6.

Table 6. Field Procedures

Parameter	Sample Type/Equipment	Procedure
Water quality samples	Grab samples/Polyethylene Bottles	Outlined in QAPP
Performance Evaluation Samples	1.0, 10.0, 35.0, and 100.0 mg/l nitrate stock solution ^a /Polyethylene Bottles	Outlined in QAPP
Field Blank Samples	Distilled water sample ^b	Outlined in QAPP
Well location Coordinates	Latitude and Longitude Readings/Field GPS Unit	Outlined in QAPP

^a: Nitrate Stock solution is purchased from independent third-party laboratory

^b: Benton Franklin Health District will supply the de-ionized water for field blanks.

8.5 Laboratory accredited for method

The Benton Franklin Health District is located in Kennewick, Washington. Accredited parameters for this lab include nitrate, using the standard method of 4500-NO₃-D, Nitrates by Ion Selective Electrode. Nitrate samples collected during the course of this study will be analyzed at the Benton Franklin Health District Laboratory.

9.0 Quality Control (QC) Procedures

9.1 Table of field quality control

9.1.1 Field quality control – water samples

A Field Duplicate (FD) sample will be collected at a sampling interval of 1/sampler/week and submitted to the laboratory as a blind sample. A field duplicate is a second sample from the same well using identical sampling procedures. Duplicate sample results will provide an estimate of overall sampling and analytical precision.

Field Blank (FB) samples will be collected at an interval of 1/sampler/week. These samples evaluate the potential for contamination of samples from containers and handling during actual sample collection. Bottles will be filled with de-ionized water in the field and are handled the same as the well samples. De-ionized water free of nitrates will be obtained by the Benton Franklin Health District laboratory for the FB sample use.

Performance Evaluation (PE) samples will be prepped at an interval of 4/ week for 4 weeks (i.e., 4 times per each Fall and Spring sampling event). These samples are used to assess the accuracy of measurement method and the handling and exposure impacts in the field. Performance Evaluation samples will be purchased from an independent laboratory and prepared in the field. Bottles will be filled with a solution of known nitrate concentration (provided by an independent laboratory) in the field and are handled the same as all well samples. Reference solutions will be purchased and provided to the field technicians ahead of time.

Trip Blank (TB) samples are pre-filled bottles with de-ionized solution supplied by the Benton Franklin Health Department ahead of time. These samples will be kept closed, taken to the field, handled the same as the well samples, and then returned with the collected samples to the laboratory for analysis. The intent of this sample is to identify any contaminants associated with the shipping and packaging protocol. One TB will be handled in the field with sample bottles and coolers as if it were a complete sample. There will be one TB per sampling event with a sampling event defined as one of the biannual sampling trips.

The Field Quality Control samples are provided in Table 7.

Table 7. Field QC Samples, Types and Frequency

Parameter	Field			
	Blanks	Duplicate	Trip Blank	Performance Evaluation
Nitrate	1/sampler/week 4%	1/sampler/week 4%	1/event* 0.5%	4/week/4weeks/Event* 8%

* An event is defined as one biannual sampling (spring or fall) and will consist of 4 weeks consecutive sampling weeks. Two samplers will be in the field for each sampling events.

9.1.2 Field quality control – field equipment

GPS units shall be inspected and tested prior to field collection activities. Inspecting and testing shall include turning the units on to assure adequate power supply and readability of the GPS screen. Maintenance of the GPS units will be based on the manufactures' written instructions.

9.2 Laboratory quality control

Routine laboratory quality control procedures maintained by the Benton Franklin Health District's laboratory are adequate in estimating laboratory precision and accuracy for this project. Laboratory quality control samples consist of blank, duplicates, matrix spikes, and check standards (laboratory control samples). The procedures are outlined in Appendix F: *Nitrates by Ion Selective Electrode (Method 4500-NO3-D)*.

Duplicates will be used to assess analytical precision. Matrix spikes will be used to indicate bias due to matrix interferences. Check standards will be used to estimate bias due to calibration. Laboratory blanks will be used to measure the response of the analytical system at a theoretical concentration of zero. The Laboratory Quality Control Samples are provided in Table 8.

Table 8. Laboratory QC Samples, Types and Frequency.

Parameter	Laboratory		
	Check Standards	Method Blanks	Matrix Spikes
Nitrate	2 per run	1 per 20 samples	2 per run

9.3 Corrective action processes

The Benton Franklin Health District conducting sample analysis for this project has specific quality control procedures that include criteria for initiating corrective action based on quality control results. These criteria are specified by the laboratory Method 4500-NO3-D and are included in Appendix F and shown in Table 3, Section 5.2 of this QAPP. The Manager will be contacted when the laboratory has to initiate corrective actions for the data results. The lab will follow prescribed procedures to resolve the problems. Options for corrective actions might include:

- Retrieving missing information.
- Recalibrating the measurement system (if standards fall outside of the established control limits).
- Reanalyzing samples (must be within holding time requirements).
- Modifying the analytical procedures.
- Requesting collection of additional samples.
- Qualifying the results when they are not within acceptable limits.

The Manager will deal with any problems associated with the field data collection. A field log will be used to record data in the field. Once back in the office, data will then be processed and analyzed for errors, discrepancies, completeness, precision, and bias. If found, errors and discrepancies will be noted to be later included in the report. Corrective measures will be taken to eliminate errors and validate the quality of the data as stated above. Data review will be performed on a quarterly basis and accordingly, adjustments with field or the measurement quality objectives may be made. The BCD District Manager will try to isolate whether the problem is associated with the sampler or the laboratory. If the problem appears associated with the sampler the BCD District Manager will evaluate the sampler's procedures and provide

additional training as necessary. If the problem is associated with the Laboratory, the BCD District Manager will contact the laboratory to resolve any problems and corrective actions will be taken as stated above.

10.0 Data Management Procedures

10.1 Data recording/reporting requirements

Following completion of each sampling trip, the BCD District Manager will review the field information that the Field Samplers have recorded on the Chain Of Custody (COC), the Field Log, Ecology Tag and the Sample Tracking Form/Checklist. These forms are to be filled out in accordance with the procedures outlined in the Sampling Procedures Section of this QAPP. Examples of the forms are provided as Appendices B-E. The intent of this review is to check for completeness, accuracy, and clarity of information entered. It is critically important that this step is performed rigorously so that the field data generated by the project is verified.

All laboratory data will be provided to the BCD in electronic format. The data package provided by the laboratory will include both sample analysis as well as reporting of QA/QC samples. If there are any problems with the analysis, corrective actions taken, or changes to the referenced method, these must be included with the result package. Explanations for flags or data qualifiers must also be reported.

10.2 Lab data package requirements

The Ecology accredited laboratory will report the nitrate results for each sample including all QA/QC field samples and all of the internal laboratory QA/QC samples. This includes laboratory blanks and duplicates. The lab data package will be flagged with qualifiers and validated prior to sending to BCD. The date and time of each sample analysis will be provided to ensure holding time requirements were met. Lab documentation will include a narrative discussing any problems with the analyses, corrective actions taken, changes to the referenced method and an explanation of the data qualifiers. Quality control results will be evaluated in the narrative to determine whether the Measurement Quality Objectives (MQOs) were met.

10.3 Electronic transfer requirements

BCD staff will transfer data to Ecology's EIM Database per completion of each sampling season (twice a year). This process will involve exporting data from Excel spreadsheets, into the EIM database per EIM's specified requirements. The data spreadsheets are submitted to the Ecology's EIM database using the online process.

BCD will be responsible for the distribution, tracking, and uploading of all data collected during the project. BCD will enter the data results into Ecology's EIM database as well as provide the data results to the project consultants, landowners, and public.

10.4 Acceptance criteria for existing data

The existing data used for selection of candidate wells will be obtained by USGS, Department of Health, and of Ecology. As such, it should have already been reviewed prior to this project and determined as usable data but all data will be reviewed first for stated quality assurance levels before being used. None of the existing nitrate data will be used in the monitoring study or utilized for decision-making purposes beyond establishing potential sampling locations. As such, acceptance criteria are not necessary for this study.

10.5 EIM data upload procedures

Data will be transferred to Ecology's EIM database annually per online submittal guidelines. To assure accurate entry of data into EIM, 10% of all values will be checked against the source data. If errors are found, an additional 10% of values will be checked; the process will continue in this manner until no errors are found or all values have been verified. The EIM data coordinator will be consulted if data submittal problems arise. The field technician will complete EIM training offered by Ecology.

11.0 Audits and Reports

11.1 Number, frequency, type, and schedule of audits

Good communication, strict adherences to standard protocols, and documentation of deviations from protocols are critical during the two-year sampling effort to maintain adherence to the QAPP. To ensure that procedures are followed, the BCD management will review this QAPP and the overall project design bi-annually and may suggest procedural refinement or additional procedures. A QA assessment carried out by the BCD staff will be performed to determine data usability prior to its use in data analysis. Any such changes will be subject to Ecology approval.

Quarterly and biannual reports will be submitted for the life of the grant and information summarized in narrative form as data becomes available. System audits will be conducted biannually for field activities following each sampling season. Field activity audits will determine whether procedures are being followed and documented. All fieldwork activities are documented using Log Book pages and these will be reviewed by the BCD District Manager and/or BCD Water Quality Specialist.

11.2 Responsible personnel

The BCD District Manager will complete all reports/audits, the BCD field technicians and Water Quality Specialist will complete all monitoring reporting requirements. Audits will occur after field work is complete and consist of a review of field data records for verification and data discrepancy. The BCD District Manager and/or Water Quality Specialist will complete this task. This review will also serve for EIM data upload verification as well as data reporting verification.

11.3 Frequency and distribution of reports

Reporting for this project will be completed according to the required reports in the contract between BCD and Ecology. Reports will be completed by the following schedule:

- January 1 through March 31
- April 1 through June 30
- July 1 through September 30
- October 1 through December 31

Reports shall be submitted within 30 days after the end of the quarter. The final closeout report will be provided 30 days after the expiration date of the project.

After the data are reviewed for each sampling episode, the results for each well will be sent to the respective well owner (and well user if different than the well owner). Additionally, reports will be sent to the newly formed Groundwater Stakeholder Management Group for each quarterly meeting for the lifetime of the grant project.

11.4 Responsibility of reports

The BCD District Manager and/or Water Quality Specialist will prepare all reports to be submitted to Ecology. The reviewed data will be included in a final groundwater monitoring

report for the project prepared by the BCD District Manager. This report will include recommendations for future work based on the collected project data.

BCD staff will be responsible for the generation and distribution of well owner reports. Well owners will receive a hard copy of the well analysis for their well. The results sent will include the date sampled, the nitrate concentration for that sampling event, and field parameter results.

BCD management will prepare and provide quarterly reports to the newly formed Groundwater Stakeholder Management Group meetings. These reports will help guide the group for development of recommendations for a Nitrate Management Plan.

12.0 Data Verification

12.1 Field data verification, requirements, and responsibilities

BCD field technicians will be responsible for reviewing log sheets for errors or omissions before leaving the monitoring site. The Water Quality Specialist is responsible for examining field data for errors or omission as well as for compliance with QC acceptance criteria in addition to verifying all field data. Review of some data such as the field information and certain field QA sample results must be performed in a short time frame to allow the project to continue. The following groups of data will be reviewed and verified by BCD staff:

- Log book.
- Accurate GPS data for well locations.
- Collection of field information other than well locations if applicable (i.e., purge times, point of collection at the well pump, well construct).
- Analytical nitrate data for field samples and field QA samples.

A data quality assessment will be performed twice a year, following completion of a monitoring season. The field records will be organized and reviewed for accuracy and completeness. At this time it will also be determined if the MQOs for precision and bias have been met. The BCD Manager and/or Water Specialist will examine the complete data package in detail to determine whether the procedures outlined in this QAPP were followed.

12.2 Laboratory data review and verification

12.2.1 Laboratory internal QA/QC of data

All laboratory data will undergo an internal quality assurance review by the Benton Franklin Health District laboratory staff to verify that quality control samples meet acceptance criteria as specified in the SOP for the nitrate method. Appropriate qualifiers will be attached to results that did not meet requirements. Data will be checked for problems with sample condition, holding times, analytical procedures, or anomalous results. The data review by the laboratory should document that the analytical MQOs have been achieved. An explanation for any data qualification will be described in a quality assurance memorandum attached with the data package.

12.2.2 Project QA/QC of data

BCD will review the data package promptly upon data receipt. The data package will be verified for completeness and adherence to the data quality objectives. The bias, precision, and accuracy for each sampling episode will be verified as outlined within the MQOs section of the QAPP. Decisions to reject or qualify data will be made by the BCD manager. Data may be rejected because of inadequate or deficient documentation or because the quality assurance samples analyzed fail to meet the data quality objectives identified in the MQOs section. Goals for completeness will be evaluated and, if needed, replacement samples will be obtained and adjustments in subsequent sampling events will be made.

The BCD manager must determine whether the field and laboratory MQOs have been achieved. It is immensely important to the success of the project that the review and verification of data be conducted rigorously. Data that does not meet the MQOs will not be incorporated into the database.

12.3.3 Project review of QC samples

BCD will review the results of the QC samples included for laboratory analysis with the field samples. The data will be reviewed for completeness and accuracy. The results will be checked as follows for:

- Check nitrate concentrations for field blanks are less than the method detection limit. Field blank results that are greater than the method detection limits indicate that these samples may not have been collected properly. Sample collection procedures should then be reviewed with the sampler.
- RPD results for sample and duplicate results need to be checked to be sure they are less than 20%. Greater RPDs are potentially attributable to sampling error. The larger RPDs, if observed, should be flagged in the database and discussed with the sampler to minimize sampling error.

If data MQOs have been met for the sampling episodes, the data will be considered acceptable for use, except as qualified during the data review and validation process. The data will be used to identify trends of nitrate concentrations in the groundwater over the two-year project period.

12.3 Validation requirements, if necessary

Completeness will be assessed through the number of samples collected compared to sampling plan, number of samples delivered to and analyzed by the Benton Franklin Health District in good condition, and within the appropriate holding times. Additionally, completeness will be assessed by the ability of the Benton Franklin Health District to produce usable results for each sample and the acceptability of sample results as determined by the BCD District Manager and/or Water Resource Specialist.

13.0 Data Quality (Usability) Assessment

13.1 Process for determining whether project objectives have been met

If measurement quality objectives have been met, the quality of the data should be useable for meeting project objectives. BCD staff will assess the data to determine if they are the right quality and quantity to support the project objectives. This will include an assessment of whether the requirements for representativeness and comparability have been met. The number of valid measurements completed will be compared with those established.

13.2 Data analysis and presentation methods

Data will be evaluated for obvious errors and the quality will be checked against the objectives described in the document for bias and precision. If data quality objectives have been met for all sampling episodes, the data will be considered acceptable for use (except where qualified during the data review and validation process). The usability of the data will be confirmed by its ability to be used in the evaluation of groundwater nitrate trends, determination of contaminated groundwater areas, and identification of domestic wells with nitrate levels exceeding drinking water MCLs. These data will be presented to the Stakeholder Community and help guide the formation of a Groundwater Nitrate Management Plan.

13.3 Treatment of non-detects

If a non-detect sample result occurs, it will be reported accordingly. During data analysis, if a non-detect sample result occurs it will be considered value of zero.

13.4 Sampling design evaluation

The data will be evaluated to determine if the sampling design has been adequate and if it needs modification for future use. This project is a monitoring effort to gather initial baseline data as the extent and magnitude of nitrate concentrations within Benton County groundwater. The sampling design is established in Section 7.0. The aspects to be evaluated prior to starting the project and again after project data collection is completed include:

- Sampling locations.
- Frequency and timing of sample collection.
- Adequate distribution of samples representing depth.
- Adequate distribution of samples representing area.

The evaluation will be considered successful if the study questions were addressed with the data collected using the established sampling design.

14.5 Documentation of assessment

The BCD District Manager and Water Quality Specialist will be responsible for the data quality assessment. The data kept in spreadsheets and databases will be available for Ecology's review. The water quality summary report will include a quality assurance section that will summarize quality control results and the procedures used to ensure data quality during the monitoring

project. Updates of data results, problems, corrections (if encountered) will be included in the quarterly grant report to Ecology.

15.0 References

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Appendices

Appendix A. Field Sampling Supplies List

To Be Secured By Local Personnel

1. GPS units with extra batteries
2. Sample packing material - bubble wrap, packing beads
3. Additional blue ice or regular ice as may be needed.
4. Additional field coolers for sample storage
5. Permanent markers/ballpoint pens
6. De-ionized water for blank solution
7. Ziploc™ bags - large and medium sizes
8. Copies of field forms
9. Cooler strapping tape
10. A 5-gal bucket
11. Basic hand tools (i.e., Pliers, screwdrivers, hammer, etc.)
12. Additional labels for bottle labeling
13. Paper dust masks
14. Maps with well locations
15. Performance Evaluation Samples (Standard Solutions)
16. Hoses
17. Laptop computer or PDA device
18. Chain of Custody Form

To Be Provided By Benton Franklin Health District

1. Blank Solution (Deionized water)

Appendix B. Field Log

GENERAL INFO	
Date	
Sampler Name	
Well Owner Name	
Name Of Owner Representative On Site	
Well Pump Operation Schedule	
Mailing Address To Send The Results (May Take Two Months)	
WELL LOCATION INFO	
Physical Well Address	
GPS Well Location Longitude (deg, min, sec)	
GPS Well Location Latitude (deg, min, sec)	
Location of previous GPS readings taken relative to well	
SAMPLING INFORMATION	
BCD Sample ID No. (BCxxxxZZ)	
Type Of Sample - Circle Applicable One	Well (WW), Well Duplicate (WD) Field Blank (FB), Trip Blank (TB), Performance Evaluation Samples (PE)
Ecology Well Tag ID No.	
Affix One Bottle Label here	
Time Start Purge, if purging	
Time Sampled	

Inline Hydraulic Components Or Treatment Tanks Between Sampling Point And Wellhead - (circle one or add as needed)	RO Unit Chemigation/Fertigation Unit Surge/Pressure Tanks Other - Specify
Sampling Point Location - Narrative or Sketch	
If not sampled, Why?	
Other Comments (note any deviations, unusual circumstances that may impact results):	

Appendix C. Ecology Chain of Custody

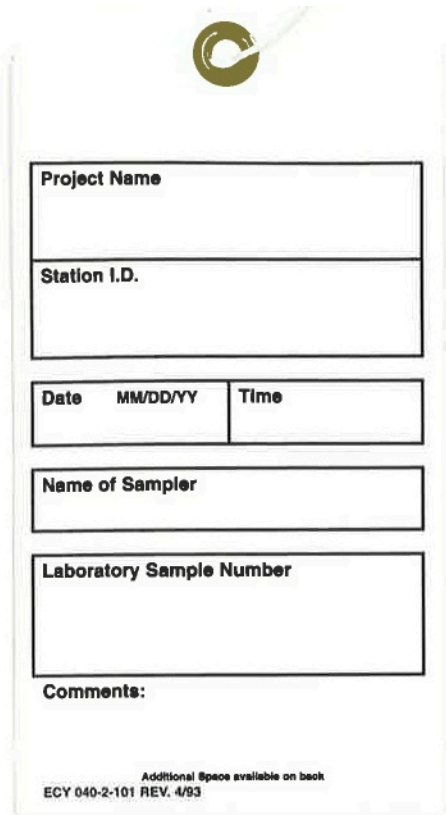
[illegible]

Appendix D. Sampling Tracking Form

Sample Collection Date:

No.	BCD Sample ID (BCD xxxxYY)	Sampler Name	Forms Completed? Check off with (✓)			Sample Condition (✓)			Delivered? (Y/N) (Date if Y)
			Field Log	COC	Ecology Well Tag & Form	Ice	Label	Tag	

Appendix E. Ecology Tag



The Ecology Tag form is a vertical document with a green circular logo at the top. It contains several fields for data entry: Project Name, Station I.D., Date (MM/DD/YY), Time, Name of Sampler, and Laboratory Sample Number. A Comments section is located at the bottom, followed by a note about additional space on the back and a version number.

Project Name		
Station I.D.		
Date	MM/DD/YY	Time
Name of Sampler		
Laboratory Sample Number		
Comments:		
<small>Additional Space available on back ECY 040-2-101 REV. 4/93</small>		

Appendix F. Benton Franklin Health District Standard Operating Procedure: Nitrates by Ion Selective Electrode (Method 4500-NO3-D)

STANDARD OPERATING PROCEDURE Signature Page

Analyte name: Nitrate _____ **Matrix** D _____
Analyte ID: 1805
Method Name SM 4500-NO3⁻ D-00
Method Code 20114107

Revised: 2-23-06 _____

Revised: 3-04-13 _____

Revised: 4-26-14 _____

Revised: _____

Revised: _____

Revised: _____

Revised: _____

Revision #: 3 By: DM Date: 4-26-14

Total Pages: 4 Pages Revised: 4

Lab Supervisor: David Miller Date: 4-26-14

**NITRATES BY ION SELECTIVE ELECTRODE
(METHOD 4500-NO3-D)**

1. Scope:

- 1.1 This procedure is used to determine nitrate activity in drinking water for providing information to public water systems for compliance. Additionally it is used to provide information to private well owners with the intent to help protect the public from adverse effects of high nitrates. The method can be used for a wide range of samples however the vast majority of our samples will be below 40 mg/l.

2. Reference Documents:

- 2.1 Standard methods for the Examination of Water and Wastewater 21st Edition
- 2.2 Orion Nitrate instruction manual

3. Interferences:

- 3.1 A variety of anions can cause interferences with the Nitrate analysis. This interference can be minimized by using an Interference suppressor buffer. The formula is found in Standard Methods, 21st Edition on page 4-123 under reagents # d

4. Sample Requirements:

- 4.1 25 to 100 mls. of drinking water is needed. Samples are diluted with interference suppressor buffer in a 1:1 ratio prior to testing.

5. Apparatus /Instruments:

- 5.1 Direct concentration readout I.S.E. or millivolt meter.
- 5.2 Nitrate electrode (Orion 93 Series, 9300BN).
- 5.3 Reference electrode, double junction (Orion Model 900200).
- 5.4 50 ml and 100 ml., Class A volumetric flasks.
- 5.5 1 and 10 ml. volumetric pipets, Class A.
- 5.6 250 ml and 1 liter poly bottles.
- 5.7 Plastic disposable specimen cups, 4 oz.
- 5.8 Stir plate/bars.
- 5.9 Timer.
- 5.10 Log / reports.
- 5.11 Pipet discard cylinder.
- 5.12 Tensette pipets and tips

6. Chemicals and Reagents:

- 6.1 Reference electrode fill solution - outer chamber (Orion Cat. #900046).
- 6.2 Reference electrode fill solution - inner chamber (Orion Cat. #900002).
- 6.3 Nitrate standard 1000 ppm as Nitrate nitrogen (Orion cat. no. 920707).
- 6.4 Nitrate interference suppressor solution (Orion cat. no. 930710) or made per Standard Methods 21st edition, section 4-123 under Reagents

7. Calibration Standard Preparation:

- 7.1 Label a 100 ml. volumetric flask w/ 50.0 mg/l and pipette 5.0 mls. of 1000 ppm stock standard into the flask, fill flask w/ DI water. Mix well.
- 7.2 Label a 2nd 100 ml volumetric flask w/ 5.0 mg/l and pipette 10.0 mls of the 50.0 mg/l standard into the flask, fill to the mark with DI water. Mix well.
- 7.3 Label a 3rd flask w/ 0.5 mg/l and pipet 10.0 mls of sample from the 5.0mg/l flask. Fill the flask w/DI water. Mix well.
- 7.4 Label 3 specimen cups with 0.5mg/l, 5.0mg/l, and 50.0 mg/l nitrate.
- 7.5 Add 25 mls. of buffer and 25mls. of the appropriate standard to each cup.

8. Meter Preparation:

- 8.1 Connect electrodes to I.S.E. meter
- 8.2 Press 2nd function 5 to select concentration mode and the proper channel.

9. Conditioning electrodes:

- 9.1 Screw electrode tip onto end of nitrate probe and shake like a clinical thermometer to dislodge any air bubbles trapped in the tip.
- 9.2 Immerse tip in distilled water for a minimum of 20 minutes.
- 9.3 Unscrew and drain the reference electrode and rinse with distilled water.
- 9.4 Fill internal chamber with fresh fill solution and replace seal over fill hole.
- 9.5 Replace the inner probe into its plastic sleeve.
- 9.6 Fill the outer chamber with fill solution and seat the probe by gently pushing the end of probe into the sleeve. Use a tissue for this process.
- 9.7 Place both probes into a 50.0 mg/l standard and buffer solution for a minimum of 30 minutes before calibration and use or longer if needed for stability.

10.0 Sample preparation:

- 10.1 Label beakers for all standards, blanks, known samples, spikes, and each sample to be measured.
- 10.2 Place 25 mls. of appropriate solution into each beaker.
- 10.3 Place 25 ml. of interference suppresser buffer into each beaker and add A stir bar to each.
- 10.4 Position magnetic stirrer and turn stir control to position number 3. heat control should remain in the OFF position.

11.0 Calibration and measurement:

- 11.1 Rinse the electrode with distilled water.
- 11.2 Place electrode in the 0.5 mg/l standard. Press measure #3 to start measurement.
- 11.3 When stable and prompted enter 0.5 on the key pad and press measure #3 to enter the standard .
- 11.4 Rinse electrode and place in the 5.0 mg/l standard start measurement. When stable enter the level of standard on the key pad. Press measure #3 to enter the standard.
- 11.5 Rinse electrode and place in the 50.0 mg/l standard, start measurement. When stable enter the level of standard on the key pad press measure #3 to stop the measurement.
- 11.6 Record slope. which should be between 58.0 and 62.0 mv.
- 11.7 Rinse electrode and place in 1.0 mg/l standard. Read and record results when stable. Press measure #3 to start and stop all measurements.
- 11.8 Repeat step 11.7 for all standards, blanks, knowns, spikes and samples.
- 11.9 When complete enter 1st function standby to enter standby mode. Rinse probes, remove the nitrate tip and put away. Place plastic cap over probe.
- 11.10 Place reference probe into cap containing outer fill solution and turn off stir plate.

12. Data Management:

- 12.1 Report all results of public water supplies to the purveyor, and a copy to Data Entry and the appropriate DOH Regional Office If an MCL violation, result over 10.0 mg/l occurs.
- 12.2 Send 1 copy of all private samples to the individual submitting sample and to other individuals as needed. Environmental Health, mortgage company, etc.
- 12.3 State standards are anything less than 10 ppm are acceptable. Anything over 10 is unacceptable and pregnant women would be advised to use an alternate water supply for drinking during the time of their pregnancy and for their children under the age of 1 year. High nitrates can cause a condition known as methemoglobinemia.
- 12.4 All blank, known samples and duplicate spike samples are recorded on control charting programs supplied by the Department of Ecology and are recorded in the QC Manual.

13. Calculations:

- 13.1 The instrument is read out in direct readout mode in mg/l. No calculations are necessary with this method.

14 Quality Assurance and Quality Control:

- 14.1 A reagent blank sample is run with each batch, additional blanks are run when carry over from samples are suspected and on runs larger than 20 samples.
- 14.2 Laboratory fortified matrix (Spikes) are run in duplicate by spiking a single sample within the run. The spike is 20.0 mg/l, approximately half way between the high and low calibration standards.
- 14.3 Two check standards of 1.0 mg/l and 10.0 mg/l are run with each batch to insure that the laboratory is in control with each batch of samples run.
- 14.4 All reagent blanks, check standards, and fortified spikes are recorded on control charts supplied by the Department of Ecology and are recorded in the QC Manual.
- 14.5 Method Detection Levels (MDL) are determined on an annual basis. The Estimated detection level used is 0.02 mg/l and a 0.2 mg/l standard is used for the determination of the MDL. Recoveries of the samples used should fall between 50 and 150% and the RSD (Relative Standard Deviation) should be < 20.0% or the test should be repeated.
- 14.6 The laboratory will report down to 0.5 mg/l. Anything below this level will be reported as < 0.5 mg/l.
- 14.7 Precision is also determined on an annual basis. Using a 2.0 mg/l standard with 7 replicates.
- 14.8 Sample data when check standards are outside of 85% to 115% recovery and spike recoveries are outside of 75% to 125% will be rerun after systems are checked and recalibrated or sample data will be reported as an estimate only and clients will be notified that the laboratories acceptance criteria has been exceeded.

Appendix G. Glossary, Acronyms, and Abbreviations

Quality Assurance Glossary

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

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, etc. (Kammin, 2010)

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

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

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

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

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

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

Continuing Calibration Verification Standard (CCV) - A 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)

Data Quality Objectives (DQO) - Data Quality Objectives are 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).

Dataset - A grouping of samples organized by date, time, analyte, etc (Kammin, 2010)

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

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

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

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

Data verification - Examination of a dataset for errors or omissions, and assessment of the Data Quality Indicators related to that dataset for compliance with acceptance criteria (MQO's). Verification is a detailed quality review of a dataset. (Ecology, 2004)

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

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

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

Laboratory Control Sample (LCS) - A sample of known composition prepared using contaminant-free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern. It is prepared and analyzed in the same batch of

regular samples using the same sample preparation method, reagents, and analytical methods employed for regular samples. (USEPA, 1997)

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

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

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

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

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

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

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

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

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

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:

$$[\text{Abs}(a-b)/((a + b)/2)] * 100$$

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).

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

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

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

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

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

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

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

Split Sample – The term split sample denotes when a discrete sample is further 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)

General Terms

Ambient: Background or away from point sources of contamination.

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

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.

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

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

Nonpoint source: Pollution that enters any waters of the state from any dispersed land-based or water-based activities. This includes, but is 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 is considered a nonpoint source. 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 is a nonpoint source.

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.

Parameter: A physical chemical or biological property whose values determine environmental characteristics or behavior.

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.

Point source: Sources of pollution that discharge 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 that clear more than 5 acres of land.

Pollution: Such 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 is 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.

Total Maximum Daily Load (TMDL): A distribution of a substance in a waterbody 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.

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.

Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this report.

BCD	Benton Conservation District
BMP	Best management practices
COC	Chain of Custody
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
FB	Field Blank sample
GIS	Geographic Information System software
GPS	Global Positioning System
i.e.	In other words
Ma	Million years ago
MQO	Measurement quality objective
PE	Performance Evaluation Sample
QA	Quality assurance
RPD	Relative percent difference
RSD	Relative standard deviation
SOP	Standard operating procedures
SRM	Standard reference materials
TMDL	(See Glossary above)
USGS	U.S. Geological Survey
WAC	Washington Administrative Code
WD	Well Duplicate sample
WRIA	Water Resources Inventory Area
WW	Well Water sample

Units of Measurement

°C	degrees centigrade
ft	feet
km	kilometer
Ma	mega-annum
mg	milligram
mg/L	milligrams per liter (parts per million)
mL	milliliters