Relation between Nitrates in Water Wells and Potential Sources in the Lower Yakima Valley, Washington

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Acronyms/Abbreviations

AOAC – Association of Analytical Communities

CAFO – Concentrated Animal Feeding Operation

CARE – Community Action for a Renewed Environment

CFC – Chlorofluorocarbon

CHHP — Center for Hispanic Health Promotion

DEHP - bis-(2-ethylehxyl)-phthalate

DOH — Department of Health

DQO – Data Quality Objectives

DG – Downgradient

EJ — Environmental Justice

EPA – U.S. Environmental Protection Agency

GIS – Geographic Information System

GPS — Global positioning system

"J" value – Compound was positively identified, but the associated numerical value is an estimate

"JN" value – There is evidence that the analyte is present. The associated numerical result is an estimate

LG – Dairy lagoon

LOE – Lines of Evidence

MCL – Maximum Contaminant Level

MDL – Method Detection Limit

MEL – EPA's Manchester Environmental Laboratory

mg/L – Milligrams per liter

MST – Microbial Source Tracking

NCEC – Northwest Communities Education Center

ng/g – Nanogram per gram

ng/L – Nanograms per liter

N_2 – Nitrogen Gas

^{14}N- Nitrogen 14

^{15}N – Nitrogen 15

NH_4^+ - Ammonium

NO_2^- - Nitrite

NO_3^- - Nitrate

ND – Not detected

NS – Not sampled

NWQL — National Water Quality Laboratory

ORD – Office of Research and Development

PCB — Polychlorinated biphenyls

ppm – Parts per million

QA/QC – Quality Assurance/Quality Control

QAPP – Quality Assurance Project Plan

QC – Quality Control

"R" value – The data are unusable for all purposes

RARE – Regionally Applied Research Effort

REDOX – Oxidation/Reduction Potential

RSKERC – Robert S. Kerr Environmental Research Center

SDWA – Safe Drinking Water Act

SF_6 – Sulfur hexafluoride

SMOW – Standard Mean Ocean Water

SOP – Standard Operating Procedure

TKN – Total Kjeldahl Nitrogen

"U" Value – The analyte was not detected at or above the reported result

µg/kg – Micrograms per kilogram

µg/L – Microgram per liter

UG – Upgradient

"UJ" Value – The analyte was not detected at or above the reported estimated results. The associated numerical value is an estimate of the quantitation limit of the analyte in the sample

UNL – University of Nebraska Laboratory

USGS – U.S. Geological Survey

VIRE – Valley Institute for Research and Education

WW – Water Well

WWTP – Wastewater Treatment Plant

EXECUTIVE SUMMARY

I. INTRODUCTION

This report presents the results for sampling conducted from February 2010 to April 2010 by the U.S. Environmental Protection Agency (EPA) in the Lower Yakima Valley in Central Washington State. The primary purpose of this study was to investigate the contribution of various sources from nearby land uses to the high nitrate levels in drinking water wells. The study looked at three likely sources of nitrate: dairies; irrigated cropland; and residential septic systems.

EPA used standard investigation and analytical methods as well as several analytical methods applied primarily for research. The sampling was conducted as part of an EPA Regionally Applied Research Effort (RARE) grant (EPA 2009). Additional funding was provided by EPA Region 10's Office of Compliance and Enforcement and by the Yakima Valley Environmental Justice (EJ) Showcase Community pilot program.[1]

EPA's sampling effort in the Lower Yakima Valley was partially in response to concerns raised by several agencies and community members who participated in the EPA Community Action for a Renewed Environment (CARE) cooperative agreement with the Northwest Communities Education Center (NCEC) in Yakima County, Washington. The objective of the cooperative agreement was to assist the Yakima Valley community to establish its priorities for environmental health concerns. There were numerous meetings held over a 2-year period from 2007 to 2009. One of the outcomes from the cooperative agreement was that community members identified their top three environmental health priorities as groundwater contamination, asthma, and children's exposure to pesticides.

In October 2008, the *Yakima Herald Republic* ran a series of articles titled "Hidden Wells, Dirty Water" in which it examined a long history of groundwater contamination affecting public and private drinking water wells, primarily in the Lower Yakima Valley. The reporter sent a letter requesting that EPA invoke Section 1431 of the Safe Drinking Water Act (SDWA) to address the problem. Section 1431 authorizes EPA to take action when a contaminant is present or may enter a public water system or underground source of drinking water that may present an imminent and substantial endangerment to human health.

EPA facilitated formation of a work group consisting of representatives from state and local agencies, EPA, and the community. The work group released a report in February 2010, "Lower Yakima Valley Groundwater Quality: Preliminary Assessment and Recommendations." One of the recommendations identified in the report was to conduct an investigation to gather information to try to link high nitrate levels in drinking water wells with potential sources.

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[1] The purpose of the RARE program is to provide EPA Regional Offices with support for near-term applied research projects and enhance interactions and connections between Regional staff and EPA's Office of Research and Development. The EJ showcase projects focus on communities experiencing disproportionate impacts from an environmental health burdens.

The report documented that groundwater data collected in the Lower Yakima Valley from 1990 to 2008 indicated that as many as 12 percent of private wells had nitrate levels above the drinking water standard for nitrate (10 milligrams per liter [mg/L]) and about 20 percent of private wells demonstrated bacterial contamination (WADOE 2010). Nitrate is a naturally occurring form of nitrogen that can be found at concentrations between 0.5 mg/L and to 1.1 mg/L in shallow groundwater (Nolan and Hitt 2003). Nitrate concentrations higher than this range typically indicate that human activities have contributed nitrate to the groundwater.

II. PURPOSE AND SCOPE

As discussed above, the primary purpose of this study was to collect data to investigate the contribution of various sources from nearby land uses to the high nitrate levels in drinking water wells. The objective of this investigation was to sample and analyze likely sources of nitrate (dairies, irrigated croplands, and residential septic systems) and private residential drinking water wells for a variety of chemicals to determine if chemicals other than nitrate can be used to link the nitrate contamination in groundwater to specific sources. The analyses included chemicals that are expected to be associated with one or more of the likely sources, such as pharmaceuticals (both veterinary and human medications), personal care products, steroids and hormones, pesticides and herbicides, as well as other indicators of water quality.

The investigation also used microbial analysis to determine whether the drinking water wells were contaminated with fecal contamination. If the water wells were found to have fecal contamination, then Microbial Source Tracking (MST) was performed to identify the source (i.e., human or ruminant) of the fecal contamination. In addition, EPA performed isotopic analysis for the water wells to determine the general source, or combination of sources, of nitrates in the water wells. Finally, an age dating analysis was completed for the water wells to determine the time since infiltration of water into the water wells.

Figure 1 provides a conceptual site model for the project. The conceptual site model (in conjunction with **Figure 2** – Nitrogen Cycle) provides a graphic description of how nitrate can reach groundwater and eventually drinking water wells. This study evaluated three likely sources of the nitrate contamination in drinking water wells (dairies; irrigated cropland, and residential septic systems). The main sources of nitrogen from the dairies include: dairy waste lagoons; manure piles; and manure applied to crops. For irrigated cropland, the main source is the synthetic fertilizers applied to the land to promote plant growth. For septic systems, it is the human waste that can migrate from the septic systems into adjacent drinking water wells.

As described in **Figure 2 (Nitrogen Cycle),** nitrogen is applied to the land from different sources. The different forms of nitrogen migrate through the unsaturated silts, sands, and gravels and arrives at the water table via different preferential pathways. The nitrogen is converted to nitrate through different chemical and biological processes. The nitrate can then be transported to drinking water wells where humans consume the water or the nitrate can migrate to surface waters (in this case the Yakima River).

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The scope of this study includes an area approximately 40 miles long ranging between 10 and 25 miles wide where EPA had previously collected several hundred samples from residential wells to determine nitrate concentrations. EPA identified areas with some of the highest nitrate concentrations to conduct additional sampling to determine whether other chemicals are traveling with the nitrate from the sources to the groundwater and drinking water wells. This report includes the results for the sampling of 29 wells (25 residential wells and four dairy supply wells), 11 dairy lagoons (15 samples), 11 soil samples (five at dairy application fields and six at irrigated/fertilized crop fields), five dairy manure samples, and three wastewater treatment plant (WWTP) influent samples.   The sampling was conducted in April 2010.

There were several constraints in the study that are important to note. Drinking water samples were collected from existing wells. No new wells or sampling points were installed for this study. Because of this, information on the well depths, screened intervals, and construction details of the wells was generally unknown. In order to analyze for certain chemicals, such as pharmaceuticals and hormones, EPA or equivalent standard methods have not been developed so methods used primarily for research purposes were ~~utilized~~used. Finally, there was limited information regarding the dairy operations. EPA requested information on specific aspects of the dairy operations to develop a better understanding of their day-to-day operations, however the dairies did not provide this information. This information would have contributed to a more complete understanding of the dairies' practices and their use of specific chemicals. These study constraints and their implications on interpreting the results of this study are discussed in Section X.

III. BACKGROUND

Nitrate is an inorganic compound that is a naturally occurring form of nitrogen that can be found at concentrations between 0.5 mg/L and ~~to~~ 1.1 mg/L in unimpacted shallow groundwater (Nolan and Hitt 2003). Nitrate concentrations higher than this range typically indicate that human activities have contributed nitrate to the groundwater. Nitrate is highly soluble in water and mobile in soil, which make it relatively easy for nitrogen from a variety of point and non-point sources to leach through the soil and into the groundwater as nitrate.

Nitrate is an acute contaminant. EPA has established a Maximum Contaminant Level (MCL) for nitrate in drinking water of 10 mg/L under the SDWA. EPA regulates nitrate in public drinking water systems because nitrate concentrations greater than the MCL may cause a number of health problems. Exposure to excess nitrate can result in methemoglobinemia (blue-baby syndrome) in infants and susceptible individuals, which can lead to death in extreme cases (Ward 2005). Methemoglobinemia is caused by the reduction of nitrate to nitrite in the body. Nitrite binds to hemoglobin and lowers the body's ability to carry oxygen in the blood. Some studies have shown a positive association between long-term exposure to nitrate in drinking water and risk of cancer and certain reproductive outcomes, while other studies have shown no association (Ward 2005).

Several water quality investigations for nitrate over the last 30 years in the Lower Yakima Valley, including the 2002 investigation by the Valley Institute for Research and Education (VIRE) were summarized in a February 2010 report entitled "Lower Yakima Valley Groundwater Quality: Preliminary Assessment and Recommendation Document" prepared by the Washington State Departments of Agriculture, Ecology and Health; Yakima County Public Works Department; and EPA (WADOE 2010). The report found nitrate levels above the EPA MCL of 10 mg/L in about 12 percent of private wells.

Nitrate contamination in groundwater is primarily a health risk for rural populations in the Lower Yakima Valley who rely on private wells for drinking water. Public water systems test regularly for nitrate and the data are reported to the Washington State Department of Health. Monitoring those systems that meet the definition of "public water systems" falls under state or federal drinking water regulations. EPA defines a public water system under SDWA Section 1401(4) as amended by the 1996 SDWA amendments as:

> A public water system is a system for the provision to the public of water for human consumption through pipes or other constructed conveyances, if such has at least fifteen service connections or regularly serves at least twenty-five people.

The State of Washington has established requirements for systems serving between 3 and less than 15 connections and fewer than 25 people. These water systems are called Group B (Chapter 246-291 of the Washington Administrative Code), and the state Department of Health (DOH) and local health jurisdictions share responsibility for administrating Group B requirements. The DOH does not regulate wells with just one or two connections that are residential systems, but some local jurisdictions regulate these systems. In 2009, the governor and state legislature set a new direction for regulating Group B systems by eliminating all state funding for this program.

Owners of drinking water wells that have fewer than three service connections (for example, a single, residential well) are not required to regularly sample their drinking water for contaminants. However, the EPA and the Washington State Departments of Ecology and Health recommend that rural residents test their well water regularly. If residents choose to sample and find contamination levels that exceed the MCL, they are not required to take action to address the situation.

IV. NITROGEN CYCLE

Nitrogen is present in many chemical forms in the environment including organic nitrogen, ammonium (NH_4^+), nitrite (NO_2-), nitrate (NO_3-), and nitrogen gas. **Figure 2** shows the nitrogen cycle (adopted from Pidriwny 2006). The processes of the nitrogen cycle transform nitrogen from one chemical form to another. Important processes in the nitrogen cycle include nitrogen fixation, mineralization, nitrification, and denitrification. The mobility of nitrogen is highly dependent on its form and the matrix it moves through. In soils, nitrate is the most mobile form of nitrogen, with the exception of the gaseous form because negatively charged soil particles repel the negatively charged nitrate (Frans 2000).

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Nitrogen is an essential nutrient critical to plant growth in the formation and function of cellular tissue, proteins, and reproductive structures. Nitrogen can be supplied to plants through the organic decomposition of plants or animal waste products or by the application of synthetic fertilizers.

Nitrogen gas composes about 78 percent of the atmosphere. Atmospheric nitrogen must be processed, or fixed, to be used by plants. Some fixation is done by lightning strikes, but the majority of fixation occurs by bacteria. Additional small quantities of nitrate may wash out of the atmosphere from aerosol salt particles from the ocean or dusts from arid regions, or from fossil fuel combustion.

Mineralization occurs when the organic nitrogen in the soil is converted by bacteria into ammonium (NH_4^+). The ammonium is then converted to nitrites and then nitrates by bacteria through nitrification. The nitrates can then be converted back into nitrogen gas (N_2) by bacteria through denitrification. Denitrification occurs in low oxygen conditions in the soil. In the absence of denitrification, nitrates moves with the groundwater until the groundwater is taken up by plants, discharged to surface water, or extracted from a well.

In human-influenced systems, there are significant increases in the amount of nitrogen released to the soil and frequently leached into groundwater from various land uses, including application of synthetic fertilizers or animal waste. While many fertilizers may be composed of nitrate, urea or ammonia are often used. The urea and ammonia is ultimately converted to nitrate by soil bacteria. Animal wastes are another source of nitrogen frequently applied to the land or they can be directly deposited by animals. Infiltrating rain or irrigation water can push excess nitrogen into groundwater from each of these sources, unless it is picked up by plants while still in the shallow subsurface. For additional information on the nitrogen cycle, see Stumm and Morgan, 1996.

V. STUDY AREA

The Yakima Basin is a watershed of great diversity in climate, vegetation, and land use. More than 30 percent of the Yakima Basin is forested, 30 percent is sage-steep steppe rangeland, and 28 percent is in agricultural production (Vaccaro and others 2009). The Yakima River flows from its headwaters near the Cascade Mountains crest to its mouth as where it joins the Columbia River, 160 miles to the east. In the rain shadow of the Cascades, precipitation diminishes to less than 9 inches annually (Yakima County 2011), and irrigation plays a key role in the viability of agriculture. A series of high mountain reservoirs capture snowmelt, which is released through the Yakima River into a complex set of irrigation diversions and canals throughout the basin. Irrigation is supplied to fields during the March through October growing season in a variety of methods including flood, furrow, sprinkler, and drip systems.

This investigation focused on a portion of the Yakima Basin referred to as the Lower Yakima Valley **(see Figure 3).** This broad valley is bounded by basalt ridgelines to the north and south, the Cascade Mountains to the west, and encompasses two counties (Yakima and Benton) and the

million-acre Confederated Tribes and Bands of the Yakama Nation Reservation. The study area includes portions of the Toppenish Basin (western area) and the Benton Basin (eastern area) along the Yakima River. Together, both areas cover approximately 368,600 acres within Yakima County. The Lower Yakima Valley has about 75,000 people, of which about 30,000 use private, unregulated residential wells (WADOE 2010).

In Yakima County, poverty afflicts greater than 20 percent of the population, and a little more than 30 percent of adults have less than a high school diploma. Approximately 41 percent of the population is Hispanic/Latino, which is more than four times the state average of nearly 10 percent. American Indians and Alaskan Natives make up a little more than 5 percent of the county's population, which is three times the state average of almost 2 percent. English is not the primary language (written or spoken) in many households in the Lower Yakima Valley (U.S. Census 2000). Economic viability depends on high-value agricultural production, irrigation, and a reliable supply of farm laborers. Yakima County leads the nation in production of milk per cow and is a top producer of apples, pears, sweet cherries, mint, and hops in the country (U.S. Census 2000).

A. Western Study Area - The Toppenish Basin

The Much of the Toppenish Basin is within the boundaries of the Yakama Nation. Land ownership in the major floodplain of the Toppenish Basin is a checkerboard of Indian trust, Indian fee, and deeded (privately held) parcels. Land use in this area is mixed, with open range and agriculture predominating. The basin is bordered on the north by the Ahtanum Ridge and on the south by the Toppenish Ridge.

B. Eastern Study Area – The Benton Basin

The Benton Basin includes the non-reservation lands along the river and to on the southeast side of the valley. Approximately 60 percent of the valley population resides in this area, which includes the Yakima County communities of Sunnyside, Granger, Grandview, and Mabton.

Comment [LE1]: ? but some of the Benton Basin is included in the reservation along the river

The Benton Basin lies in the southeastern part of the Lower Yakima Valley. The western boundary of the basin abuts the eastern boundary of the Toppenish Basin. The southern boundary is bordered by the Horse Heaven Hills, and the northeastern boundary generally follows the northern flank of the Cold Creek Syncline.

C. Geology, Hydrogeology, and Geochemistry of the Study Area

The information presented below, unless otherwise noted, is summarized from the USGS publication "Hydrogeologic Framework of the Yakima River Basin Aquifer System, Washington" (Vaccaro and others 2009).

The Toppenish and Benton Basins consists of fine- and coarse-grained sediments overlying a sequence of three major basalt flows (see **Figure 4** and **Figure 5** for a general overview of the hydrogeology for the Toppenish and Benton Basins). The structural setting for the study area is created by bounding ridges such as the Rattlesnake Mountains, Ahtanum Ridge, Toppenish

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Ridge, and Horse Heaven Hills. The uppermost basalts of the Saddle Mountain Unit of the Columbia River Basalt Group are typically exposed in these upland ridges. This unit averages more than 500 feet thick. The underlying Wanapum unit averages 600 feet thick. These units are separated by the Mabton Interbed with an average thickness of 70 feet.

> **Comment [LE2]:** These last two sentences are not needed if the basalts are not discussed again by name. Just say how thick they are.

The valley is filled with a variety of sediments that pinch out along the flanks of the ridges. These sediments range from include Touchet Beds, loess and thick alluvial sands and gravels, and significant thickness of Ellensburg Formation. The thickness of these sedimentary units decreases from an average of more than 500 feet in the Toppenish Basin to less than 200 feet in the lower Benton Basin.

Water is found in fractures and interbeds bounded by clinkers (a mass of vitrified material ejected from a volcano) and may be first found at significant depths in the upland ridges, such as Horse Heaven Hills, and especially in the basalts. The water table approaches the surface as the valley is approached from these ridges. Near the Yakima River, it may be less than 10 feet to water, especially during the irrigation season.

There are two main aquifer types underlying the study area. They include a surficial unconfined to semi-confined alluvial aquifer and an extensive basalt aquifer of great thickness underlying the sedimentary deposits. The basalt aquifer is believed to be semi-isolated from the surficial aquifer and stream systems. Groundwater flow within the surficial aquifer generally follows topography, with natural recharge occurring within the headlands and on the sides of the valley and discharge occurring to the Yakima River. Flow within the uppermost portions of the deeper basaltic aquifer can similarly followalso generally follows this pattern.

However, since the basalts extend to great depths, those deeper basaltic layers may convey waters across local flow divides to more regionally significant discharge locations such as the Columbia River. This produces a major flow direction from northwest to southeast as water moves down the valley parallel to the course of the Yakima River. Other, more localized directions of flow — typically at shallower depths in the uppermost sediments — tend to flow toward the Yakima River with components of flow northeast to southwest on the north of the river and southwest to northeast on the south.

It is likely that even more localized and minor components of flow are significantly modified by irrigation practices upland from the Yakima River. These modifications of groundwater flow are not true present in the deeper basalt aquifer in the Benton Basin, where regional flow may be more regional beneath structures such as Rattlesnake Ridge and more generally flowingflows generally toward the Columbia River. In this upland area, predominant groundwater flow is from the northwest toward the southeast. Locally, the flow direction may be modified by geologic structures and by drains, ditches, canals, and other hydrologic features.

> **Comment [LE3]:** These two paragraphs say the same thing: regional flow toward Columbia vs localized flow affected by irrigation, etc. They could be combined.

Sediments such as those shed by the ridges at the margins of the study area and those sediments deposited in the valley bottom by the Yakima River have an internal structure that strongly controls groundwater movement. As the water moves through these sediments, it tends to follow preferential flow paths composed of coarser sediments. Very frequently, there are 10- to 100-fold

differences in velocities ~~from one area to another~~among aquifer materials of such contrasting grain sizes (Freeze and Cherry 1979). These different preferential flow paths can have different water chemistry depending on their location below a source of contamination.   A well that is located along a preferential flow path may draw a substantial portion of its water from a particular source. A well located on an adjacent, but different, preferential flow path may have markedly different chemistry. For this reason, it is anticipated that upgradient sources of nitrates could produce different downgradient effects (such as nitrate in water wells), even in wells from neighboring homes.

> **Comment [LE4]:** Freeze and Cherry citation is about the materials, not this specific area

In addition to the variability caused by the physical ~~makeup~~ characteristics of the aquifer, many compounds react with the aquifer materials in a way that changes their mobility. Some compounds like nitrate or ions like chloride interact very little and are transported nearly as fast as the water itself flows in the aquifer. Chloride tends to minimally adsorb to the aquifer material. Nitrate similarly minimally adsorbs and does not break down unless it encounters areas with very low oxygen in the aquifer and high concentrations of denitrifying bacteria. Other compounds, such as iron or manganese, often participate in chemical reactions and can create immobile minerals, which can change their concentrations as measured in water wells in unpredictable ways (Fetter 1980).

Organic compounds, which are any gaseous, liquid, or solid chemical compounds containing carbon, are typically less mobile in water than inorganic compounds. Organic compounds tend to adsorb to organic carbon in the aquifer material and may be degraded by bacteria and either disappear entirely or may be greatly reduced in concentrations. Even if not broken down, most organic compounds will move much slower than nitrate because they tend to adsorb to other organic matter in the aquifer. As a result, in general, they are unlikely to be transported as far or as fast as the nitrate (Stumm and Morgan 1996).

VI. THREE STUDY PHASES

Sampling efforts conducted to date in the Lower Yakima Valley by various agencies and groups have focused on nitrate. While these studies have been useful to document the problem of high nitrate levels in groundwater and private wells, they did not evaluate the link between the various sources and the high nitrate levels. The objective of this study was to sample and analyze sources of nitrate (dairies, irrigated crop lands, and residential septic systems) and private residential drinking water wells for a variety of chemicals to determine if chemicals other than nitrate can be used to connect the nitrate contamination in groundwater and drinking water wells to specific sources. Also, the study used several other analytical techniques (i.e., microbial source tracking, isotopic analysis, and age dating) to evaluate the contribution of various sources to high nitrate levels in drinking water wells.

To accomplish these objectives, EPA designed a three-phased study within two contiguous segments of the Yakima River Basin extending approximately 40 miles from the town of Union Gap to the Yakima County line near the town of Byron. The upper segment comprises the entire

Toppenish Basin, and the lower segment comprises the northern portion of the Benton Basin. The width of the study area was defined by the width of the Toppenish and Benton Basins along the selected segment, which varies between approximately 10 ~~to~~ and 25 miles **(Figure 3).**

The purpose of Phase 1 was to identify and map major sources of nitrate in the study area, based on historical records. In Phase 2, the residential wells in closest proximity to the potential sources were identified, sampled, and analyzed for nitrates using screening-level analytical protocols and confirmatory laboratory analysis.

Phase 3 of this study involved using the results of Phases 1 and 2 to identify residential wells with high nitrate concentrations and locate upgradient nitrogen sources. Once these source areas were selected, Phase 3 involved the collection and analyses of numerous samplesfrom the potential source areas, downgradient wells, and upgradient wells (which were not available in some areas). The following subsections provide details about each phase of the study.

A. Phase 1: Geographic Information System (GIS) Tool Development and Screening Analysis for Nitrogen Sources

The purpose of Phase 1 was to identify and map major sources of nitrate in the study area, based on historical records. Phase 1 included the development of a GIS tool to organize a large amount of historical information and allow the examination of the landscape for spatial patterns in that data. EPA used the GIS tool to identify sites to be sampled in Phases 2 and 3 of the project. The tool incorporates information from the Lower Yakima Valley about known nitrate, bacteria, and general chemistry data. It also includes information on locations of wells, parcels with septic systems, land elevation, depth to groundwater, crop type, estimated fertilizer application rates, dairy and animal feeding operation locations, roads, and an aerial photo layer.

Phase 1 included a screening analysis to determine the potential sources of nitrogen in Yakima County. The screening analysis, described in more detail below, combined information on land use with some simple calculations in order to estimate the amount of "potential nitrogen available" from several sources. The estimates indicate that three sources; dairies, irrigated cropland and septic/wastewater, can account for as much as 98% of the nitrogen available to be delivered to the aquifer.

The screening analysis showed that about 63 percent of the potential nitrogen available comes from dairies, about 32 percent from inorganic fertilizers applied to irrigated crops, about 3 percent from septic and wastewater systems, and the rest from relatively minor sources such as nitrogen deposited by precipitation (EPA 2011a). These estimates did not account for losses from various biological, physical, and chemical processes.

Based on this screening, EPA focused the Phase 3 sampling on three sources: dairies; irrigated cropland; and residential septic systems. Although there are other sources of nitrogen in the Lower Yakima Valley, EPA focused on the three areas believed to have the largest potential nitrogen contribution **(see Figure 6).**

Comment [LE5]: Don't jump from this general statement to "63% …." It implies a lot more precision and certainty than appropriate. This is where you need to say that the estimates are only for relative comparisons and to make sure you've captured all of the potentially significant sources.

Comment [LE6]: Or something like this. It might actually help a lot to include a table showing these calculations in one place.

Comment [LE7]: Without the info I added above, at this point in the document, the reader has no idea what you mean by this term. You need to introduce the topic in general, then explain that you used some simple, but reasonable assumptions, and only then say what the resulting numbers were.

Comment [LE8]: This makes it sound like a much harder number than it really is

Comment [LE9]: This is one of the qualifying statements that needs to be read in advance of the numbers

Comment [LE10]: Figure 6 needs to be way smaller and integrated into the text. It currently has a very low ratio of information per square inch!

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EPA is working to further refine these estimates and evaluate nitrogen fate and transport, in a collaborative project between EPA and the U.S. Geological Survey (USGS). A report is due in the fall of 2012. The project focuses on better characterizing the sources of nitrogen applied to the land and the relationship between ~~increasing or decreasing nitrogen~~changes in nitrogen loading on the land ~~and~~ to ~~to~~ levels of nitrate in drinking water wells.

1. Dairies

~~A trend over the past several decades has led to larger and larger dairies~~

Average dairy size has increased significantly in the last several decades (EPA 1998). Currently, 68 dairies in the Lower Yakima Valley are registered with the Washington State Department of Agriculture **(see Figure 8).** These facilities have a total of approximately 133,000 milking animal units (EPA 2011a), an average of almost 2,000 milking animal units per dairy. Modern dairies generate large quantities of animal wastes, which must be managed appropriately to prevent pollution, including pollution of surface and groundwater. Greater concentrations of animals and the scarcity of available land have made it increasingly challenging to effectively manage animal wastes to prevent adverse impacts to public resources.

In addition to generating large quantities of manure, dairies also generate large amounts of liquid waste from cleaning activities. Liquid wastes are typically flushed into a series of lagoons before they are sprayed on nearby fields as fertilizer.

Dairy wastes contain key components of fertilizer, including nitrogen, phosphorous, and potassium. When used as a fertilizer, dairy wastes are often supplemented with synthetic fertilizer to meet specific nutrient needs of the crop being grown. In the lower parts of the Yakima Valley dairies are concentrated around the cities of Sunnyside, Grandview, Mabton and Granger, although some are in more ~~sparcely~~ sparsely populated areas of the valley and on the Yakama Reservation.

The total annual nitrogen production associated with dairies in Yakima County, without accounting for estimated losses, is approximately 36 million pounds per year. This amount was calculated by multiplying the number of dairy cows by the estimated nitrogen production rate per cow provided by the Washington Department of Agriculture (EPA 2011a).

> **Comment [LE11]:** This is the type of info that needs to be included in the introduction explaining how these numbers were derived (before the pie chart.)

2. Irrigated Cropland

Yakima County is one of the world's most fertile growing regions, with more than 240,000 acres of cropland. Agriculture is the primary economic activity in Yakima County, accounting for approximately 70 to 80 percent of land use. Most of the crop land in the area is irrigated. The major irrigation districts include the Roza, Sunnyside Valley, Wapato Irrigation Project, Grandview, and Zillah. Major commodities grown in the valley include apples, alfalfa, corn for silage and grain, grapes, hops, cherries, and mint **(see Figure 9).**

> **Comment [LE12]:** Figure 9 needs a great deal of simplifying and clarifying. There are just way too many categories and they are way too hard to tell apart. Get rid of those that are land uses and not crops (fallow, golf course, research.) Make sure to highlight the ones you used in the analysis (corn, hops, mint). Either lump the rest into some logical categories (flowers, nursery crops and opiates, assuming those are poppy fields, for example) OR keep them separate, but use a similar color family for them, and a different one for other groups. Right now all the pinks are too similar, all the baby blues are too similar, and so on. Nothing is emphasized and almost everything is hard to identify. Fix typo in "wheat."

Inorganic fertilizers contain high amounts of nitrogen. Nitrogen application is essential to crop growth and development, but crops can be treated with more nitrogen fertilizer than they are able

to take up through their roots. Application can result in excess nitrogen infiltrating through the soil below the root zone into the groundwater. However, it is not just the use of fertilizer that can contribute nitrate to the groundwater, but rather the amount, timing, frequency, and type of fertilizer, as well as the timing and amount of irrigation relative to the application of fertilizer. Other factors such as denitrification in the soil by microorganisms, soil type, and volatilization to the atmosphere, also affect the amount of nitrate in groundwater.

EPA estimates that about 18.5 million pounds of nitrogen are added to the land each year in the form of inorganic fertilizers in Yakima County. This estimate was derived by taking the total acreage for each crop in Yakima County in 2007 and multiplying the acreage by the Washington State University-recommended average nitrogen application rate for each crop (EPA 2011a). These rates are general and the specific application rates and management practices by farmers could vary greatly. In addition, this estimate is the amount of nitrogen that is potentially applied to the land and does not include the uptake by plants nor the nitrogen removed at harvest or returned to the soil as crop residue.

As with the estimates for the dairies, the estimates were used as a relative value to compare with other estimates to assist in the study design. EPA is working to refine these estimates in a separate work effort discussed above.

Comment [LE13]: This is really important. Needs to be stated at the very beginning of the discussion of the screening phase of the project

3. Septic Systems and Wastewater

Domestic wastewater is managed by city wastewater treatment plants in Yakima County, but a large percentage of the mostly rural population relies on septic systems **(see Figure 10)**. As of 2009, there were about 22,000 septic systems registered with Yakima County (EPA 2011a). Septic systems in Yakima County are permitted based on the average number of occupants per home square footage. Septic system use could exceed the design capacity in poor rural areas. Poor or deferred maintenance also could lead to improperly functioning septic systems, which could lead to increased concentrations of nitrogen moving into groundwater.

There are 16 permitted wastewater treatment facilities in Yakima County (EPA 2011a). Wastewater As wastewater treatment facilities process and treat wastewater, to they produce biosolids, which are nutrient-rich organic material. After the solids have been processed and treated, they are recycled as fertilizer and soil amendment. There are about 200,000 pounds per year of biosolids applied in Yakima County, which includes biosolids imported from metropolitan municipalities in Western Washington State (EPA 2011a).

An estimated 1.4 million pounds per year of potential anthropogenic nitrogen was calculated by multiplying the 2007 population in Yakima County (234,564) by the rate of 6 pounds of nitrogen per person per year (EPA 2011a). This approach provides an overall estimate of 1.6 million pounds per year of nitrogen from biosoilds and septic systems or about 3 percent from septic systems and wastewater.

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4. **Other Sources**

Other sources of nitrogen, which are considered relatively minor, include nitrogen deposited by precipitation and non-cropland application of fertilizer to lawns, public parks, and golf courses. Application of nitrogen fertilizers was not estimated for the dryland wheat crops grown in the valley since they are not irrigated and the natural precipitation for the area likely limits nitrate leaching potential.

> **Comment [LE14]:** After the discussion of the separate pieces, this is where I would summarize the numbers and show the pie chart.

B. **Phase 2: Identification of Wells with High Nitrate Concentrations**

The objective of Phase 2 was to determine the extent and magnitude of nitrate contamination downgradient of likely sources and to provide residents with information on the nitrate levels in their drinking water wells. The GIS tool developed in Phase 1 was used to help identify sampling locations for Phase 2. The sampling took place between February 22 and March 6, 2010. This time period corresponds to the pre-irrigation season when the aquifer is least influenced by recharge with irrigation-delivered surface water. **Figure 7** provides a map of the locations and nitrate concentrations for the Phase 2 sampling, **Appendix A16** contains a summary of the results for the compounds evaluated in Phase 2.

EPA developed a Quality Assurance Project Plan (QAPP) for Phase 2 (USEPA, 2010a). It identifies the data quality objectives, sampling process design, sample collection procedures, sample handling and custody requirements, analytical methods, instrument calibration, data management, and standard operating procedures for instrument calibration, shipping container preparation, and chain-of-custody process. The Center for Hispanic Health Promotion (CHHP), a local bilingual, bicultural organization affiliated with the Fred Hutchinson Cancer Research Center, was contracted to assist in recruiting residences for sampling, scheduling, and Spanish interpretation assistance.

A series of public meetings, newspaper articles, and radio announcements notified the community of the Phase 2 work. Samples were collected by two-person teams trained for the project. Sample teams verified access from the homeowner, collected a global positioning system (GPS) location at the well, and completed a data collection form developed by EPA. Each sampling team maintained a field logbook to document sampling activities. For each well, water quality parameters were measured in the field using a Horiba multi-parameter probe.

The parameters measured included dissolved oxygen, oxidation/reduction potential, total dissolved solids, pH, and temperature. Measurements were taken at 1-minute intervals. At 5 minutes, the sampling team used nitrate colorimetric test strips as a field screening tool to provide an indication of whether the water exceeded the MCL of 10 mg/L for nitrate. The Hach test strips measure nitrate concentrations in increments of 0, 1, 2, 5, 10, 20, and 50 mg/L. If the test strip indicated the water may exceed the MCL (10 mg/L), samples were collected for analysis by EPA's Manchester Environmental Laboratory (MEL).

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Samples submitted to the laboratory were also analyzed for enumeration and quantification of total coliform using EPA's mobile microbiology laboratory. If total coliform bacteria were present, the samples were also analyzed for *E. coli* and fecal coliform bacteria. If *E. coli* or fecal coliform ~~was~~ were detected, an additional sample was collected from the same well and analyzed using Microbial Source Tracking. Microbial Source Tracking is a molecular technology tool capable of differentiating human and ruminant sources of fecal contamination.

During the 2 weeks EPA was in the field, about 330 homes were visited and all were screened for nitrate levels using the Hach tests strip. Seventy of those homes, or just over 24 percent, were found to exceed the MCL of 10 mg/L for nitrate **(Figure 7).** The percentage of homes with nitrate levels above the MCL in this study may be higher than the 12 percent from historical records because the homes sampled in Phase 2 of this study were selected ~~because they are in close~~ due to their proximity to likely sources. This method of selection would bias the results compared with a study where the sampling locations were selected randomly. Another possible explanation is that the previous studies were completed several years ago and the area with nitrate levels above the MCL ~~could~~ may have increased in size.

Eight wells, or 2 percent, were found to have fecal coliform bacterial contamination or contamination with *E.coli.* This result is less than the 20 percent frequency found in past studies. Residents were informed of the results from the test strips immediately. Residents of all of the homes with nitrate levels greater than 10 mg/L or with bacterial contamination were provided with written laboratory results.

The Phase 2 sampling was informative in several ways. The results confirmed that nitrate concentrations in many domestic drinking water wells were above the EPA drinking water standard of 10 mg/L and provided information to the residents on the levels of nitrate in their wells. In addition, the Phase 2 results were used to identify the Phase 3 sampling locations.

C. Phase 3: Investigating Contribution of Sources to High Nitrate Concentrations in Drinking Water Wells

The objective of Phase 3 was to investigate the contribution of various sources from nearby land uses to high nitrate levels found in water wells using a wide array of sampling and analysis techniques. The wells shown in **Figure 7** with the highest nitrate concentrations were selected for more extensive Phase 3 sampling and analyses. In addition, the specific sources associated with each well were selected for Phase 3 sampling and analysis. Representative upgradient wells also were selected for the locations where they were available.

After selecting all the sampling points, EPA grouped them into three basic types of sources (dairy waste, septic system wastes, and irrigated/fertilized crops) at five general sampling areas shown in **Figure 11**. Each area contains a number of nitrate-contaminated residential wells (above MCLs) and potential sources. Two of these areas contain only dairy-farm contamination sources (such as manure piles, lagoons, and application fields), and the three other areas contain both septic systems sources and irrigated cropland sources. The three source types and five sampling areas are shown in the **Table 1** (see attachment). **Table 1** also illustrates how the experimental

> **Comment [LE15]:** There are 3 distinct called-out areas shown in Figure 11. It would help to name all 5 and show them on the map.
>
> This actually gets more confusing as I read along. 8 areas are described—2 dairy, 3 septic, 3 irrigated. Everything that is a "sampling area" on Table 1 should be labeled on the map.

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design of the study varied, depending on the waste source type (dairy, septic system, or irrigated cropland).   In general:

1. Investigation of each of the two dairy waste areas included sampling one upgradient well and a number of downgradient wells that are associated generally, but not individually, to a number of waste samples collected from lagoons, waste application fields, and manure piles. The well and waste samples were analyzed for many different chemicals, microbiology and using several different analytical techniques. The data for the downgradient wells were compared to the data for the upgradient wells and the various waste sources to determine if the different compounds can be used to identify specific sources.

2. The investigation of the three septic waste areas included sampling residential wells downgradient from septic systems. The chemicals detected in the downgradient wells were compared to samples collected from the influent to wastewater treatment plants (WWTPs) located in Toppenish, Mabton and Zillah. These WWTP influent samples were selected to be representative of the types of chemicals that could be released from residential septic systems.

3. The investigation of the three irrigated cropland areas (hops, mint, and corn) included sampling a total of six downgradient wells. Each well was exclusively paired with a soil sample from a specific type of crop. The chemicals detected in the downgradient well were compared to the chemicals detected in the corresponding soil sample from each of the six cropfields.

Each of the sampling areas was evaluated looking at five different groups of chemicals or analytical techniques. The five groups included: general chemistry, microbiology, and organic chemicals. In addition, the well samples, lagoons, and WWTP samples were evaluated using isotopic analysis and the water wells were evaluated using age dating techniques.

1.   **Phase 3 Sampling Locations**

EPA used the Phase 1 GIS tool, Phase 2 sampling results, and a set of selection criteria to identify 63 sampling locations for Phase 3 (see **Figure 11** for the location for each of the sampling sites). **Appendix A1** provides the sample location, sample location type, description of the sample medium, and a summary of analytes at each location.

Criteria for Selection of Dairies and Associated Sampling Locations

EPA collected samples at seven dairies. Dairy selection was based on data from Phases 1 and 2 of the project using the following criteria:

- High concentration of animals per unit area of available land.

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- Indication of over-application of nutrients to application fields based on information contained in Washington Department of Agriculture inspection reports *(need cite)*
- Relatively consistent direction of groundwater flow from season to season.
- Minimal upgradient nitrate sources.
- Existence of private drinking water wells along the downgradient side, or sides, of the dairy.
- History of nitrates levels above the MCL in downgradient drinking water wells.

Samples were collected from dairy lagoons, manure piles, application fields, and supply wells associated with the dairies. Wells upgradient and downgradient of the dairies also were identified for sampling. One sample was collected at the influent to each lagoon, and two samples were collected at the outlet from the lagoons. The manure pile samples were collected on site at each dairy. The application field samples were collected at the nearest field where lagoon waste recently had been applied.

Criteria for Selection of Residential Septic System Areas and Associated Sampling Locations

Samples were collected from four private drinking water wells that had high nitrate concentrations in Phase 2 and are located downgradient of areas with a concentration high density of residential septic systems in close proximity to one another. Additionally, samples were collected from the influent stream to three small wastewater treatment plants in the Lower Yakima Valley (Zillah, Mabton, and Toppenish) to serve as a surrogate for septic system influent and to characterize compounds found in rural septic systems. The criteria used to select the water well sampling locations in the residential septic system areas included:

- High concentration density of homes not served by sanitary sewers.
- Relatively consistent direction of groundwater flow from season to season.
- Minimal upgradient nitrate sources other than septic.

Criteria for Selection of Irrigated Cropland Areas and Associated Sampling Locations

Soil samples were collected from two fields each of corn, hop, and mint. Corn, hop, and mint were the crops selected because they require significant nitrogen to produce the large amounts of plant biomass for yield in contrast with other crops such as tree fruit. Thirty sub-samples per field were collected and composited to obtain a representative soil sample. One well was selected for sampling for each crop that was downgradient to the field. The criteria used for the site selection for the three crop fields were as follows:

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- Presumed history of high fertilizer application rates and use of agricultural chemicals.

- Relatively consistent direction of groundwater flow from season to season.

- Minimal upgradient nitrate sources.

- History of nitrates levels above the MCL in downgradient drinking water wells.

VII. PHASE 3: COMPOUNDS AND ANALYTICAL TECHNIQUES

EPA analyzed for nearly 200 chemicals and ~~utilized~~ used several analytical techniques to investigate the high levels of nitrate in water wells to likely nitrate sources: The chemical analyses and analytical techniques were grouped as follows: general chemistry; microbial data; organic compounds; isotopic analysis; and age dating/gas studies. Each of the five groups are evaluated independently in an effort to connect specific sources to the nitrate found in residential drinking water wells.

This section describes the analyses that make up each of the five groups, why each of the analyses was conducted, and the issues or challenges associated with specific analyses and techniques. The data for the study are summarized in appendices referenced in each section below. A discussion of the analytical results is included in Section IX.

A. General Chemistry

The study evaluated four ~~areas~~ aspects of general chemistry: nitrate and other forms of nitrogen; major ions; minor and trace inorganic elements; and perchlorate. Each is discussed below.

1. Nitrate and Other Forms of Nitrogen

Samples from all water wells were analyzed for nitrate. All water wells, dairy lagoons, and WWTP influent samples were analyzed by EPA's Manchester Laboratory for nitrate plus nitrite, ammonia, and total Kjeldahl nitrogen (TKN). TKN is the sum of organic nitrogen and free ammonia. EPA conducted this analysis to ensure all major forms of nitrogen were identified, regardless of what form the nitrogen took.

For example, nitrate is generally not detected in a dairy lagoon because the chemistry of the dairy lagoon is anoxic (lack of oxygen) based on the large amounts of organic matter present. Nitrogen is present in the dairy lagoon, but in the form of organic nitrogen and as ammonia or ammonium released by bacterial action on the organic matter. Some of this ammonia can volatilize from the surface of the dairy lagoon. The ammonia is then converted to nitrite and then nitrate once it comes into contact with oxygen and bacteria.

In addition, total nitrogen was measured for each sample. Total nitrogen is the sum of nitrate, nitrite, and TKN. The concentrations of total nitrogen can be compared and evaluated for

Comment [LE16]: What I would have found handy in this section = summary tables!
  1.List sample type (wells, lagoons, etc.) in column A followed by columns for each analysis type. Place X in boxes where appropriate.
  2. For each category (major ions, minor and trace organics, pesticides, etc) a table listing what those analytes are—as in Tables 2 and 3.

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patterns in concentrations between upgradient water wells and downgradient water wells with likely sources, such as dairy lagoons and manure stockpiles that receive dairy waste located between these points. The results for the water wells, dairy lagoons, and WWTPs are included in **Appendix A2**.

All manure piles and application field samples were analyzed by Cascade Analytical Laboratory for extractable nitrate, extractable ammonia, and total nitrogen by combustion. These analyses were conducted to provide an indication of fertilization practices and the potential for leaching of nitrogen from the fields containing manure or inorganic fertilizer and to quantify the potential for these materials to act as sources of nitrate to the groundwater. The nitrogen not taken up by the plants would be available for mobilization by infiltrating rainwater or irrigation and could be delivered to the groundwater. The results for the manure piles and application field samples are included in **Appendix A3**.

Nitrate was analyzed at three different labs for different purposes. Cascade Analytical Laboratory in Union Gap analyzed the water wells samples for nitrate using EPA Method 300.0. Method 300.0 provides for measurement of nitrate alone. Method 300.0 requires the sample to be analyzed within 48 hours after it is collected. This method was used for the water well samples because it is specified as the method for evaluating the MCL for nitrate and Cascade Analytical Laboratory was used because of its proximity to the study area. The short holding time for Method 300.0 (48 hours) made it a challenge to get the samples to EPA's Manchester Laboratory in the required time.

EPA's Manchester Laboratory analyzed for nitrate as part of the general chemistry suite using Method 353.3. Method 353.3 measures nitrate plus nitrite and is one of several analytes measured in Method 353.3. This method has a holding time of 28 days because the samples are preserved. Finally, the University of Nebraska analyzed samples for nitrate using Method 353.3 to complete the isotopic analysis.

Appendix A4 provides a comparison of the nitrate concentrations reported by each of the three laboratories for the water wells sampled in Phase 3. The results for the nitrate analysis are similar among the three laboratories, which suggest the analyses are accurate. (One exception was sample WW-18.) Even for WW-18, two of the labs reported consistent concentrations of 72.2 mg/L (Cascade) and 72.3 mg/L (UNL).

4.2. Major Ions

All water wells, dairy lagoons, and WWTP influent samples were analyzed for the major ions by EPA's Manchester Environmental Laboratory. The major ions were not analyzed for soil and manure samples because, in general, the purpose for analyzing the major ions is to track the chemical evolution of migrating groundwater.

An ion is an electrically charged species consisting of a single atom or a group of atoms. It is formed when a neutral atom or group of atoms either gains or losses electrons. The major ions

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evaluated included. calcium,; chloride,; fluoride,; iron,; magnesium,; nitrate,; potassium,; sodium,; and sulfate. The results for the major ions are included in **Appendix A5.**

Different ions have different chemistries and transport mechanisms. For example, chloride does not generally sorb to particles or participate in reactions with the aquifer material. Other ions, such as potassium and sodium, are much more likely to react with minerals and sorb to aquifer materials. Because of the absence of oxygen, sulfate would not be expected to be found in the dairy lagoons. The expected form of sulfur in the dairy lagoons would be sulfide or sulfur still bound in the organic matter. Sulfate would be formed after the dairy lagoon waste escapes from the lagoon and has the opportunity to react with oxygen, oxidizing the forms of sulfur to mobile sulfate in the groundwater.

For this study, the major ions were evaluated for spatial patterns in concentrations from upgradient wells to downgradient wells. If the concentrations in the downgradient wells are higher for specific ions than in the upgradient wells, and those same ions are abundant in a specific source such as a dairy lagoon, then the source is a likely contributor to those higher levels.   For example, if chloride is detected at high levels in a dairy lagoon and the concentrations of chloride in a water well downgradient of the dairy lagoon are higher than in compared with a well upgradient of the dairy lagoon is higher, it is an indication the dairy lagoon is contributing chloride to the downgradient well.

5.3. Minor and Trace Inorganic Elements

All water wells, dairy lagoons, and WWTP influent samples were analyzed for minor and trace inorganic elements by EPA's Manchester Laboratory. Twelve minor and trace inorganic elements were evaluated: arsenic, barium, bromide, cadmium, chromium, copper, lead, manganese, mercury, selenium, silver, and zinc. Minor and trace inorganic elements were not analyzed in the soil or manure samples for similar reasons cited above for the major ions. The results for the minor and trace inorganic elements are included in **Appendix A5.**

The trace inorganic elements were included in this study because the sensitivity of certain metals to oxidation/reduction potential (how oxygen rich the waters are) can provide indications of releases from dairy lagoons. For example, the change in oxygen can lead to the increased mobility of metals such as arsenic and manganese. Oxygen is consumed in microbial reactions that use organic carbon. If an increased concentration of arsenic and manganese in downgradient water wells in comparison to upgradient water wells was seen, then it could provide an indication of the influence of an organic carbon source such as dairy lagoons.

Comment [LE17]: But it is not the "sensitivity" that gets measured. So I'm hoping the rest of the paragraph explains this.

Comment [LE18]: Specify increase or decrease since this is so specific

Comment [LE19]: I really don't understand this paragraph.

6.4. Perchlorate

All wells was tested for perchlorate and analyzed by the EPA's Robert S. Kerr Environmental Research Center (RSKERC) in Ada, Oklahoma. The results for perchlorate are in **Appendix A6.** Perchlorate is the most highly oxidized form of chlorine and tends to accumulate in caliche associated soils in arid regions such as Eastern Washington and Oregon (Rao and others 2007). In this study, it was used as an indicator for potential naturally occurring nitrates.

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There is a very slight, but steady, deposition of nitrate and perchlorate from the atmosphere. Much of it starts as aerosol salt particles released from combustion in transportation or power generation or carried off the oceans as aerosols or dust particles from deserts by winds (Prospero and Lamb 2003). In this region, the National Atmospheric Deposition Program (http://nadp.sws.uiuc.edu/) calculates aerial deposition of atmospherically derived nitrate at approximately 0.9 pounds per acre per year. Perchlorate accumulates at much lower rates but has not been studied to the same extent, so data are lacking.

This accumulation of nitrate and perchlorate has been occurring since the end of the last glacial period, approximately 10,000 years ago. In higher rainfall areas, both these compounds are sufficiently soluble to be carried into the subsurface and potentially into groundwater. However, these compounds can build up in the shallow subsurface with the calcium carbonate that forms the cement-like caliche layer in arid regions such as the Lower Yakima Valley.

The same conditions that would wash the nitrate out of a caliche soil horizon – the first application of irrigation water to a new field converted from sage habitat – would flush out perchlorate as well. These two compounds, nitrate and perchlorate, are somewhat differentially extractable and it is more common to find conditions where nitrate persists but the perchlorate has been mobilized and lost to the underlying groundwater. As shown in the results section, only a few of the wells showed high values of perchlorate despite the presence of significant amounts of nitrate with an isotopic signature suggesting an atmospheric origin.

> **Comment [LE20]:** Are you trying to say the data are often difficult to interpret?

> **Comment [LE21]:** Results are not discussed for other parameters in this section. Why for this one?

~~D.~~B. Microbiology

All water wells, dairy lagoons, and WWTP influent sample were analyzed for either total coliform, fecal coliform, or ***Escherichia coli*** (*E. coli*) as an indicator of fecal contamination. The results for microbiology are in **Appendix A7**. EPA's Manchester mobile microbiology laboratory or Cascade Analytical Laboratory in Union Gap conducted the analysis. Microbial Source Tracking (MST) was performed in samples that tested positive for fecal coliform. MST was not completed for the water wells because fecal coliform was not detected in any of the water wells. MST was not completed on nine of the 15 dairy lagoons ~~and all~~or any of the three WWTP influent samples because of limited resources.

MST is a means of identifying the source of the fecal contamination in a water sample. The method used in this study is genotypic and is used to detect the presence of host-specific Bacteroides species shed in the fecal material of humans or ruminants. This method allows a presence or absence reporting format for these two sources. A common way of referring to the host-specific genetic identifier for each of these species is a "biomarker."

Because this method is limited to presence or absence reporting for only human and ruminant sources, the data cannot be used to: (1) identify the quantity or proportional levels of contamination from either source; (2) identify specific sources other than human or ruminant; or (3) differentiate between the various kinds of ruminants — cattle, goats, sheep, deer, or elk.

However, the data can be used to: (1) identify the frequency of identification of either of the sources from a particular sampling site if more than one set of samples is collected from the same site; (2) identify human or ruminant source contamination; and (3) confirm that recent fecal contamination has occurred.

E.C.   Organic Compounds

The study looked at four groups of organic compounds: pesticides; trace organics; pharmaceuticals; and hormones. Each of the four is discussed below.

1. Pesticides

Fifty pesticides were analyzed in water wells, dairy lagoons, WWTP influents, manure piles, and application field samples by EPA's Manchester Environmental Laboratory. The term "pesticide" refers to insecticides, herbicides, fungicides, and various other substances used to control pests. The pesticide analysis conducted as part of this investigation included insecticides and herbicides. The results for the pesticides are included in **Appendix A8.**

The pesticides selected for analysis were those that USGS reported had been used in the Yakima Valley and are considered mobile in groundwater, persistent, or both (Nakagaki and Wolock 2005). These compounds were considered possible tracers that might provide further information in support of the link of nitrate introduced with irrigated crop production and from field application of waste from dairies to the nitrate detected in water wells.

Many of the pesticides are used on specific crops and during specific times of the year. This pattern of usage can be an advantage as it can assist to identify the specific crop where the pesticide was applied. At the same time, it is possible that a particular pesticide, though used in the area, was not applied recently and so not detected in the soil samples collected by EPA because EPA collected samples over a limited time period (February to April).

EPA's Manchester Laboratory reported that the sample matrices provided significant interferences that made pesticide analysis difficult for dairy lagoons and WWTP influent samples. Because of this problem, the pesticide concentrations could not be quantified in the dairy lagoons or WWTP influent samples. The laboratory attempted to develop an extraction and cleanup procedure for the dairy lagoon and WWTP matrix; however, a procedure to resolve the matrix interference could not be developed within the maximum holding time specified for these samples. By the time the laboratory could have developed and tested an effective and reliable procedure, the maximum sample holding times would have been exceeded. Therefore, the pesticide results for the dairy lagoon and WWTP samples are considered unusable.

7.2. Trace Organics

Each water well, dairy lagoon, and WWTP influent sample was tested for 67 trace organic compounds by the USGS National Water Quality Laboratory in Denver. The trace organics were

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> **Comment [LE22]:** I can't parse this sentence enough to be able to suggest how to fix it. I got lost in all the phrases and couldn't tell what was modifying what.
> of… with… from… of.. from.. to… in…

not analyzed in soil or manure samples because the USGS laboratory was not equipped for this type of analysis and the methods for extraction of such samples are complex. The results for the trace organics and a description of their main use are included in **Appendix A9**.

The USGS developed a method for analyzing a large number of trace organics because they and other researchers had found them in domestic and industrial wastewater (Zaugg and others 2006) as well as groundwater and surface waters (Kolpin and others 2002; Barnes and others 2008). EPA believed the trace organics would help to differentiate water wells affected by septic systems (humans) from water wells influenced by other sources such as dairy lagoons or irrigated cropland. The compounds analyzed include many that can be associated with human usage, including caffeine, bisphenol A; cholesterol; menthol; phenol; various flame retardants; acetophenone (fragrance in detergent); benzophenone (fixative for perfumes); camphor (flavor, oxidant); isoborneol (fragrance in perfume); and many others.

8.3. Pharmaceuticals

The sample from each water well, dairy lagoon, WWTP influent, manure pile, and application field was analyzed for 14 wastewater pharmaceuticals **(Table 2).** The University of Nebraska Water Sciences Laboratory in Lincoln, Nebraska (UNL), performed the analysis. The results are included in **Appendix A10**.

Table 2: UNL - Wastewater Pharmaceuticals Evaluated

Compound Name	Description
Acetaminophen	Pain Reliever (Tylenol)
Amphetamine	Psychostimulant (Dexedrine)
Azithromycin	Antibiotics (Zithromax)
Caffeine	Stimulant
Carbamazepine	Anticonvulsant
Cotinine	Metabolite of nicotine
DEET	Insect repellent
Diphenhydramine	Antihistamine
Ibuprofen	Pain reliever
Methamphetamine	Psychostimulant
Naproxen	Pain reliever (Aleve)
Paraxanthine	Stimulant (metabolite of caffeine)
Thiabendazole	Parasiticide (mintezol)
Triclosan	Antibacterial

The group is identified as "wastewater pharmaceuticals" because they are generally used by humans for therapeutic reasons and have been detected in municipal wastewater (Ternes and others 2004), surface waters (Kolpin and others 2002), groundwater (Barnes and others 2008), and drinking water (Benotti and others 2009). Many of the compounds are for over-the-counter

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use (for example, acetaminophen and ibuprofen) and are ingested, but a few are applied topically (DEET and triclosan). Two of the compounds can be used in other animals (thiabendazole and DEET).

Humans typically excrete 50 to 90 percent of the active ingredients in ingested drugs, either as unmetabolized pharmaceuticals or as metabolites (McGovern and McDonald 2003). These excreted compounds can enter a municipal WWTP or a septic system. Detection of these compounds in water wells may provide evidence that septic systems are the primary source of nitrate.

In addition, the sample from each water well, dairy lagoon, WWTP influent, manure pile, and application field was analyzed for 17 additional pharmaceuticals and ~~labeled~~ classified as "veterinary pharmaceuticals" for this study. **Table 3** lists the compounds and the current FDA-approved uses (FDA, 2011(a) and FDA, 2011(b)). Many of the pharmaceuticals shown in **Table 3** do not require a veterinarian's prescription and are available for over-the-counter purchase (FDA, 2011(a) and FDA, 2011 (b)).[2] The majority of the over-the-counter pharmaceuticals are included in the feed for the animals. The University of Nebraska Water Sciences Laboratory in Lincoln, Nebraska, also conducted these analyses. The results are included in **Appendix A11**.

Detections of the compounds in **Table 3** in water wells would provide evidence that dairies are a likely source of those compounds. For example, if monesin is detected in water wells, then it is coming from a source other than humans. (Monesin is not approved for use in humans.) If the compounds are detected in dairy lagoons, manure piles, or application fields, it is a good indication that the dairy is using the compound. If detected in the influent to the WWTPs, it can establish whether these compounds are being excreted by humans and ending up in municipal sewage waste. If the compounds are detected in the WWTP influent, they can be compared with detected compounds in water wells to evaluate whether septic systems may contribute to the presence of these compounds in well water.

Table 3: Veterinary Pharmaceuticals Evaluated and FDA Approved Uses as of November 2011

Compound Name	Current FDA Approved Use
Chlortetracycline (total)	Cattle (beef, dairy), poultry, swine, and sheep
Erythromycin	Cattle (beef, dairy) and humans
Lincomycin	Swine, poultry, and humans
Monesin	Cattle (beef, dairy), and poultry
Oxytetracycline	Cattle (beef, dairy), poultry, sheep, and humans
Ractopamine	Cattle (beef), swine, and poultry.
Sulfachloropyridazine	Cattle (beef), swine, and sheep

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[2] Compounds that can be obtained over-the-counter include chlorotetracycline; erythromycin;lincomycin; monesin; ractopamine; sulfadimethoxine; sulfamethazine; sulfathiazole; tetracycline; tiamulin; trenbolone; tylosin; and virginiamycin.

Compound Name	Current FDA Approved Use
Sulfadimethoxine	Cattle (beef, dairy), and poultry
Sulfamerazine	Poultry
Sulfamethazine	Cattle (beef, dairy), poultry, and swine
Sulfamethizole	Dogs and cats
Sulfamethoxazole	Humans
Sulfathiazole	Swine
Tetracycline	Cattle (beef, dairy), poultry, sheep, swine, and humans
Tiamulin	Swine
Tylosin	Cattle (beef, dairy), poultry, and swine
Virginiamycin	Poultry, swine, and poultry

The UNL analyzed the compounds in **Table 3** because they are used in livestock production at
therapeutic doses to treat and prevent disease and at sub-therapeutic doses as prophylactics and
growth promoters (Meyer 2004) and have been found at low levels in different environmental
media: groundwater (Barnes and others 2008 and Kummerer, 2009); surface water (Koplin and
others 2002; Christian and others 2003; and Kummerer, 2009); and wastewater treatment
facilities (Ternes and others 2004; and Lubliner and others 2010). More specifically, several of
the compounds have been found in dairy lagoons (Watananbe and others 2008 and Watananbe
and others 2010); soil and surface samples from dairies (Watanabe and others 2010); private
wells nearby a beef cattle operation (Batt and others 2006); and in groundwater underlying swine
and beef cattle facilities (Bartlet-Hunt and others 2011). Some of the compounds in **Table 3** are
used by humans (Kummerer 2009).

The U.S. Department of Agriculture's National Animal Health Monitoring System conducted a
survey to evaluate the use of antibiotics in dairy operations for disease prevention, disease
treatment, and growth promotion in preweaned heifers, weaned heifers, and mature cows (USDA
2008). The survey represented 17 of the nation's major dairy states (Washington was included)
and represented about 82 percent of the U.S. dairy cows. The results indicate that the majority of
dairy operations use antibiotics to treat for diarrhea, digestive problems, respiratory problems,
mastitis, reproductive disorders, and lameness.

To identify which of the pharmaceuticals might be used by the dairies in this study, EPA
requested information from the dairies on the use of pharmaceuticals in their operations. The
dairies declined to provide this information to EPA and therefore there is no specific information
on the use of these compounds by the dairies that are included in this project.

9.4. Hormones

Each water well, lagoon, and WWTP plant influent sample was analyzed for five hormonally
active compounds (17-a-estradiol, 17-a-ethynyl-estradiol; 17-b-estradiol; Estriol; and Estrone) by
EPA's Subsurface Characterization Laboratory in Ada, Oklahoma The results for these
hormones are in **Appendix A12.**

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In addition, each water well, lagoon, WWTP plant influent, and soil/manure sample was tested
for 18 hormonally active compounds by the UNL Water Sciences Laboratory in Lincoln,
Nebraska, including the five analyzed by Ada. The results for these analytes are in **Appendix
A13.** **Table 4** shows all the compounds evaluated and their natural source or general use. The
table also provides information on the FDA-approved uses for the analytes as of November 1,
2011 (FDA 2011a and FDA 2011b).

Table 4: Ada and UNL – Hormonally Active Compounds Evaluated

Compound Name	Description (Current FDA Approved Use)
Analyzed at both Ada and UNL	
17βeta-estradiol	Natural female sex hormone (beef cattle)
α-Estradiol	Predominant sex hormone in females (beef cattle)
Estriol	One of three main estrogens produced in mammals
Estrone	One of three main estrogens produced in mammals
17-α-Ethynyl Estradiol	Synthetic analogue of estradiol (human)
Analyzed at UNL Only	
11-Keto Testosterone	Oxidized form of testosterone
17α-Hydroxyprogesterone	Natural progestogen
4-Androstenedione	Intermediate step in producing testosterone and estrogens
Androsterone	Metabolite of testosterone
Epitestosterone	Naturally occurring form of testosterone
Progesterone	Natural female sex hormone (beef cattle and human)
Testosterone	Natural male sex hormone (beef cattle and human)
17α-trenbolone	Synthetic growth promoter (beef cattle)
17β-trenbolone	Synthetic growth promoter (beef cattle)
Androstanedienedione	Precursor to boldenone (boldenone: horse)
α-Zearalanol	Metabolite of zeranol (zeranol: beef cattle and sheep)
α-Zearalenol	Metabolite of zeranol (zeranol: beef cattle and sheep)
β-Zearalanol	Metabolite of zeranol (zeranol: beef cattle and sheep)
β-Zearalenol	Metabolite of zeranol (xeranol: beef cattle and sheep)
Melengesterol Acetate	Synthetic growth promoter (beef cattle)

UNL developed a method for analysis of these hormones in order to detect the compounds at the
low levels of detection in environmental samples. Many of the hormones are naturally excreted
by animals and can be used as pharmaceuticals in human and veterinary clinical practices (Zheng
and others 2007). Many of the compounds have been detected at low levels in different
environmental media or sources including: surface waters (Kolpin and others 2002); dairy
lagoons (Kolodziej and others 2004; Arnon and others 2008; Hutchins and others 2007, and
Zheng and others 2008); groundwater associated with dairies (Kolodziej and others 2004 and
Arnon and others 2008); and manure at dairy facilities (Raman and others 2004).

Since many of the compounds are produced naturally by both humans and animals, it is challenging to identify the source of the hormones if detected in water wells. One compound (17-α-ethynyl-estradiol) is a synthetic analogue of estradiol that is primarily used in hormonal contraception and would not be expected to be found in lagoons, unless the lagoons are impacted by human waste, but maybe found in WWTP influent and septic systems, given its use by humans.

Several of the compounds analyzed by UNL are synthetic growth hormones (e.g., metabolites of zeranol, trenbolone, and melengesterol acetate) and are not approved for use in dairy cows. These compounds would not be expected to be detected in dairy lagoons, manure piles, or application fields associated with dairy operations. However, they can be used in other animals such as beef cattle. If these compounds are detected in water wells, it may be an indication that a source other than dairy cows or humans may be responsible.

F.D.   Isotopic Analysis

Samples from all the water well, dairy lagoon, and WWTP influent were submitted to the University of Nebraska, Lincoln Laboratory for isotopic analysis. The results of the isotopic analyses are presented in **Appendix A14.** A more detailed discussion regarding the interpretation of the isotopic data can be found in Appendix B.

The isotopic analysis is used to identify the general source, or combination of sources, or dominant processes that have contributed nitrates to the drinking water wells evaluated in this study (Kendall and McDonnell 1998 and Michener and Lajtha 2007). Most of the literature on isotopic fractionation, particularly the part attributing specific samples to specific sources, makes clear that the science is still evolving and that this tool is most appropriately to as a supplement to other methods used to investigate the source of nitrates (Kendall and others 2007).

Isotopes are forms of the same element that have a different number of neutrons. As an example, the atomic weight of nitrogen is 14.0067 because the most common isotope of nitrogen is the form with seven neutrons and seven protons and a mass number of 14, written as ^{14}N. ^{14}N makes up 99.636 percent of the total nitrogen in the atmosphere and is referred to as the "light isotope." Nitrogen 15 consists of seven protons and eight neutrons and is written as ^{15}N. ^{15}N makes up the rest of the total nitrogen in the atmosphere at 0.364 percent and is referred to as the "heavy" isotope.

Isotopic values are reported as the ratio of the heavy isotope (in this case, ^{15}N) to the light isotope (in this case, ^{14}N) in the sample compared with that ratio in a chosen standard. For nitrogen, the standard is the pool of nitrogen in the earth's atmosphere or, referred to as the atmospheric standard. Nitrogen isotopic composition is expressed in terms of "delta ^{15}N," which is written as $\delta^{15}N$ and   is expressed as parts per thousand differences from the atmospheric standard stated as, "per mil" or written as ‰.

$$\delta^{15}N\ (‰) = (^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{standard} * 1000$$

$$({}^{15}\text{N}/{}^{14}\text{N})_{\text{standard}}$$

δ^{15}N will be positive (e.g., +6.1‰) and therefore heavier if there is more of the ^{15}N compared with the atmospheric standard in the sample. δ^{15}N will be negative (e.g., -0.2‰), or lighter, if there is less of ^{15}N in the sample compared with the atmospheric standard.

Isotopes of oxygen (^{18}O) have also been used to provide information on the source of the nitrate in a sample. The standard for ^{18}O is "Standard Mean Ocean Water," or SMOW. The δ^{18}O in the atmosphere is heavier at 23.5‰. Nitrate derived from atmospheric deposition is therefore heavier with a δ^{18}O of 60‰ to 70‰.

~~G.~~E.   Age Dating and Gas Study

Several methods are available to measure the age of groundwater in a well, meaning the amount of time between the initial infiltration of the water into the ground~~,~~ and the time it was sampled in the well. For this study, EPA selected a method involving sampling for sulfur hexafluoride (SF_6). SF_6 was selected because some of the wells in this study were anoxic, and SF_6 is stable in anoxic groundwater. SF_6 is useful in age-dating because it has been increasing in the atmosphere as it is released by human activities.

SF_6 is a liquid at room temperature and is used in high voltage switches and capacitors as a replacement for polychlorinated biphenyls (PCBs). Significant production of SF_6 began in the 1960s for use in high-voltage electrical switches. SF_6 is extremely stable, with an estimated atmospheric lifetime of 800 years (Morris and others 1995) to 3200 years (Ravishankara and others 1993). As more of it is used, more of it escapes into the atmosphere. It is very persistent in the atmosphere, so the concentration has been steadily increasing. Additionally, SF_6 does not biodegrade even in areas of low oxygen, which is true for some of the Yakima Basin. Due to this increase, laboratory measurements of the concentration in groundwater can indicate the time since the groundwater was last in contact with the atmosphere. Measurement of the concentration in groundwater indicates the time when the sample infiltrated into the ground.

All water wells were sampled for SF_6. The analysis was completed by the USGS laboratory in Reston, Virginia. SF_6 is not an analysis done by commercial laboratories. The Reston laboratory was selected because it had developed a method that had been used successfully by the USGS in Washington State. The purpose of using age dating was to determine the time since infiltration into the water wells and to attempt to evaluate whether the nitrate found in water wells could be associated with either legacy or current practices. A summary of the results for the age dating and gas study are in **Appendix A15**.

In addition to the SF_6 samples, five gas studies were conducted. These studies involved filling containers with water for the analysis of nitrogen and argon gas to measure the temperature and elevation of the recharge zone for the groundwater. These data are used to correct the SF_6 measurement for excess nitrogen, which can be dissolved when groundwater elevations fluctuate rapidly. It also provides a means to determine if nitrogen gas has been added to the sample from

Comment [LE23]: this confused me when I first read it. I thought "there are easier ways to measure temperature and elevation" before I realized this analysis was intended to figure out where the recharge zone was! So there needs to be some other introductory text here. You are using the nitrogen and argon measurements to characterize the temp and elevation? To infer the temp and elevation? I'm not sure of the best way to say it.

denitrifying bacteria breaking down nitrate in an anoxic setting. None of the EPA samples showed evidence of denitrification based on measured nitrogen to argon ratios.

As seen in **Appendix A15**, there were no reported SF_6 values for WW-01, WW-11, WW-12, WW-23, WW-27, and WW-28. Values were not reported because the concentration of SF_6 in the groundwater exceeded the highest expected concentration based on average atmospheric concentrations of SF_6. EPA determined as a result that the SF_6 results for those wells were not meaningful. These samples may indicate areas where localized human caused releases of SF_6 occured. For example, they could include the accidental release during servicing of high voltage equipment or the intentional introduction of SF_6 into water for localized fate and transport studies or for tracing leaking pipes. Alternatively, volcanic rocks can contain more SF_6 than the average atmospheric concentrations and the volcanic terrain and mineralogy of the sediments in the local aquifer may be the source of the SF_6. Based on the high values of SF_6 observed in the groundwater, the USGS Reston Laboratory believes that the concentrations were from human caused releases and not related to natural levels associated with volcanic regions.

VIII. QUALITY ASSURANCE AND QUALITY CONTROL

As discussed previously, the project was implemented in three phases. In Phase 1, a GIS screening application was developed and used to identify potential sample locations and sites in the Lower Yakima Valley for Phase 2 sampling and screening. Phase 1 also developed estimates of the relative nitrogen available for application to the land from different sources. Phase 2 and Phase 3 involved sampling and analysis as described in Sections V, VI and VII. A discussion of the quality assurance and quality control (QA/QC) procedures followed in Phase 2 and Phase 3 and a summary of the data validation process conducted by EPA QA chemists is presented in **Appendix C.**

IX. ANALYTICAL RESULTS AND DISCUSSION

This section presents the analytical results for the Phase 3 sampling conducted at the three source areas previously described: the dairies, residential septic systems, and irrigated croplands. The results are presented Sections A through E below present the results from sampling at the five locations identified for this study (See **Figure 11**), including:

- Haak Dairy (one location)
- Dairy Cluster (one location with six dairies in close proximity)
- Septic Systems Wastes (three locations: Mabton [one site], N. Harrah [one site], and Sunnyside [two sites and three WWTPs (Zillah, Mabton, and Toppenish)
- Irrigated/fertilized crop fields (three locations: Mabton [three separate crops], N. Harrah [one crop], and Sunnyside [two separate crops])

Comment [LE24]: Another result reported in this section. Seems like it should be all or none.

Comment [LE25]: But later in the paragaraph, there is a conclusion based on them? Seems contradictory unless you explain later that although the actual concentrations are not usable, the fact that they were elevated implies human-caused releases.

Comment [LE26]: This is the structure I needed to see back on about page 15 (comment 28)

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B. • Two sites WW-18 and WW-30 that were not apart of the original study design but which were sampled during the study.

Each section listed above contains five subsections to address each of the different compounds or analytical techniques used to evaluate whether there is a link between the high nitrate levels and different sources: general chemistry; microbiology; organic chemicals; isotopic analyses and age dating. In addition, each of the four main sections provides a summary of the results.

•**A. R&M Haak Dairy**

The R&M Haak Dairy ("Dairy") is located in an agricultural area north of the Yakima River, about four miles north of the city of Sunnyside. It is in the Benton groundwater basin, which includes the communities of Sunnyside, Grandview, Satus, Kiona, Prosser, Mabton and Richland. This dDairy was selected as one of the sampling locations because it is relatively high on the landscape with very few other sources of nitrate above the dairy. The Dairy A ditch runs from north to south through the dDairy. Cow pens, a milking parlor, and three waste lagoons lie west of the ditch. There are several large structures where cows are kept. East of the ditch, a center-pivot irrigation system is installed on a large sprayfield which is used by the dDairy as a disposal location for liquid wastes. The dDairy operator stated that corn and triticale were alternately grown on the sprayfield. See Appendix D for a more detailed description of the Haak Dairy and its operations.

Figure 11 and Figure 12 shows the Phase 3 sample locations associated with the Haak Dairy. The sampling locations include:

- One residential drinking water well upgradient of the dairy (WW-01);

- One dairy supply well (WW-02);

- One dairy manure pile located on the dairy (SO-01);

- Two dairy lagoons with three samples collected (LG-01, LG-02, and LG-03). Lagoon samples LG-02 and LG-03 are from the same lagoon;

- One application field sample (SO-02) and;

- Three downgradient residential drinking water wells (WW-03, WW-04, and WW-05).

1. Haak Dairy: General Chemistry

The four types of general chemistry data collected at the Haak Dairy were nitrate and other forms of nitrogen; major ions; minor ions and trace inorganic elements; and perchlorate. Each of these is discussed below.

Haak Dairy: Nitrate and Other Forms of Nitrogen

All five water well samples, three dairy lagoon samples, one manure pile sample, and one application field sample were analyzed for several forms of nitrogen. The water wells and lagoons were analyzed for nitrate, nitrate plus nitrite, ammonia or ammonium (if in an aqueous solution), and TKN. The manure samples and the application field samples that were receiving dairy waste were analyzed for extractable nitrate-N (Nitrate-N Solid), extractable ammonia-N (Ammonia-N Solid), and total nitrogen by combustion (Total Nitrogen Solid).

In addition, the total nitrogen in all forms was calculated for each sample and the value presented summed as "Calculated Total Nitrogen." The manure sample, SO-01, had only 22 percent solids and was analyzed for TKN rather than total nitrogen by combustion. For SO-02, the total nitrogen equals the nitrate plus the TKN value. For all other solid samples, the total nitrogen equals the nitrogen by combustion result.

Figure 12 and **Table 5** show the concentration of total nitrogen in parts per million at each of these sampling locations. Total nitrogen is the sum of nitrate, nitrite, and TKN. Using total nitrogen values allows a comparison between among different locations.

Table 5: Haak Dairy – Concentrations of Different Forms of Nitrogen Including Total Nitrogen Values for Water Wells, Lagoons, Manure Piles, and Application Fields

Location	Nitrate as N (mg/L)	Nitrate + Nitrite as N (mg/L)	Ammonia as N (mg/L)	TKN as N (mg/L)	Calculated Total Nitrogen (mg/L)
Water Wells and Lagoons					
WW-01: Upgradient Well	0.4	0.4	ND	ND	0.4
WW-02: Supply Well	3.1	3.4	ND	ND	3.4
LG-03: Lagoon Influent	NA	ND	920	1200	1200
LG-04: Lagoon Outlet	NA	1.2	1200	1400	1401
LG-05: Lagoon Outlet	NA	1.0	1200	1400	1401
WW-03: Downgradient Well	33.1	35.5	ND	ND	35.5
WW-04: Downgradient Well	51.9	55.0	ND	ND	55.0
WW-05: Downgradient Well	12.8	13.4	ND	ND	13.4

	Manure pile			
Location	Ammonia-N Solid (mg/kg)	Nitrate-N solid (mg/kg)	Total Nitrogen Solid (mg/kg)	Calculated Total N (ppm)
SO-01: Manure	10,100	0.32	29,700 (as TKN)	29,700

	Application Field			
Location	Ammonium as N (mg/kg)	Nitrate + Nitrate as N (mg/kg)	Total Nitrogen Solid (mg/kg)	Calculated Total N (ppm)
SO-02: Application	4.6	71.7	2760	2760

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Field				

NA: Not Analyzed ND: Not Detected

TKN was not detected in the five water wells and therefore the total nitrogen value is the sum of the nitrate plus nitrite concentrations. For WW-01, the total nitrogen value is 0.4 parts per million (ppm) which is within the "background" nitrogen levels. The downgradient water wells that were sampled (WW-03, WW-04 and WW-05) had total nitrogen concentrations of 35.5 ppm, 55.0 ppm and 13.4 ppm, respectively. These levels are well over background nitrogen levels, and the nitrate levels exceed the drinking water MCL of 10 ppm (mg/L)

Nitrate and nitrite were not detected and therefore the total nitrogen values for the lagoons are reflected by the TKN value. The total nitrogen concentrations in LG-01 were 1,200 ppm and in LG-02 and LG-03 was 1,401 ppm. The total nitrogen concentration for the manure sample was 29,700 ppm and the soil sample was 2,760 ppm.

Figure 12 and **Table 5** show an increase in concentrations of total nitrogen between the upgradient well and the downgradient wells with likely sources, such as dairy lagoons, manure piles, and application fields receiving dairy waste located between these points. The lagoons, manure piles, and application fields from the Haak Dairy are a likely source of the increased nitrogen levels in the downgradient wells. Other sources of nitrogen, such as inorganic fertilizer, may also be contributing to the nitrogen in the downgradient wells. A Washington State Department of Agriculture inspection report indicates the Haak Dairy has utilized inorganic fertilizer on it application fields, in addition to animal wastes (WSDA, 2010).

> **Comment [LE27]:** It is a little unusual to see all these sample types plotted on the same graph, but I get what you are trying to show. It would help if the bars were color or pattern-coded to indicate the different media. Maybe upgradient wells, potential sources, and downgradient wells. Not sure how you'd classify the production wells, however.
>
> This comment applies to all similar figures—I think it would help to illustrate the point

Information on the construction and depth of both the upgradient and downgradient wells would be useful to further confirm the hydraulic connection between the upgradient well, dairy lagoons, and downgradient wells. In addition, information on the construction of the dairy lagoons (if they are lined, and if so, with what material) would be useful to determine the extent to which they may be contributing to the increase in nitrogen concentrations. EPA requested this information from the Haak Dairy via a letter, but it declined to provide it.

Haak Dairy: Major Ions

All five wells and three dairy lagoons were sampled for analysis of the major ions. **Figure 13** shows the concentrations of six major ions (calcium, chloride, magnesium, potassium, sodium, and sulfate) in the upgradient well, the dairy lagoons, and the downgradient wells. The concentrations of these six ions all show similar patterns of having higher concentrations in the downgradient wells than the upgradient well.

The difference in concentrations from the upgradient well to downgradient wells ranges from up to: a 3-fold increase for potassium; an 8–fold increase for magnesium; a 10-fold increase for calcium; and more than a 30-fold increase for chloride. Chloride is generally accepted as the most conservatively transported ion and therefore an excellent tracer and possible linking

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candidate. "Conservative" in this case means that the negative chloride ion typically flows with the groundwater unchanged. It is unlikely to participate in reactions or be electrically attracted to minerals such as clays making up the aquifer matrix.

One possible explanation for the observed increase in these major ions, especially for the conservatively transported chloride, is that the dairy lagoons are introducing these ions to the groundwater. After this release, the ions are changing the chemistry and producing the observed higher concentrations in the downgradient wells. As with total nitrogen, this is another indicator of the source of nitrate, although information on the construction and depth of the water wells would be helpful to confirm the hydraulic connection along with information on the construction of the lagoons.

Haak Dairy: Minor and Trace Inorganic Elements

All five water wells and three dairy lagoons were sampled for analysis of minor and trace inorganic elements. The only metals found in both the water wells and dairy lagoons were barium and zinc (see **Table 6**). Other metals detected in dairy lagoons (chromium, copper, iron, and manganese) were not found in the water wells. The manure and application field samples were not evaluated for minor or trace inorganic elements.

Table 6: Haak Dairy - Concentrations of Barium and Zinc in Water Wells and Dairy Lagoons (µg/L)

Location	Barium	Zinc
WW-01 – Upgradient Well	13.5	Not detected
WW-02 – Supply Well	32.7	5.4
LG-01 – Dairy lagoon	297	1790
LG-02 – Dairy lagoon	931	5410
LG-03 – Dairy lagoon	907	5260
WW-03 – Downgradient Well	135	21
WW-04 – Downgradient Well	178	12
WW-05 – Downgradient Well	164	15

There is an increase in the concentrations from the upgradient to the downgradient wells for both barium and zinc, and the concentrations are higher than seen in other studies for surface water in the area. However, this increase may not be solely attributable to the dairy lagoons, given that barium and zinc are both naturally occurring and their concentrations can vary greatly.

As discussed before, the trace inorganic elements tend to react with aquifer materials. As a result, they are difficult to evaluate as indicators of the linkage between likely sources and downgradient wells. However, some of the elements have been successfully used in similar studies (Davis and others 1998) by evaluating the ratios of specific ions such as bromide to chloride. The ratios can provide evidence that a particular nitrate source has altered the groundwater quality.

EPA looked for ionic ratios between bromide and chloride, but it was not possible to quantify the amount of bromide in the dairy lagoons because of the concentration and complexity of the dairy lagoon sampless. Without the quantification of the concentration of bromide, it was not possible to develop the ratio for the lagoons. The use of the ratio as an indicator of linkage to downgradient wells was therefore not possible despite the detection of these ions in most of the water wells.

Haak Dairy: Perchlorate

Perchlorate was analyzed only in the water well samples (see **Appendix A6**). The concentrations ranged from 0.14 µg/L (WW-01) to 1.96 µg/L (WW-03). The results for the perchlorate analysis are evaluated together with the isotopic data because perchlorate was used as an indicator of potential accumulation of atmospherically derived nitrate associated with caliche soils. Perchlorate was not evaluated in the dairy lagoon system, but this compound is not expected to persist in the anoxic environment of a dairy lagoon.

10.2. Haak Dairy: Microbiology

All the wells were sampled for analysis of total coliform and *E. coli*. (see **Appendix A7**). One well (WW-04) had a detectable level of total coliform, but *E. coli* was not detected. MST was not completed for the wells as *E. coli* was not detected in any of the wells. The manure piles and application field samples were not analyzed.

Samples from the three dairy lagoons were analyzed for fecal coliform. High concentrations of fecal coliform were found in the dairy lagoons. MST was performed on the samples from the three dairy lagoons. One of the samples (LG-01) indicated a ruminant source, while two of the samples (LG-02 and LG-03) indicated both human and ruminant sources. As stated before, LG-02 and LG-03 are co-located so the same findings for these two dairy lagoons are not surprising. It is unknown why the two dairy lagoons had an indication of human sources though it is possible that the lagoons are impacted by human waste given the Haak Dairy is on a septic system and has several employees.

11.3. Haak Dairy: Organic Compounds

The organic compounds evaluated included pesticides; trace organics; pharmaceuticals, and hormones.

Haak Dairy: Pesticides

Atrazine was the only pesticide detected in the water wells. It was detected in the well upgradient of the Haak Dairy (WW-01), the dairy supply well (WW-02), and two wells downgradient from the Haak Dairy (WW-04 and WW-05). The pesticides were not reported for lagoons because of problems with matrix interference.

The concentrations of atrazine were 0.015 µg/L (WW-01); 0.041 µg/L (WW-02); 0.015 µg/L (WW-04); and 0.11 µg/L (WW-05). Atrazine was detected in the application field sample for the Haak Dairy (SO-02) and the other two corn fields sampled in this study (SO-13 and SO-14). Atrazine is a commonly used herbicide for corn fields and is frequently detected in groundwater beneath both urban and agricultural land uses (Barbash and others 1999).

Both grain and silage corn are is a significant feedstocks in dairy and other cattle livestock operations, and corn has been grown on fields surrounding the water wells in the past. The detection of atrazine in the application field sample and its presence in the downgradient wells is a likely indication that the application field samples are a contributing source. However, its presence in the upgradient well indicates at least one source of atrazine is upgradient of the dairy.

Three pesticides (Dicamba, Dacthal-DCPA, and 2,4-D) were found in the manure pile sample from the Haak Dairy (SO-01). Atrazine was not detected in any manure pile sample. Given that the three compounds detected are common herbicides, a possible source is the feed given to the dairy cows.

Six pesticides (atrazine; 4-nitrophenol; pentachlorophenol; endosulfan sulfate; chlorpyrifos ethyl; and diuron) were found in the application field sample collected adjacent to the Haak Dairy (SO-02). The application field was historically planted in corn.

Haak Dairy: Trace Organics

The only trace organic compound detected in the five water wells was bis-(2-ethylehxyl)-phthalate (DEHP) in WW-01 (upgradient well) and WW-03 (downgradient well). It was not detected in any of the dairy lagoon samples (see **Appendix A9**). The trace organics were not analyzed in the manure or soil samples.

Other trace organics were detected in the three dairy lagoons but not detected in any of the downgradient wells: LG-01 (10 compounds); LG-02 (12 compounds); and LG-03 (11 compounds). Compounds found in all three dairy lagoons included: fecal indicators (such as 3-beta-coprostanol and 3-methyl-1h-indole); plant sterols (for example, beta-sitosterol, beta-sigmastanol, and cholesterol); and phenol. Phthlates, such as DEHP, are compounds used in the manufacture of plastics to decrease the brittleness of containers and other objects. They are increasingly ubiquitous in the environment and are being widely detected in water wells (EPA 2011(b)). Given their widespread occurrence and detection in water wells, and their absence in the dairy lagoons, it would be difficult to attribute them with to any source from the Haak Dairy at this time.

Haak Dairy: Pharmaceuticals

The UNL completed analysis for two lists of compounds in this study referred to as "wastewater pharmaceuticals" and "veterinary pharmaceuticals." The wastewater pharmaceuticals analyzed in

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this study are generally used by humans. Many of "veterinary pharmaceuticals" can be used in both veterinary practice and to treat humans.

There were no detections in the water wells, manure pile sample, or application field sample for any of the wastewater pharmaceuticals. Thiabenzadole was detected in one dairy lagoon (LG-01) sample and DEET was detected in one dairy lagoon (LG-03) sample. Thiabenzadole is used to treat worm infections in both livestock and humans and can be used as a pesticide (Mayo Clinic 2011). DEET is a common insect repellent.

Three veterinary pharmaceuticals were detected in one or more water wells (tetracycline, chlorotetracycline, and monesin). Several veterinary compounds were detected in the dairy lagoons: LG-01 (eight compounds); LG-02 (nine compounds) and LG-03 (six compounds). Several compounds were also detected in the manure sample (SO-01: four compounds) and application field sample (SO-02: five compounds).

Table 7 provides the concentrations of the three ~~compounds~~ veterinary pharmaceuticals detected in the water wells and the concentrations for these compounds in the dairy lagoons, manure sample, and soil sample from the application field associated with the Haak Dairy. **Appendix A11** provides the concentrations of all the pharmaceuticals detected in the dairy lagoons, manure pile sample, and application field sample.

Table 7: Haak Dairy - Concentrations of Veterinary Pharmaceuticals Detected in Water Wells, Dairy Lagoons, Manure Pile, and Application Field Samples

Location	Tetracycline	Chlorotetracycline	Monesin
WW-01 – Upgradient Well	ND	ND	**0.027**
WW-02 – Supply Well	ND	ND	ND
LG-01 – Dairy Lagoon	**1.96 (J)**	R	**44.97**
LG-02 – Dairy Lagoon	**5.83 (J)**	**0.067 (J)**	**1086**
LG-03 – Dairy Lagoon	**2.88 (J)**	ND	**420**
WW-03 – Downgradient Well	**0.041 (J)**	ND	ND
WW-04 – Downgradient Well	**0.075 (J)**	**0.049**	ND
WW-05 – Downgradient Well	ND	ND	ND
SO-01 –Manure Sample	**178**	ND	**441**
SO-02 – Application Field Sample	**26.9**	**45.6**	**2.9**

µg/L for wells/dairy lagoons and µg/g for manure/soil samples
Method Detection Limit = 0.02 µg/L for wells/dairy lagoons and 0.5 ug/g for manure/soil samples.
ND = Not detected
"J" values mean the compound was positively identified, but the associated numerical value is an estimate.
"R"values mean the data is unusable for all purposes because of analytical problems with the sample.

Tetracycline was detected in two of the downgradient wells (WW-03 and WW-04) and in the dairy lagoons, manure sample, and application field samples. This detection ~~provides a good~~

~~indication~~ indicates that tetracycline is used at the Haak Dairy and suggests the lagoons, manure piles, or application fields could be the source of the tetracycline in the wells, especially given that the concentrations in the dairy lagoons was considerably higher than in the downgradient wells.

Chlorotetracycline was detected in one downgradient well (WW-04), one dairy lagoon (LG-02), and the application field sample (SO-02). The detection of chlorotetracyline in one lagoon and the application field sample indicates that the Haak Dairy is using chlorotetracycline,

Monesin was detected in the upgradient well (WW-01), dairy lagoons, manure sample, and application field sample, but not in any downgradient wells. The concentrations of monesin seen in the samples indicate that it is used at the Haak Dairy.

As stated before, organic molecules are subject to a number of factors that affect their fate and transport properties and may cause them to travel differently from nitrate in groundwater. As organic molecules, they are much more likely to sorb to materials in the aquifer, which can greatly retard their migration with respect to nitrate. Their concentrations are also much more likely to decrease during migration by microbial degradation.

<u>Haak Dairy: Hormones</u>

EPA's Ada laboratory analyzed five hormones in water wells and dairy lagoon samples associated with the Haak Dairy. The laboratory did not analyze the manure pile or application field samples associated with the Haak Dairy because the laboratory specializes in liquid samples and did not have solid extraction techniques developed at the time of the study. However, soil and manure samples were analyzed by UNL and included the five hormones evaluated by the Ada laboratory.

No hormones analyzed by the Ada Laboratory were detected in the water well samples associated with the Haak Dairy; however, three compounds were detected in each of the three dairy lagoons sampled (see **Appendix A12).**

UNL analyzed 18 hormones in water wells, dairy lagoons, manure pile, and application field sample associated with the Haak Dairy, including the same five hormones as Ada. In the water wells, testosterone was the only hormone detected, and it was detected in all five wells, including the upgradient well.

Several hormones were detected in the three dairy lagoons by UNL **(see Appendix A13),** but testosterone was detected in only LG-01. Seven hormones were detected in LG-01, five in LG-02, and four in LG-03. Several hormones were detected in the manure and application field samples, but testosterone was not detected. Six compounds were detected in SO-01 and two in SO-02.

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Comment [LE28]: And the downgradient well concentrations indicate that some of it is moving into ground water. (I'm not sure why some sections include conclusions here and some don't.)

The concentrations of testosterone in the water wells and LG-01 are 21 nanograms per liter (ng/L) (WW-01); 16 ng/L (WW-02); 32 ng/L (LG-01); 9 ng/L (WW-03); 12 ng/L (WW-04); and 7 ng/L (WW-05).

The concentration of testosterone in the upgradient well (WW-01) was greater than in the downgradient wells (WW-03 to WW-05), although the highest concentration was in LG-01. While other hormones were detected in the dairy lagoons, manure pile, and application field samples, they were not found in the water wells. Given that the concentration of testosterone in the upgradient well is greater than the downgradient wells, it is difficult to determine the likely source of the testosterone, although the concentration in one dairy lagoon sample was higher than in the downgradient wells.

12.4.   Haak Dairy - Isotopic Analyses

Table 8 provides the results for the isotopic data for water wells for the Haak Dairy, and **Table 9** below provides the results for the isotopic data for the Haak Dairy lagoons. See **Appendix C** for more details on the interpretation of the isotopic data.

Location	Nitrate-N (mg/L)	δ^{15}N-NO3 (‰)	Dominant Source	δ^{18}O-NO3 (‰)	Overall Assessment
WW-01	0.2	NM	NM	NM	NM
WW-02	3.0	2.7	Soil Cycling	15	Soil Cycling
WW-03	34	2.3	Fertilizer/Animal Waste	29	Fertilizer & Atmospheric & Animal Waste
WW-04	49.9	3.5	Fertilizer/Animal Waste	-4.5	Fertilizer & Animal Waste
WW-05	12.8	9.7	Animal Waste	7.1	Animal Waste

δ^{15}N-NO3. Values less than 2.0 = dominated by fertilizer; values between 2.0 to 8.4= undetermined mixture of fertilizer and/or animal waste; values greater than 8.4 = dominated by animal.
δ^{18}O-NO3. Values greater than 20 considered strong atmospheric contribution.

WW-01 had insufficient nitrate to allow analysis. The dominant source of the nitrates for the other wells is attributed to either soil nitrogen from plant natural degradation (WW-02); undetermined mixture of fertilizer, animal waste, and atmospheric deposition (WW-03); undetermined mixture of fertilizer and animal waste (WW-04); or animal waste (WW-05).

Table 9: Isotopic Analysis - Summary Results for Lagoons

Location	Position in System	Ammonia (mg/L)	δ^{15}N-NH4 (‰)	Assessment
LG-01: Haak	Influent	907	3.4	Fresh Animal Waste
LG-02:Haak	Discharge	923	10.1	Volatilized animal waste
LG-03: Haak	Discharge	896	9.9	Volatilized animal waste

The information for the lagoons supports a conclusion that the source of the nitrogen in the dairy lagoons is associated with animal waste. For the three dairy lagoons, LG-01 was the nearest point of entry to the dairy lagoon system. Dairy lagoon samples LG-02 and LG-03 were collected at the end of the system just before it was pumped onto the application fields.

These samples are considered co-located and similar values would be expected. The expected trend would be for the isotopic weight fractions to increase in δ^{15}N-NH4 as the ammonia is volatilized in the dairy lagoons farther from the entry point to the dairy lagoon system. This trend would result in larger numbers for the δ^{15}N-NH4and is seen for the three dairy lagoons at the Haak Dairy (LO-01 3.37‰ compared with 10.07‰ for LG-02).

13.5. Haak Dairy: Age Dating

Age dating data were collected for the water wells. Two samples were collected from each well and the values were averaged **(see Table 10).**

Table 10: Haak Dairy – Summary of Age Dating Analyses for Water Wells (Years)

Location	Sample Age	Duplicate Age	Average
WW-01: Upgradient Well	Over Value	Over Value	NA
WW-02: Supply Well	15.8	16.3	16.1
WW-03: Downgradient Well	24.8	25.8	25.3
WW-04: Downgradient Well	21.8	23.3	22.6
WW-05: Downgradient Well	18.3	20.8	19.6

Over Value: These samples contained more SF_6 than can be explained by equilibrium with modern air.

No values were reported for WW-01 (reported as an over value – see above). The supply well had an average age of 16.1 years and the average age of the downgradient wells ranged from 19.6 to 25.3. Typically, the supply well would be deeper, yielding water from deeper zones in the aquifer, which have traveled farther and are presumably older. In the case of the supply well at the Haak Dairy (WW-02) the age was measured as younger. The younger than expected age could be the case because the supply well is screened in the same shallow zone as the downgradient wells and the time difference in the age may correspond to the travel time between the wells.

Comment [LE29]: So here there are conclusions regarding the sources in the lagoons, but not the groundwater, even though only the 3 downgradient wells were linked to animal waste in Table 8.

Comment [LE30]: That doesn't explain it. What is an over-value? How far back can the method go—does this just mean the water is older than that?

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14.6.   **Haak Dairy – Summary of Results for Residential Water Wells**

Table 11 provides a summary of the groups of compounds and analytical techniques (general chemistry, organic compounds, and isotopic analyses) that provide the most useful information to address the question of the likely sources of the nitrate for the four residential water wells associated with the Haak Dairy. No conclusions using the microbial data is possible given the three downgradient wells did not exhibit any microbial contamination. In addition, the age dating data do not provide any specific evidence to connect specific sources to high nitrate levels.

Table 11: Haak Dairy – Summary of Results for Residential Water Wells

Sample Location	General Chemistry	Organic Compounds Detected in Wells	Organic Compounds also Detected in Dairy Sources	Isotopic Analyses
WW-01 Upgradient Well	Nitrate level = 0.4 mg/L No trends in total nitrogen or major ions as this is an upgradient well	Atrazine, DEHP, testosterone, and monesin.	Not applicable as because this is an upgradient well	Not measured because lack of nitrate in sample
WW-03 – Down-gradient Well	Nitrate level = 34 mg/L. Total nitrogen concentrations increased substantially between WW-01 and WW-03 Ten to 45-fold increase in concentration in four major ions between WW-01 to WW-03.	Atrazine, DEHP Tetracycline Testosterone,	Atrazine (SO-01) DEHP (ND) Tetracycline (LG-01, LG-02, LG-03, SO-01, and S0-02) Testosterone (LG-01)	Fertilizer & Animal & Atmospheric
WW-04 – Down-gradient Well	Nitrate level = 49.9 mg/L Total nitrogen concentrations increased substantially between WW-01 and WW-04 Ten to 20-fold increase in concentration in four major ions between WW-01 and WW-04.	Atrazine Tetracycline Chlorotetracycline Testosterone	Atrazine (S0-01) Tetracycline (LG-01, LG-02, LG-03, SO-01, and SO-02) Chlorotetracycline (LG-02 and SO-02) Testosterone (LG-01)	Fertilizer & Animal Waste

Sample Location	General Chemistry	Organic Compounds Detected in Wells	Organic Compounds also Detected in Dairy Sources	Isotopic Analyses
WW-05 – Down-gradient Well	Nitrate level = 12.8 mg/L Total nitrogen concentrations increased substantially between WW-01 and WW-05 Five to 10-fold increase in concentrations in four major ions between WW-01 and WW-05.	Atrazine Testosterone	Atrazine (SO-01) Testosterone (LG-01)	Animal waste

ND = No Detects

All of the residential water wells, except WW-01 have nitrate levels greater than EPA's MCL of 10 mg/ L. In two cases, the concentrations are substantially greater than the MCL (WW-03 and WW-04). The total nitrogen and major ions data indicated that the dairies are likely contributing to higher levels of nitrogen and major ions in the three downgradient wells associated from the Haak Dairy. The total nitrogen and major ion data indicate an increasing trend in the concentrations from upgradient to downgradient wells, with higher concentrations in the dairy lagoons, manure samples, and application field samples.

Atrazine was the only pesticide detected in the water well samples for the organic chemicals. Atrazine is widely used throughout the area, and the source is likely historical and current use of the pesticide. DEHP was the only trace organic detected in the water wells, but it was not detected in any of the dairy lagoons.

Tetracycline was detected in two of the three downgradient wells and in all three dairy lagoons and the manure and application field samples. It is possible that the source of the tetracycline is the various upgradient sources from the Haak Dairy or it could be septic systems, given tetracycline is used by humans. Monesin was detected in the upgradient well but not in any of the downgradient wells. Monesin was detected in all the dairy lagoons and manure and application field samples.

Testosterone was the only hormone detected in water wells, with higher concentrations in the upgradient well than the downgradient wells; the sources could be from any animal.

It appears that the source of nitrate for each of the wells is different for the isotopic data. For WW-02, the dominant source appears to be soil cycling, while the possible sources in WW-03 are fertilizer, animal waste, and atmospheric. For WW-04, the possible sources are fertilizer and animal waste, while the dominant source for WW-05 is animal waste.

Comment [LE31]: This well really doesn't look to be downgradient of many of the dairy sources—is it? If not, it would make sense that it looks different.

In conclusion, all of the residential water wells except WW-01 have high nitrate levels. Data from the total nitrogen and major ion data indicate an increasing trend in the concentrations from the upgradient well to the downgradient wells. Information on the construction and depth of the wells would be helpful to confirm the contributions of sources to the higher concentrations seen from the upgradient well to the downgradient wells. The tetracycline in the wells could be a contributing source related to the Haak Dairy, but could also be from a human source. The isotopic data provide ~~good~~ strong evidence that animal waste is a dominant contributor to the nitrate contamination for WW-05.

1.F. Dairy Cluster

The "Dairy Cluster" refers to a group of dairies in close proximity to each other. EPA regards them as three facilities because some of the dairies are adjacent and have common ownership. The Liberty Dairy and the Hank Bosma Dairy are regarded by EPA as a single facility, as are the Cow Palace 1&2 Dairies, and the George DeRuyter/D&A Farms Dairies. Together they occupy about eight square miles of land (roughly 5,100 acres) north of the Yakima River and the town of Liberty, near the northern edge of the irrigated area in the Yakima Valley.

For this study sampling was organized into four areas: (1) George DeRuyter Dairy; (2) D&A Farms; (3) Cow Palace #1and Cow Palace #2; and (4) Henry Bosma and Liberty Dairy. Appendix E provides a more detailed description of the Dairy Cluster and their operations.

Figure 11 show the sample locations for the Dairy Cluster. The sampling locations include:

- One upgradient drinking water well (WW-06) located north of all the other samples in the Dairy Cluster, with the exception of SO-05;

- Three dairy supply wells located on each of the dairies except for Henry Bosma and Liberty Dairies. The supply well at the Bosma dairy was not sampled because they used an ion-exchange system which modified the water chemistry of the sample and made it unsuitable for sampling for this study. A residential water well owned by the dairy was sampled instead (WW-10). The three dairy supply wells included: George DeRuyter Dairy (WW-07); D&A Farms (WW-08); and Cow Palace #1 and #2 (WW-09);

- Four dairy manure pile samples located on each dairy: George DeRuyter (SO-03), D&A Farms (SO-05); Cow Palace #1 and #2 (SO-07); and Henry Bosma and Liberty Dairy (SO-09);

- Twelve dairy lagoon samples;

  - George DeRuyter (LG-04, LG-05, and LG-06. LG-05 and LG-06 were taken from the same lagoon);

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- D&A Farms (LG-07, LG-08, and LG-09. LG-08 and LG-09 were taken from the same lagoon);

- Cow Palace #1 and #2 (LG-10, LG-11, and LG-12). LG-11 and LG-12 were taken from the same lagoon); and

- Henry Bosma and Liberty Dairy (LG-13, LG-14, and LG-15) (these were three separate lagoons);

- Four dairy application field samples;

  - George DeRuyter (SO-04);

  - D&A Farms (SO-06);

  - Cow Palace #1 and #2 (SO-08); and

  - Henry Bosma and Liberty Dairy (SO-10).

- Eight downgradient residential drinking water wells (WW-10 to WW-17

Dairy Cluster: General Chemistry

The four types of general chemistry data collected at the Dairy Cluster were: nitrate and other forms of nitrogen; major ions; minor ions and trace inorganic elements; and perchlorate. Each of these is discussed below.

Dairy Cluster: Nitrate and other forms of nitrogen

Twelve water wells and 12 dairy lagoon samples were analyzed for nitrate, nitrate plus nitrite, ammonia or ammonium, and TKN. The manure samples and agricultural field samples that were receiving dairy waste were analyzed for extractable nitrate-N (Nitrate-N Solid), extractable ammonia-N (Ammonia-N Solid), and total nitrogen by combustion (Total Nitrogen Solid). In addition, total nitrogen from all forms was calculated for each sample and is present as "Calculated Total Nitrogen." **Table 12** shows the values measured for total nitrogen for all the dairy cluster samples.

Table 12: Dairy Cluster - Concentrations of Forms of Nitrogen Including Total Nitrogen Values for Water Wells, Lagoons, Manure Piles, and Application Fields

Location	Nitrate as N (mg/L)	Nitrate + Nitrite as N (mg/L)	Ammonia as N (mg/L)	TKN as N (mg/L)	Total Nitrogen (mg/L)
Water Wells and Lagoons					
WW-06: Upgradient Well	0.71	0.73	ND	ND	0.73

WW-07: Supply Well	1.02	1.19	ND	ND	1.19
WW-08: Supply Well	11.7	12.9	ND	ND	12.9
WW-09: Supply Well	ND	ND	ND	ND	ND
LG-04: Lagoon Influent	ND	ND	920	1600	1600
LG-05: Lagoon Outlet	ND	ND	1200	1600	1600
LG-06: Lagoon Outlet	ND	3.1	1200	1800	1803
LG-07: Lagoon Influent	3.1	3.1	950	1700	1703
LG-08: Lagoon Outlet	ND	ND	730	1200	1200
LG-09: Lagoon Outlet	ND	ND	760	1100	1100
LG-10: Lagoon Influent	ND	ND	190	380	380
LG-11: Lagoon Outlet	ND	ND	240	500	500
LG-12: Lagoon Outlet	ND	ND	240	290	290
LG-13: Lagoon Influent	2.5	2.5	970	1700	1703
LG-14: Lagoon Outlet	ND	ND	860	1400	1400
LG-15: Lagoon Outlet	ND	ND	560	900	900
WW-10: Downgradient Well	ND	ND	ND	ND	ND
WW-11: Downgradient Well	22.3	23	ND	ND	23
WW-12: Downgradient Well	45	46.7	ND	ND	46.7
WW-13: Downgradient Well	41.4	44	ND	ND	44
WW-14: Downgradient Well	40.9	43.4	ND	ND	43.4
WW-15: Downgradient Well	29.4	30.2	ND	ND	30.2
WW-16: Downgradient Well	22.3	23.4	ND	ND	23.4
WW-17: Downgradient Well	21.7	22.7	ND	ND	22.7

Manure Piles				
Location	Ammonia-N Solid (mg/kg)	Nitrate-N solid (mg/kg)	Total Nitrogen Solid (mg/kg)	Calculated Total N (ppm)
SO-03: Manure	1470	32.8	9210	9210
SO-05: Manure	1060	43.1	13600	13600
SO-07: Manure	3600	18.9	16100	16100
SO-09: Manure	1700	5.69	13700	13700

Application Fields				
Location	Ammonium as N (mg/kg)	Nitrate + Nitrate as N (mg/kg)	Total Nitrogen Solid (mg/kg)	Calculated Total N (ppm)
SO-04: Application field	7.3	247	2110	2110
SO-06: Application field	6.8	45.6	960	960
SO-08: Application field	2.9	84.3	3040	3040
SO-10: Application field	7.1	139	3590	3590

Figures 14a, 14b, 14c, and 14d shows the concentration of total nitrogen for the DeRuyter Dairy, D&A Dairy, Cow Palace # 1 and #2 Dairy, and Bosma and Liberty Dairy. As with the Haak Dairy, there is an increasing trend in concentration of total nitrogen from the upgradient

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well to the downgradient wells, with several likely sources of nitrogen in between (dairy lagoons, manure piles, and application fields). The attribution to a specific source is complicated given the lack of information on water wells, but it does suggest the lagoons, manure piles, or application fields are a likely source contributing to the higher total nitrogen concentrations observed downgradient from these sources.

<u>Dairy Cluster: Major Ions</u>

Figures 15a, 15b, and 15c show the concentrations of several major ion in the upgradient water wells, the supply wells, the lagoons, and the downgradient wells. An average concentration for the lagoons for each area was calculated: LG-04, LG-05, and LG-06: LG-07, LG-08, and LG-09; LG-10, LG-11, and LG-12; and LG-13, LG-14, and LG-15. The averages for the lagoons were calculated for each area because they are in close proximity and they allow easier comparison.

 The figures show a similar pattern to that observed at the Haak Dairy of elevated concentrations in the downgradient wells (WW-10 to WW-17) compared with the upgradient wells (WW-06) and supply wells (WW-07 to WW-09). The increase in the concentrations ranges from up to: seven-fold for sodium; nine-fold for magnesium; ten-fold for calcium; and almost 40-fold increase for chloride. Potassium did not show any clear increase.

Sulfate ~~saw~~ showed a large increase in concentration in the downgradient wells compared to the upgradient well, but also ~~saw~~ showed an increase in the concentrations ~~from~~ compared to the lagoons. The reason for this pattern is that ~~similar to~~ as with nitrogen, sulfur comes in many different forms. This study only evaluated sulfate, which is the oxidized form of sulfur. The levels of sulfate in the lagoons is less than in the downgradient wells because the form of sulfur in the lagoons is sulfide. The sulfide to sulfate transformation occurs outside the lagoon when it is exposed to oxygen. This accounts for the higher levels of sulfate in the downgradient wells.

As with the Haak Dairy, one possible explanation for the observed increase in these major ions, especially for the conservatively transported chloride, is that the dairy lagoons are introducing these ions to the groundwater. After the release, the ions are then changing the ground water chemistry and producing the observed higher concentrations in the downgradient wells.

<u>Dairy Cluster: Minor and Trace Inorganic Elements</u>

All water wells and dairy lagoons were sampled for analysis of minor and trace inorganic elements **(see Appendix A5)**. The manure and application field samples were not evaluated for minor or trace inorganic elements. The trace inorganic elements found in the water wells and dairy lagoons were barium, iron, manganese, mercury, and zinc. Barium was detected in all 11 wells, iron was detected in five wells, manganese was detected in four wells, mercury was detected in one well, and zinc was detected in eight wells. No discernible pattern of increasing concentrations from the upgradient wells to the downgradient wells was evident for any of these compounds with the possible exception of barium. This lack of a pattern is not surprising, since

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minor ions and trace inorganic elements are not generally used as linking compounds because they are ubiquitous and are frequently not conservatively transported with groundwater.

<u>Dairy Cluster: Perchlorate</u>

Perchlorate analysis was performed on all the water well samples (see **Appendix A6**). The concentrations ranged from less than the detection limit (0.003 µg/L) to 3.08 µg/L (WW-17). Perchlorate was intended to augment the isotopic data as an indicator of potential accumulation of atmospherically derived nitrate associated with caliche soils. However, elevated levels of perchlorate were seen in only two wells. None of those wells was part of the Dairy Cluster. Perchlorate was not evaluated in the dairy lagoon system because this compound is rapidly degraded in the anoxic environment of a dairy lagoon.

1. **Dairy Cluster: Microbiology**

There were no detections of total coliform, fecal coliform, or *E.coli* at any of the water wells either upgradient of the Dairy Cluster, in the supply wells, or downgradient of the Dairy Cluster. MST was not performed because there was no indication of fecal contamination.

All the dairy lagoons in the Dairy Cluster were analyzed for fecal coliform. LG-04 through LG-09 were also analyzed for *E.coli* and MST was performed. The other dairy lagoons did not have *E. coli* or MST performed because the Manchester mobile laboratory was only able to participate in the sampling effort for a limited period **(see Appendix A7).**

All the dairy lagoons had high levels of fecal coliform. Of the six dairy lagoons evaluated using MST, five indicated a ruminant source (LG-04, LG-05, LG-06, LG-07, and LG-08) while one indicated both a ruminant and a human source (LG-09). The five dairy lagoons indicative of ruminant sources are expected, but LG-09 indicated both a ruminant and a human source and is unexpected. It is unknown why LG-09 had an indication of human sources though it is possible that the lagoons are impacted by human waste given the Dairy is on septic systems and they have several employees.

15.2. **Dairy Cluster: Organic Compounds**

<u>Dairy Cluster: Pesticides</u>

Four pesticides were detected in the water wells associated with the Dairy Cluster (atrazine, bentazon, alachlor, and ioxynil). Atrazine, bentazon, and alachlor are all common pesticides used in agricultural production. Ioxynil is not registered for use in the United States (PAN 2011).

- Atrazine: WW-12, WW-13, WW-14, WW-15, WW-16, and WW-17
- Bentazon:WW-08 (supply well)
- Alachlor:WW-13 and WW-17
- Ioxynil: WW-13

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As stated before, there are no results for pesticides in dairy lagoons or WWTPs because of problems with matrix interference from the wastes. The four pesticides detected in the water wells were not detected in the manure or application field samples. The concentrations of atrazine found in the water wells ranged from 0.016 µg/L to 0.18 µg/L.

The concentration of bentazon in WW-08 was 0.036 µg/L. Alachlor levels found in the water wells were 0.048 µg/L and 0.057 µg/L. The concentration of Ioxynil in this study was 0.063.ug/L The four pesticides are not anticipated to be used in animal operations at the dairies for pest control (Pike 2004), but atrazine, alachlor, and bentazon may be used in corn fields that produce grain for dairy feedstock. Each of the dairies includes crop land where pesticides may have been applied. Given the historical use of these pesticides and the detection of these compounds in other studies, it is likely that these pesticides are from the current and historical use of pesticides for agricultural purposes, which could include application by the dairies.

Seven pesticides were detected in one of more of the manure samples. These pesticides were not detected in the water well samples. One possible source of these pesticides is from the feed given to the animals. Seven pesticides were also detected in one or more of the field application samples, but they were not detected in the water well samples.

<u>Dairy Cluster: Trace organics</u>

For the trace organics, three compounds were detected in water well samples associated with the dairy cluster:

- Bis-(2-ethylhexyl)-phthalate (DEHP) in WW-06 (upgradient well), WW-11, and WW-17

- Naphthalene in WW-07 (supply well)

- Tetrachloroethylene in WW-07 (supply well).

All 12 dairy lagoons associated with the dairy cluster had one or more detections for trace organics **(see Appendix A9).** Eight compounds were detected in all 12 dairy lagoons associated with the dairy cluster. These compounds are generally the same as were detected in at the Haak Dairy: 3-beta-coprostanol; 3-methyl-ih-indole (skatol); 4-nonyphenol monoethoxylate; beta-sitosterol; beta-stigmastanol; cholestrol; p-cresol; and phenol. Trace organics were not analyzed in manure or soil samples.

Of the three compounds found in water wells, only DEHP was found in one dairy lagoon sample (LG-10). Naphthalene and tetrachloroethylene were not detected in any of the dairy lagoons. The source for these compounds could be septic systems or some other source, given their common usage. DEHP is a common plasticizer and it could come from multiple sources.

<u>Dairy Cluster: Pharmaceuticals</u>

DEET was the only wastewater pharmaceutical detected in ~~one~~ any well (WW-10 – downgradient well). There were no detections of any of the wastewater pharmaceuticals in the manure pile or field application samples.

Three wastewater pharmaceutical compounds were detected in dairy lagoons associated with the Dairy Cluster: DEET (eight dairy lagoons); diphenhydramine (two dairy lagoons); and thiabendazole (three dairy lagoons). The source of the DEET could be its use as an insect repellent. The source of the diphenhydramine in the dairy lagoons is unknown. Diphenhydramine is a common antihistamine used by humans and can be used in dogs and cats. Thiabenzadole is a parasticide that is used to treat worm infections in both livestock and humans and can be used as a pesticide (Mayo Clinic 2011). It is possible that the source of thiabenzadole is its use to treat worm infections.

Eight compounds were detected in water wells with five detected in downgradient wells for the veterinary pharmaceuticals (see **Table 13 - attached**). Three of the eight compounds were detected only in supply wells (erythromycin, sulfadimethoxine, and sulfamethazine). Three residential wells had no detections (WW-12, WW-15, and WW-16). Veterinary pharmaceuticals were detected in the following residential water wells.

Chlorotetracycline: WW-13 and WW-14

Monesin: WW-14

Tetracycline: WW-11, and WW-17

Tylosin: WW-11

Virginiamycin: WW-13

Several of the veterinary pharmaceuticals were detected in the majority of dairy lagoons, manure samples, and application field samples (ractopamine, sulfachloropyridazine, sulfadimethoxine, sulfamethazine, and sulfathiazole) but were not detected in downgradient water wells. The presence of these compounds in the dairy lagoons, manure samples, and application field samples indicates these compounds are used at the dairies but were not transported or were not transported at detectable levels to the downgradient wells during the study period..

The concentration of chlorotetracycline in the downgradient wells was greater than the concentrations in the two dairy lagoons with detections of this compound **(Table 13 – attached).** The two dairy lagoons (LG-05 and LG-10) with detected levels of chlorotetracycline are a considerable distance from WW-13 and WW-14. Chlorotetracycline was detected in the majority of the manure and application field samples, although some of these samples are a considerable distance from WW-13 and WW-14 (such as SO-07 and SO-05). It is possible the source of the chlorotetracycline in the water wells could be the manure piles or application fields.

Monesin was detected in WW-14 and was also detected in high concentrations in the dairy lagoons, manure piles, and application field samples. These detections would indicate that monesin is used at the dairies. Monesin is not used by humans, but is used in dairy cows. Thus, the source of monesin in WW-14 is probably from its use in one or more of the upgradient dairies. This is reinforced by the isotopic findings, which indicate that the source of nitrate for WW-14 is animal waste (although animal waste can be aincludes human sources).

Tetracycline was detected in upgradient well WW-06 (0.051 µg/L) and in two downgradient wells, which had lower concentrations than the upgradient well (0.038 µg/L for WW-11; and 0.049 µg/L for WW-17). Tetracycline was detected in all of the dairy lagoon samples, manure samples, and application field samples, indicating that tetracycline is used at the dairies. It is possible that tetracycline in the downgradient wells was from one of the sources in the dairy cluster.

Tylosin was detected in one downgradient well (WW-11) and five of the dairy lagoons along with several manure and application field samples. These detections indicate that tylosin is used at the dairies. Similar to monesin, this compound is not approved for use in humans, but it can be used in different livestock, including dairy cattle.

Dairy Cluster: Hormones

EPA's Ada laboratory analyzed for five hormones in water wells and dairy lagoons associated with the dairy cluster. The laboratory did not analyze the manure pile or application fields samples associated with the Dairy Cluster. The Ada laboratory did not detect any of the five hormones in water wells associated with the Dairy Cluster. The 12 dairy lagoons all had detected levels of 17-α-estradiol, 17-β-estradiol, and estrone, while 17-α-ethyl-estradiol and estriol were not detected in any of the dairy lagoons **(see Appendix A11).**

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The UNL analyzed 18 hormones in water well, dairy lagoon, manure pile, and application field samples associated with the Dairy Cluster, including the same five hormones as Ada analyzed. **Table 14** (attached) provides the results of these analyses for those hormones detected in water wells and also in either the dairy lagoons, manure piles, or application field samples associated with Dairy Cluster.

Hormones were not detected in water wells WW-10, WW-13, WWW-14, and WW-16. Nine hormones from the UNL analysis were detected in water wells (**see Table 14 - attached**) with three detected in downgradient wells (WW-11, WW-12, WW-15, and WW-17).

- Androsterone: WW-12, WW-15, and WW-17
- Androstanedienedione: WW-12.
- Testosterone: WW-11.

The six compounds detected in dairy supply wells, but not the downgradient wells, include α-estradiol; 17-β-estradiol; 17-β-trenbolone; α-zearalanol; epitestosterone; and 11-keto–testosterone.   The following is a discussion on the likely sources for the three compounds detected in the downgradient wells.

Androsterone was not detected in any of the dairy lagoons, manure, or application field samples. The source of the androsterone is unknown. Androsterone is a metabolite of testosterone, so it could come from either humans or other animals or from the dairy lagoons since testosterone was detected in the dairy lagoons.

Androstanedienedione was detected in three dairy lagoons and all of the manure samples, indicating its likely usage at the dairies. The three dairy lagoons (LG-05, LG-11, and LG-12) with detections of the compounds are a considerable distance from WW-12. Androstanedienedione is a precursor to boldenone (a synthetic growth promoter) and is used mainly to treat horses and cattle.

Testosterone was detected in nine dairy lagoons and one manure sample (SO-03).   The detection of testosterone in the dairy lagoons is not surprising given it is a natural sex hormone. The source of the testosterone in WW-11 could be the Dairy Cluster.

16.3.   Dairy Cluster: Isotopic Analysis

Isotopic analyses were completed for WW-06 to WW-17 (see **Table 15 -below**). There was insufficient nitrate in WW-06, WW-09, and WW-10 to complete the analysis. Additional details on the results of isotopic analyses conducted for this study are provided in Appendix B of this report.

Table 15: Dairy Cluster – Summary of Isotopic Analysis for Water Wells

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Location	Nitrate-N (mg/L)	δ^{15}N-NO3 (‰)	Dominant Source	δ^{18}O-NO3 (‰)	Overall Assessment
WW-06	0.6	NM	NM	NM	NM
WW-07	1.1	-0.1	Fertilizer	NM	Fertilizer
WW-08	11.7	5.3	Fertilizer & Animal Waste	23	Fertilizer & Atmospheric & Animal Waste
WW-09	NM	NM	NM	NM	NM
WW-10	NM	NM	NM	NM	NM
WW-11	21.6	3.0	Fertilizer & Animal Waste	18	Fertilizer & Animal Waste
WW-12	43.6	6.2	Fertilizer & Animal Waste	-1.4	Fertilizer & Animal Waste
WW-13	42	11	Animal Waste	16	Animal Waste
WW-14	40.7	10	Animal Waste	8.5	Animal Waste
WW-15	27.4	5.2	Fertilizer & Animal Waste	30	Fertilizer & Atmospheric & Animal Waste
WW-16	23	5.9	Fertilizer & Animal Waste	5.8	Fertilizer & Animal Waste
WW-17	23.3	6.9	Fertilizer & Animal Waste	2.5	Fertilizer & Animal Waste

δ^{15}N-NO3. Values less than 2.0 = dominated by fertilizer; values between 2.0 to 8.4= undetermined mixture of fertilizer and/or animal waste; values greater than 8.4 = dominated by animal.
δ^{18}O-NO3.Values greater than 20 considered strong atmospheric contribution.
.
The dominant source of nitrate for two wells (WW-13 and WW-14) is animal waste. The dominant source of nitrate for one well (WW-07) is fertilizer. For the other wells, it is not possible to determine the dominant source. For WW-08 and WW-15 the atmospheric contribution is strong.

Table 16: Isotopic Analysis - Summary Results for Lagoons

Location	Position in System	Ammonia (mg/L)	δ^{15}N-NH4 (‰)	Assessment
LG-04: DeRuyter	Influent	899	6.7	Volatilization Animal Waste
LG-05:DeRuyter	Discharge	1151	10.6	Volatilization Animal Waste
LG-06: DeRuyter	Discharge	1293	10.3	Volatilization Animal Waste
LG-07:D&A	Influent	869	5.4	Fresh Animal Waste
LG-08: D&A	Discharge	696	10.3	Volatilization Animal Waste

LG-09: D&A	Discharge	658	10.1	Volatilization Animal Waste
LG-10: Cow Palace	Influent	NM	NM	NM
LG-11:Cow Palace	Discharge	274	3.1	Fresh Animal Waste
LG-12: Cow Palace	Discharge	222	2.0	Fresh Animal Waste
LG-13:Bosma	Influent	469	4.4	Fresh Animal Waste
LG-14:Bosma	Discharge	600	3.3	Fresh Animal Waste
LG-15:Bosma	Discharge	658	13.9	Volatilization Animal Waste

Isotopic analyses were completed for the dairy lagoon samples (LG-04 to LG-15). **Table 16**
indicates the source of nitrate in dairy lagoons is animal waste. Additional details on the results
of isotopic analyses conducted for this study are provided in Appendix B of this report.

17.4.   **Dairy Cluster: Age Dating**

Table 17 presents the age dating data, and similar to the Haak Dairy, two samples were collected
for each water well.

Table 17: Dairy Cluster – Summary of Age Dating for Water Wells (Years)

Location	Sample Age	Duplicate Age	Average of Samples	Average of Group
WW-06l	16.3	15.8	16.1	16.1
WW-07	36.3	32.8	34.6	42.5
WW-08	35.3	40.8	38.1	
WW-09	58.3	51.3	54.8	
WW-10	44.3	44.8	44.6	34.2
WW-11	Over Value	Over Value	NA	
WW-12	Over Value	Over Value	NA	
WW-13	24.3	23.8	24.1	
WW-14	30.8	29.3	45.5	
WW-15	27.8	28.3	28.1	
WW-16	29.8	28.8	29.3	
WW-17l	33.3	33.8	33.6	

Over Value: These samples contained more SF_6 than can be explained by equilibrium with modern air.

For evaluation, averages were calculated for the upgradient well (WW-06), three supply wells
(WW-07, WW-08, and WW-09), and the six downgradient wells with reported values (WW-10,
WW-13, WW-14, WW-15, WW-16, and WW-17). The results indicate the "youngest" water was
sampled in the upgradient well, with an average age of 16.1 years. The "oldest" waters were in
supply wells associated with the Dairy Cluster, with an average age of 42.5 years. The average
age of the waters in the downgradient wells was 34.2.

18.5. **Dairy Cluster – Summary of Results for Residential Water Wells**

Table 18 provides a summary of the groups of compounds (general chemistry and organic compounds) and analytical techniques (isotopic analyses) that provide information useful to address the question of the likely sources of the nitrate for the nine residential water wells associated with the dairy cluster. No conclusions using the microbial data is possible given the downgradient wells did not exhibit any microbial contamination. In addition, the age dating data do not provide any specific evidence to connect specific sources to high nitrate levels.

Table 18: Dairy Cluster – Summary of Results for Residential Water Wells

General Chemistry	Organic Compounds Detected in Water Wells	Organic Compounds Also Detected in Dairy Sources	Isotopic Analyses
WW-06 – Upgradient Well			
Nitrate level = 0.6 mg/L No trends in total nitrogen or major ions as upgradient well	Atrazine and DEHP	No comparsion because upgradient well	Not sufficient nitrate
WW-10 – Downgradient Well			
Nitrate level = Not detected No large trends in total nitrogen or major ions between WW-06 and WW-10	DEET Monesin	DEET (8 lagoons) Monensin (All the dairy sources except LG-07)	Not sufficient nitrate
WW-11 – Downgradient Well			
Nitrate levels = 21.6 mg/L Total nitrogen increased 20-fold between WW-06 and WW-11 Three to 25-fold increase in concentration of five major ions between WW-06 and WW-11.	DEHP Tetracycline Tylosin	DEHP (LG-10) Tetracycline (All dairy sources) Tylosin (5 lagoons, 2 manure samples, and one application field sample)	Fertilizer & Animal Waste
WW-12 – Downgradient Well			
Nitrate level = 43.6 mg/L Total nitrogen increased 50-fold between WW-06 and WW-12 Five to 25-fold increase in concentration of five major ions between WW-06 and WW-12.	Atrazine Androstenedienedione Androsterone	Atrazine (ND) Androstenedienedione (three lagoons and 4 manure samples) Androsterone (ND)	Fertilizer & Animal Waste

WW-13 – Downgradient Well			
Nitrate level = 42.0 mg/L Total nitrogen increased 40-fold between WW-06 and WW-13 Seven to 40-fold increase in concentration of five major ions between WW-06 and WW-13.	Alachlor Atrazine Ioxynil Virginiamycin	Alachlor (ND) Atrazine (ND) Ioxynil (ND) Virginiamycin (5 lagoons)	Animal waste

WW-14 – Downgradient Well			
Nitrate level = 40.7 mg/L Total nitrogen increased 40-fold between WW-06 and WW-14 Two to 50-fold increase in concentration of six major ions between WW-06 and WW-14.	Atrazine Monesin	Atrazine (ND) Monesin (All the dairy sources except LG-07)	Animal waste

WW-15 – Downgradient Well			
Nitrate level = 27.4 mg/L Total nitrogen increased 30-fold between WW-06 and WW-15 Two to 20-fold increase in concentration of six major ions between WW-06 and WW-15.	Atrazine Chlorotetracycline Androsterone	Atrazine (ND) Chlorotetracycline (LG-10, all manure and application fields except SO-09 and SO-10) Androsterone (ND)	Fertilizer & Animal Waster& atmospheric

WW-16 – Downgradient Well			
Nitrate level = 23.0 mg/L Total nitrogen increased 20-fold between WW-06 and WW-16 Four to 30-fold increase in concentration of five major ions between WW-06 and WW-16.	Atrazine	Atrazine (ND)	Fertilizer & animal waste

WW-17 – Downgradient Well			
Nitrate level = 23.3 mg/L Total nitrogen increased 20-fold between WW-06 and WW-11 Four to 30-fold increase in concentration of five major ions between WW-06 and WW-17.	Alachlor	Alachlor (ND)	Fertilizer & Animal waste
	Atrazine	Atrazine (ND)	
	DEHP	DEHP (LG-10)	
	Tetracycline	Tetracycline (All dairy sources)	
	Androsterone	Androsterone (ND)	

ND = Not Detected

As with the Haak Dairy, the nitrate levels in the downgradient residential wells are substantially greater than EPA's MCL for nitrate with the exception of WW-06 and WW-10. The total nitrogen and major ions data show increasing concentrations from the upgradient well, WW-06, past several sources of nitrogen, and to the downgradient wells. The downgradient wells contain substantially more nitrogen than is present in the upgradient well (or in some wells elsewhere in the this area such as WW-09 and WW-10). The upgradient well, WW-06, shows low nitrate levels within "background" range. The age of the water in WW-10 is significantly greater than the other downgradient wells, suggesting that, this well may be substantially deeper than the other residential wells and less exposed to contamination from the shallow aquifer.

The major ion data, especially for calcium and chloride, show an increasing trend between the dairy waste (dairy lagoons, manure piles, and application fields) and the downgradient wells with high nitrate.

Four pesticides were detected in the water wells associated with the Dairy Cluster. However, none of these pesticides was detected in the manure or application field samples. Because of problems with matrix interference, no results for pesticides in dairy lagoons or WWTPs influent are available. Three trace organics were detected in water wells, but only one (DEHP) was detected in a downgradient well (WW-17). The pesticides data indicate that the source is probably the past or current application for agriculture.

Pharmaceuticals were detected in four downgradient wells. Several of the compounds — tetracycline (WW-11 and WW17); oxytetracycline (WW13 and WW-14); and monesin (W-14) — were detected in dairy lagoons, manure samples, and application fields associated with the dairy cluster. It is possible that the source of the three compounds is one of the Dairy Cluster sources, especially likely for monesin, which is used in dairy cows but not by humans.

Nine hormones were detected in water wells associated with the dairy cluster, with three detected in downgradient wells: androsterone (WW-12, WW-15, and WW-17); androstenedienendione (WW-12); and testosterone (WW-11). The source of the androsterone and testosterone could be the dairy cluster, although androsterone was not detected in any of the dairy lagoons, manure piles, or application field samples. Androsterone is a metabolite of testosterone so could come

from either humans or other animals, but in this case it was not detected in any of the other samples from the dairy cluster. Testosterone was detected in nine dairy lagoons and one manure sample and therefore its source could be from the dairy cluster or from a human source. The detection of androstenedienendione in the well is unexpected as it is a precursor to boldenone (a synthetic growth promoter) and is not intended for human use and is used mainly to treat horses and cattle.

The isotopic analysis indicates that the dominant nitrogen source for two wells is animal waste (WW-13 and WW-14) while the dominant source for WW-07 is fertilizer. For the other wells, it is not possible to determine the dominant source. For WW-08 and WW-15 the atmospheric contribution is strong.

In conclusion, all the downgradient residential water wells (with the exception of WW-10) associated with the Dairy Cluster have high nitrate levels. The data for total nitrogen and major ions indicate an increase in concentrations from the upgradient wells to the downgradient wells, with the likely sources being dairy lagoons, manure piles, and application fields.

The dominate nitrate source for the pharmaceuticals in WW-13 and WW-14 is animal waste and in WW-17 is predicted to be a mix of fertilizer and animal waste. Compounds were detected in these three wells that could be from sources associated with the dairy cluster, but could also be from human sources (tetracycline and oxytetracycline), with the exception of monesin.

It is possible for that the hormones that the compoundsfound in WW-12 or WW-17 came from sources associated with the dairy cluster. The isotopic evaluation predicted the source for WW-12 and WW-17 is probably a mix of fertilizer and animal waste. Again, a human source cannot be ruled out, as humans produce both testosterone and androsterone. For WW-11 and WW-15, it appears that the source is a mixture of fertilizer and atmospheric sources.

C.G.   Residential Septic Systems

Instead of sampling septic systems directly, samples were collected from the influent stream of three small WWTP (Zillah, Mabton, and Toppenish) as surrogate samples for septic systems. This approach allows characterization of the typical compounds introduced with rural septage without having to sample the septic systems directly. This approach was used to determine whether the compounds found in the influent to the WWTP were similar or different to those found in downgradient water wells showing high nitrate concentrations in areas with significant numbers of septic systems.

Each of the five groups of compounds or analytical techniques is discussed for the septic systems. Because of the mixture of large numbers of different water sources to the flow entering the WWTP, age dating was not done on these samples. Four wells were specifically targeted to evaluate for linkage to septic systems (WW-19, WW-20, WW-21, and WW-22 – see **Figure 7**). However, while these four wells were targeted, all of the water wells were evaluated to determine whether septic systems could be the source of the nitrate found in any well in the study.

1. **Septic Systems: General Chemistry**

Septic Systems: Nitrate and other Forms of Nitrogen

The WWTP influents were not analyzed for nitrate because it was anticipated that there would be very little formation of nitrate from the organic nitrogen in the waste during its rapid transport to the treatment plant. This is the case because of the low oxygen environment of the sewer combined with the short residence time between the waste streams. The wells were evaluated for nitrate and the different forms of nitrogen. However, no analysis is possible because there are no upgradient wells to compare for comparison and no specific sources between the upgradient and downgradient wells.

Septic Systems: Major Ions

Water quality parameters such as dissolved oxygen and conductivity were not collected from WWTPs because of concern that they could become easily contaminated. However, other studies (Pescod 1987) and a general knowledge of the nature of sewage indicates that sewage is very low in dissolved oxygen with high concentrations of dissolved solids compared with the groundwater or surface waters from which it is derived. Other general chemistry data were collected to characterize the WWTP influent as a surrogate for residential septic effluent. However, no pattern that might tie a specific well to a residential septic source is apparent when the major ion data from the treatment plants and water wells are compared.

As stated previously, the major ions for distinguishing waters are typically used to observe the evolution of water along a flow path. For the four wells identified as downgradient for the septic systemssystem analysis, upgradient wells that can be used to compare to downgradient wells were not available. Therefore, no specific analysis was conducted for the major ions.

Septic Systems: Trace Elements

Four metals were found in the water wells and WWTPs (barium, iron, manganese, and zinc). However, each of these metals is naturally occurring elements and is not unique to septic systems. Any water sample would be expected to have detectable concentrations of each of these elements and the concentrations observed are similar for natural waters (Hem 1970).

Septic Systems: Perchlorate

Perchlorate was analyzed to aid in the evaluation of the isotopic data. Perchlorate was not analyzed at the WWTP because it is not expected to persist in wastewater effluent as a result of bacterial activity and it is of value only when evaluating a particular water source, and not a mixture of sources such as is present in waste water. As stated earlier, perchlorate was used in this study as a potential indicator of the first flush of irrigation water moving through the caliche soils in the Lower Yakima Valley. The results for the perchlorate analysis are evaluated together with the isotopic data.

~~19.~~2.   **Septic Systems: Microbiology**

~~Similar to~~ As found with other water wells in the study, neither fecal coliform nor *E. coil* was detected in the four targeted water wells. The WWTPs were analyzed for fecal coliform and *E.coli*. **(see Appendix A7).** As expected, v~~V~~ery high concentrations of both fecal coliform and *E.coli* were found in the influent to the WWTPs. Samples were also analyzed using MST to identify the source of the fecal contamination. Three of the samples were indicative of human sources, while one sample was indicative of both human and ruminant sources.

~~20.~~3.   **Septic Systems: Organic Compounds**

Septic Systems: Pesticides

Samples were collected for analysis of pesticides in WWTPs by EPA's Manchester Laboratory. However, the laboratory reported that the WWTP sample matrix was too difficult to analyze because of significant interferences from the large number of organic compounds present in the waste. Therefore, the pesticide concentrations could not be quantified from the WWTP influent. No manure or application field samples are associated with these six sites.

Atrazine and bentazon were detected in WW-20 (**Appendix A8)**. Similar to the other wells with atrazine and bentazon, the most likely source of the pesticides is past or current use of these compounds in agricultural production.

Septic Systems: Trace Organics

The trace organics were one class of compounds most likely to be associated with septic systems. The compounds sampled included those associated with human activities such as caffeine, fragrances, and disinfectants.

Thirty-seven trace organics were detected in the influent to the WWTPs (see **Appendix A9**). Nineteen of the trace organics were detected in all of the WWTP sample~~s~~s. There were no detected trace organics in the four wells.

Septic Systems: Pharmaceuticals

Nine compounds were detected in the influent to the WWTPs for the wastewater pharmaceuticals, with six compounds detected in all three WWTP~~s~~ influent samples (acetaminophen, cotinine, DEET, ibuprofen, naproxen, and tricolsan) (see **Appendix A10**). None of these compounds was detected in the four wells.

Table 19 shows the veterinary pharmaceuticals detected in the WWTP influent~~s~~s and the four wells targeted for evaluating septage. WW-22 contained no detected veterinary pharmaceuticals.

Table 19: Veterinary Pharmaceutical Detected in WWTP Samples

Compound	WW-19	WW-20	WW-21	SP-01	SP-02	SP-03
Erythromycin	ND	ND	0.11	ND	ND	ND
Lincoymycin	ND	ND	0.371	ND	ND	ND
Monesin	0.194	ND	0.194	ND	ND	ND
Ractopamine	ND	ND	0.079	ND	ND	ND
Sulfachloropyridazine	ND	ND	0.334	ND	ND	ND
Sulfamethazine	ND	ND	0.053	ND	ND	0.086
Sulfamethoxazole	ND	ND	0.04	ND	0.106 (J)	0.662
Sulfathiazole	ND	ND	0.051	ND	ND	ND
Tetracycline	ND	242.6	ND	0.55 (J)	ND	ND
Tiamulin	ND	ND	0.05	ND	ND	ND
Virginiamycin	ND	ND	0.162	ND	ND	ND

Units = µg/L. Detection limit = 0.02 µg/L.

J values mean the compound was positively identified, but the associated numerical value is an estimate.
ND = Not detected.

Three compounds were detected in the water wells and at least one WWTP influent (sulfamethazine, sulfamethoxazole, and tetracycline). Eight compounds were detected in the water wells, but not in the WWTPs. WW-21 had the highest number of compounds detected (10) of any water well. Water well WW-21 is surrounded by possible septic sources; it is also downgradient from several hop yards and although at a greater distance, also downgradient from several large dairies. These factors make it challenging to identify the potential source of the veterinary pharmaceuticals at WW-21.

Many of the compounds detected in the WW-21 were not found in the WWTPs. Many of these compounds are used by humans (for example, tetracycline, lincomycin, and the sulfonamides), and it is possible that they are excreted and possibly end up in septic systems. In this case, it would be anticipated that they would be detected in WWTPs. One possible explanation is that the WWTP matrix is much more complex, with an increased possibility of interferences than the cleaner water wells. When large numbers of organic molecules are present, it makes it difficult to detect these compounds in the WWTP influent.

Septic Systems: Hormones

EPA's Ada laboratory analyzed all four water wells and the WWTP influentss for five hormones.. The laboratory did not detect any of the five hormones in the water wells, but did detect three of the hormones in WWTP sampless: 17-β-estradiol, estriol, and estrone **(see Appendix A12).**

The UNL analyzed samples for the four water wells and the WWTPs for 18 hormones, including the same five hormones as Ada **(see Appendix A13).**   No hormones were detected in WW-19 and WW-21. Androsterone was detected in WW-20. Eight compounds were detected in WW-22. **Table 20** shows the concentrations of the compounds detected in these wells and their corresponding concentrations in the WWTPs.

Table 20: Results for Hormones from UNL

Compound [(*)]	WW-20	WW-22	SP-01	SP-02	SP-03
17-β-estradiol	ND	**0.006**	**0.012**	**0.035**	**0.034**
α-estradiol	ND	**0.005**	**0.263**	ND	ND
Androsterone	**0.004(J)**	ND	**5.049(J)**	**2.137(J)**	**3.187(J)**
Androstenedienendione	ND	**0.005**	**0.255(J)**	**0.614(J)**	**14.1 (J)**
β-Zearalanol	ND	**0.003**	ND	ND	ND
Estrone	ND	**0.004**	ND	ND	ND
Testosterone	ND	**0.01**	**0.053**	**0.059**	**0.045**
Keto Testosterone	ND	**0.005**	**0.1**	**0.043**	ND
Epitestosterone	ND	**0.004**	ND	**0.06**	ND

*Both Ada and UNL analyzed for 17-β-estradiol, α-estradiol, and estrone. UNL detected 17-β-estradiol, α-estradiol, and estrone in WW-22. Only Ada detected these two compounds for the WWTP (SP01-SP03). UNL analyzed for the other compounds.

Units = µg/L. Detection limit = 0.02 µg/L. J values mean the compound was positively identified, but the associated numerical value is an estimate. ND = Not detected.

WW-20 is not located in close proximity to a dairy, so the potential source of androsterone in these samples could be a septic system or another source.

WW-22 had detections of multiple compounds. Several of the compounds detected in WW-22 were also detected in the WWTPs (17-β-estradiol, α-estradiol, testosterone, keto-testosterone, and epitestosterone). These compounds would be expected to be detected in WWTP given they are natural sex hormones or are produced in mammals. WW-22 is not in close proximity to a dairy, which would reduce the chance that the source of these compounds is a dairy, although the agricultural land use upgradient of the well could be using dairy manure as fertilizer. It is possible that the compounds detected in WW-22 are coming from septic systems that are in the vicinity of this well.

21.4. Septic Systems: Isotopic Analysis

Isotopic analysis was completed for all water well samples. **Table 20** provides the results for these four wells.

Location	Nitrate -N (mg/L)	$\delta^{15}N$-NO3 (‰)	Dominant Source	$\delta^{18}O$-NO3 (‰)	Overall Assessment
WW-19	36.4	8.7	Fertilizer & Animal Waste	15.4	Fertilizer & Animal Waste
WW-20	15	6.3	Fertilizer &Animal Waste	52.9	Fertilizer &Animal Waste &Atmospheric
WW-21	36.5	7.7	Fertilizer & Animal Waste	12.2	Fertilizer & Animal Waste
WW-22	16.6	10	Animal Waste	11.0	Animal Waste

δ^{15}N-NO3. Values less than 2.0 = dominated by fertilizer; values between 2.0 to 8.4= undetermined mixture of fertilizer and/or animal waste; values greater than 8.4 = dominated by animal.
δ^{18}O-NO3.Values greater than 20 considered strong atmospheric contribution.

The dominant source of nitrate in WW-22 appears to be animal waste. For the other water wells, the potential sources are likely to be a combination of fertilizer and/or animal waste for WW-19 and WW-21 and a combination of fertilizer and/or animal waste with a strong atmospheric contribution for WW-20. The probabley sources of nitrate for these water wells match the variety of land uses surrounding these highly scattered water wells.

22.5. Septic Systems: Age Dating

Table 21 provides the age dating results for all four water wells.

Table 21: Septic Systems – Summary of Age Dating Analyses for WW-19 to WW-22 (Years)

Location	Sample Age	Duplicate Age	Average
WW-19	44.3	34.3	39.3
WW-20	14.3	14.3	14.3
WW-21	31.3	28.8	30.1
WW-22	29.3	29.3	29.3

There is a wide scatter of ages in the water wells with age measurements ranging from 14.3 years to 44.3 years with no discernible spatial pattern.

23.6. Septic Systems – Summary of Results for Residential Water Wells

Table 22 provides a summary of the groups of compounds (general chemistry and organic compounds) and analytical techniques (isotopic analyses) that provide information useful to address the question of the likely sources of the nitrate for the four residential water wells associated with the septic systems. No conclusions using the microbial data is possible given the downgradient wells did not exhibit any microbial contamination. In addition, the age dating data do not provide any specific evidence to connect specific sources to high nitrate levels.

Table 22: Septic Systems – Summary of Results for Residential Water Wells

General Water Chemistry	Organic Compounds Detected	Organic Compounds Detected in WWTPs	Isotopic Analyses
WW-19			
Nitrate level = 38.2 mg/L	Monesin	Monesin not detected in WWTPs	Fertilizer & Animal Waste
WW-20			

Nitrate level = 15 mg/L	Atrazine and bentazon	Atrazine and Bentazon not analyzed	Animal waste & Fertilizer & Atmospheric
	Tetracycline	Tetracycline (SP-01)	
	Androsteronene	Androsterone (All WWTPs)	
WW-21			
Nitrate level = 38 mg/L	Erythromycin, lincomycin, monesin, ractopamine, sulfamethazine, sulfamethoxazole, sulfathiazole, tiamulin, and virginiamcyin	Sulfamethazine (SP-03) Sulfamethoxazole (SP-02 and SP-03) Others not detected in WWTP influents	Fertilizer & Animal Waste
WW-22			
Nitrate level = 16.4 mg/L	11-Keto testosterone	11-keto Testosterone (SP-01; SP-02)	
	17-β-estradiol α-estradiol, Androstendienendione	17-β-estradiol (All WWTPs) α-estradiol (SP-01) Androstendienendione (All WWTPs)	Animal waste
	β-zearalanol Estrone Testosterone Epitesterone	β-zearalanol (No detects) Estrone (No detects) Testosterone (All WWTPs) Epitestosterone (SP-02)	

The main information anticipated to provide a connection with septic systems was from the organic compounds, microbiological data, and possibly the isotopic data. The major ions, minor and trace inorganic elements, and forms of nitrogen analyses are not useful because of the highly variable results from these spatially distributed wells of unknown construction. As discussed above, the trace inorganic elements are ubiquitous in the environment and highly variable in concentration.

In addition, these wells were sampled in isolation – that is, without a pairing with an upgradient well with a specific source separating them. For this reason, no chemical or temporal evolution along a flow path can be demonstrated from these data. Age dating results are similarly highly variable, likely for the same reasons of spatial distribution and unknown well construction.

The pesticides atrazine and bentazon were detected in WW-20. Trace organics were the class of compounds anticipated to provide data to possible link to septic systems. There were no detections of any trace organics for the water wells targeted for the septic systems. Five trace organic compounds were found for all the water wells in the study: bis-(2-ethylhexyl) phthalate

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(DEHP); 5-methyl-1h-benzotrizole; napthelene; tetrachloroethylene, and phenol.   DEHP was the only trace organic detected in the three WWTPs. DEHP was the only trace organic detected in any of the residential water wells. The other trace organics were detected in dairy supply wells.

For pharmaceuticals, WW-21 had the highest number of compounds (10) detected of any wells. WW-21 is surrounded by possible septic sources; it is also downgradient from several hop yards and also at a greater distance downgradient from a dairy. The isotopic data indicate that the source of nitrate is a probably a combination of fertilizer and animal waste.

WW-22 had detections for eight compounds for hormones. WW-22 is not in close proximity to a dairy, which would reduce the chance that the source is a dairy, although the agricultural land upgradient of the well could be using dairy manure as fertilizer. It is also possible that the detections for WW-22 are from a septic system, although the detection of androstenedienendione and β-Zearalanol was not expected given they are not approved for human or dairy cow use. However, androstenedienendione was detected in the WWTP, indicating there is a source within the area for this compound.

In conclusion, all of the residential wells had high levels of nitrate. Other evidence to link septic systems are the pharmaceutical, hormone, and isotopic data. Compounds were detected in several wells that are associated with humans.

D.H.   Irrigated Cropland

Another likely source of nitrates is irrigated croplands. The likely inputs examined in this study are inorganic fertilizer and manure applied to the land from dairies. This study looked at three crops: mint, hops, and corn. Soil samples were collected from six fields that were located upgradient from six residential drinking water wells. Corn and hop fields typically receive both manure and synthetic fertilizer inputs at different times during the year. Mint fields typically receive only synthetic fertilizer. Each soil sample and associated water well sample is shown in **Figure 7 and Table 23**.

Table 23: Irrigated Cropland – Soil Samples and Associated Water Wells

Soil Sample	Associated Water Well	Crop
SO-11	WW-23	Mint
SO-12	WW-24	Mint
SO-13	WW-25	Corn
SO-14	WW-28	Corn
SO-15	WW-26	Hops
SO-16	WW-27	Hops

The soil samples were analyzed for: nitrogen species,; pesticides,; pharmaceuticals,; and hormones. They were not analyzed for general chemistry,; microbiology,; trace organics,; isotopic analysis,; or age dating. It was concluded that Tthe compound classes evaluated would provide the best information to link irrigated cropland with high nitrate levels in nearby water wells. Some of the analyses are not usually performed on soil samples (perchlorate, major ions, isotopic analysis, and age dating), while others were not completed because of resource constraints (trace organics).

1. **Irrigated Cropland: General Chemistry**

Irrigated Cropland: Nitrate and Other Forms of Nitrogen

The water wells associated with the irrigated cropland had high levels of nitrate and were all above the nitrate MCL of 10 mg/L. Soil samples were analyzed for several forms of nitrogen, including extractable nitrate: extractable ammonium, and total nitrogen by combustion. The values measured in the soil samples for extractable nitrate (nitrate-N) and extractable ammonium (ammonia-N) can be compared with limits recommended by the Washington Department of Agriculture for fields under National Pollutant Discharge Elimination System permits. The recommendations are that the concentration of nitrate-N in the post-harvest soil should be no more than 45 milligrams per kilogram (mg/kg) or parts per million. **Table 24** shows the measured values for these forms of nitrogen in these crop soils.

Table 24: Irrigated Cropland – Concentrations of Nitrogen Forms in Soil Samples

Soil Sample/Crop	Nitrate-N (ppm)	Ammonium-N (ppm)	Total N by Combustion (ppm)
SO-11 – Mint	245	210	3330
SO-12 – Mint	191	8.2	2350
SO-13 – Corn	24.3	7.5	1100
SO-14 – Corn	6.3	12	1180
SO-15 – Hops	83.5	21	2210
SO-16 – Hops	26.5	7.7	3000

The cropland soil samples were collected at the beginning of the growing season. As such, they are not directly comparable to post-harvest soil monitoring guidelines. However, values of nitrate-N measured in the soils during the study were five times the guidelines. These levels, if not reduced by either uptake by growing plants, volatilization, or denitrification, would ultimately move out of the root zone where they could become a source of groundwater contamination.

24.2. Irrigated Cropland: Organic Compounds

Irrigated Cropland: Pesticides

Fifteen pesticides were detected in one or more of the six soil samples targeted for crops **(see Appendix A8).** Several pesticides were detected in more than two soil samples (2,4-D was detected in four soil samples; 4-nitrophenol in six soil samples; and pentachlorophenol in five soil samples).

Of the 15 pesticides detected in the six soil samples, only two were detected in the six water wells targeted for impact from crops**:** bentazon (WW-23 and W-24) and atrazine (WW-24 and WW-26). **Table 25** indicates that bentazon was detected in soil samples related to water wells at two of the three associated sites: SO-11/WW-23 and SO-12/WW-24. Atrazine was not detected in any of the soil samples associated with the water wells that had detections of atrazine.

Table 25: Irrigated Cropland – Concentrations of Pesticides in Soil Samples and Associated Water Wells (soil sample values are reported first and then water well associated with the soil samples are reported in each cell)

Compound	Mint SO-11 WW-23	Mint SO-12 WW-24	Corn SO-13 WW-25	Corn SO-14 WW-28	Hops SO-15 WW-26	Hops SO-16 WW-27
Atrazine	ND ND	ND **0.017 (J)**	**1.6(J)** ND	**0.7(J)** ND	ND **0.025(J)**	ND ND
Bentazon	**38** **0.028 (J)**	**2 (J)** **0.033(J)**	ND ND	ND ND	ND ND	ND ND

Units for water wells = µg/L. Units for soil samples = Micrograms per kilogram (µg/kg).
ND = Not detected. Detection limit for soil and water well samples vary depending on the analysis.
"J" values mean the compound was positively identified, but the associated numerical value is an estimate.

Given the widespread use of both atrazine and bentazon, it is likely that the detections in the water wells are ~~coming~~ the result of past and current use of these pesticides.

Irrigated Cropland: Pharmaceuticals

Veterinary pharmaceuticals were detected in one well (WW-26). Nine compounds were detected. No veterinary pharmaceuticals were detected in the other wells. Monesin was the only compound detected in both a water well (WW-26 at 0.319 µg/L) and its associated soil sample (SO-15 at 4.5 micrograms per kilogram [µg/kg]). Veterinary pharmaceuticals were detected in five of the soil samples, but these compounds were not detected in the associated water well samples (SO-13 had no detections).

In addition to monesin, erythromycin, lincomycin, ractopamine, sulfamethazine, sulfamethoxazole, sulfathiazole, tiamulin, and virginiamycin were detected in WW-26. None of these compounds was detected in the soil samples.

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WW-26 is surrounded by hop yards that receive manure applications. There is also a dairy generally upgradient from the well, although it is at some distance. It is possible that the compounds detected in WW-26 came from the application of manure. This would be especially true for monesin. However, it is also possible that at least some compounds came from septic fields, given that several of the compounds are used by humans.

Irrigated Cropland: Hormones

Water well WW-27 was the only water well with any compounds detected. There were three compounds detected in WW-27 (androstandienedione, 17-β-trenbolone, and testosterone). These compounds were not detected in the soil sample (SO-16) associated with WW-27.

Five hormones were detected in soil samples (**see Appendix A13**).

- SO-11: Androstandienedione and progesterone
- SO-12: Androstandienedione, 17-α-estradiol, and progesterone
- SO-13: Melengesterol acetate
- SO-15: 4-androstenedione and androstandienedione
- SO-16: 4-androstenedione and progesterone

All of the hormones in the soil samples (except for melegensterol acetate) are naturally produced by animals and can be expected to be found in septic systems, manure piles, and dairy lagoons.

25.3. Irrigated Cropland: Isotopic Analyses

An isotopic analysis was completed for six wells associated with the irrigated croplands. One mint field (WW-24) and one corn field (WW-25) showed nitrate originating predominantly from a fertilizer source. Fertilizer and atmospheric deposition were the dominant sources for WW-23. Water well WW-26 had a mixed animal waste and fertilizer source, while water wells WW-27and WW-28 had a dominant source of fertilizer, animal waste, and atmospheric (**Table 26**).

Table 26: Irrigated Cropland – Summary of Isotopic Analysis for Water Wells

Location	Nitrate-N (mg/L)	$\delta^{15}N$-NO3 (‰)	Dominant Source	$\delta^{18}O$-NO3 (‰)	Overall Assessment
WW-23 (Mint)	17.3	2.2	Fertilizer & Animal Waste	18.0	Fertilizer & Animal Waste
WW-24 (Mint)	14	-0.3	Fertilizer	12	Fertilizer
WW-25 (Corn)	32.9	2.4	Fertilizer & Animal Waste	15	Fertilizer & Animal Waste
WW-26 (Hops)	15.1	7.5	Fertilizer & Animal Waste	6.3	Fertilizer & Animal Waste

| WW-27 (Hops) | 19.9 | 8.8 | Animal Waste | 17 | Animal Waste |
| WW-28 (Corn) | 69.6 | 5.5 | Fertilizer & Animal Waste | 44 | Fertilizer & Atmospheric & Animal Waste |

δ^{15}N-NO3. Values less than 2.0 = dominated by fertilizer; values between 2.0 to 8.4= undetermined mixture of fertilizer and/or animal waste; values greater than 8.4 = dominated by animal.
δ^{18}O-NO3.Values greater than 20 considered strong atmospheric contribution.

The dominant source for WW-24 is fertilizer while the dominant source for WW-27 is animal waste. For the other water wells, the potential sources are likely to be a combination of fertilizer and/or animal waste for WW-23, WW-25, and WW-26 and a combination of fertilizer and/or animal waste with a strong atmospheric contribution for WW-28.

26.4. Irrigated Cropland: Age Dating

The age dating date for the six wells associated with the irrigated crops is presented in **Table 27**.

Table 27: Irrigated Cropland – Summary of Age Dating Analyses for Water Wells (Years)

Location	Sample Age	Duplicate Age	Average
WW-23: Mint Field	Over Value	Over Value	NA
WW-24: Mint Field	14.8	15.8	15.3
WW-25: Corn Field	10.3	9.8	10.1
WW-26- Hops Field	12.8	11.8	12.3
WW-27: Hops Field	Over Value	14.3	14.3
WW-28: Corn Field	Over Value	Overvalue	NA

Over Value: These samples contained more SF_6 than can be explained by equilibrium with modern air.

Comment [LE34]: This is the explanation I was looking for earlier, even though I'm not sure what it means

While downgradient wells were paired with soil samples from the crop fields, they were not paired with wells upgradient of crop fields. For this reason, no pattern emerges from review of the age dating data beyond the observation that the values are younger than for any other group of samples in the study. This finding could be due to the very young age of the because irrigation water was used on the crop fields and the very young age of that water.

27.5. Irrigated Cropland – Summary of Results for Residential Wells

Table 28 provides a summary of the groups of compounds (general chemistry and organic compounds) and analytical techniques (isotopic analyses) that provide information useful to address the question of the likely sources of the nitrate for the four residential water wells associated with the septic systems. No conclusions using the microbial data is possible given the downgradient wells did not exhibit any microbial contamination. In addition, the age dating data do not provide any specific evidence to connect specific sources to high nitrate levels.

Table 28: Irrigated Cropland – Summary of Results for Residential Water Wells

General Chemistry	Organic Compounds in Water Wells	Organic Compounds Also in Associated Soil Samples	Isotopic Analyses
WW-23 and SO-11 (mint)			
Nitrate level = 16.0 mg/L	Bentazon	Bentazon	Fertilizer & Animal Waste
WW-24 and SO-12 (Mint)			
Nitrate level = 13.8 mg/L	Atrazine Bentazon	Bentazon	Fertilizer
WW-25 and SO-13 (Corn)			
Nitrate level = 33.4 mg/L	No detects	Nothing to compare	Fertilizer & Animal Waste
WW-26 and SO-15 (Hops)			
Nitrate level = 15.3	Atrazine, erythromycin, lincomycin, monesin, ractopamine, sulfamethazine, sulfathiazole, itamulin, and virginiamycin	Monesin only compound also detected in soil sample	Fertilizer & Animal Waste
WW-27 and SO-16 (Hops)			
Nitrate level = 19.8 mg/L	Androstandienedione 17- β-Trenbolone Testosterone	These compounds were not detected in soil samples	Animal Waste
WW-28 and SO-14 (Corn)			
Nitrate level = 71.2 mg/L	No detects	Nothing to compare	Fertilizer & Atmospheric & Animal Waste

Bentazon and atrazine were the only pesticides detected in the water wells associated with the six soil samples. Bentazon was detected in the soil samples associated with the water wells at two sites: SO-11/WW-23 and SO-12/WW-24. This is significant and indicates that the bentazon applied to the crop fields is being associated with concentrations in nearby wells. Atrazine was not detected in any of the soil samples associated with the water wells with detections of atrazine.

WW-26 was the only well with detected concentrations for the pharmaceuticals (eight compounds detected). None of these compounds was detected in the associated soil sample (SO15). WW-26 is surrounded by hop yards that receive manure applications. There is also a dairy generally upgradient from the well, although it is at some distance. It is possible that the compounds detected in WW-26 came from the application of manure. However, it is also possible that they came from septic fields, given these compounds are used by humans.

Three hormones were detected in one well (WW-27). The three hormones were not detected in the associated soil sample (SO-16).

In conclusion, several compounds were detected in the water wells (WW-23, WW-24, WW-26, and WW-27). However, with the exception of bentazon, none of these compounds was detected in the associated soil samples.

E.I.   Water Wells WW-18 and WW-30

Two other residential water wells were evaluated: WW-18 and WW-30. WW-18 was sampled because the owner was aware of the study and volunteered his property for sampling. WW-30 was sampled because it was located in an area not otherwise sampled and was high in nitrate.

WW-18 was analyzed for all the compounds and for isotopic and age dating. WW-30 was not evaluated for hormones, pharmaceuticals, isotopic, or age dating as the site was added later in the study.   The results for the two wells are included in Table 29.

Table 29: Results for WW-18 and WW-30

Compounds	WW-18	WW-30
Nitrate	72.2 ug/L	23.4 ug/L
Microbiology	No detects	No detects
Organic Compounds	Atrazine, tetracycline, and testosterone	Atrazine, bentazon, and phenol
Isotopic Analysis	Fertilizer & Animal Waste	Not conducted
Age Dating	28.1 years	Not conducted

While the major ions and different nitrogen forms were measured for both of these samples, the results are not included because they are used to observe the evolution of water along a flow path. There were no upgradient wells that can be used to compare and no specific source with which to compare for WW-18 and WW-30. Therefore, no specific analysis was conducted for the major ions and total nitrogen.

Neither fecal coliform nor *E. Coli* were detected in the WW-18 or WW-30. Atrazine, tetracycline, and testosterone were detected in WW-18. Atrazine, bentazon, and phenol were detected in WW-30. Phenol was abundant in the dairy lagoons sampled and can also be found in household wastewater. The source of the phenol in the water well could be septic systems. WW-30 is not located in the vicinity of a dairy. WW-30 was not analyzed for wastewater pharmaceuticals based on its late addition at the end of the study.

X. STUDY LIMITATIONS AND UNCERTAINTIES

There were several constraints in the study that are important to highlight. Primary sources of uncertainty stem from inadequate or absent information on well construction, the lack of standard analytical methods for all parameters, and the absence of specific knowledge of dairy operations. Combined with the complex matrices of some of the samples, these factors limit the certainty with which connections can be made between specific sources and downgradient sampling locations. .

First and perhaps most importantly, the well depths, screened intervals, and construction details of the wells sampled were generally unknown. An attempt was made to locate the wells logs, but it was not possible to match the well log information with the specific sampling sites in the study for the majority of the wells. For this reason, it is generally unknown whether the water chemistry in water wells represents shallow groundwater, deeper groundwater, or more than one zone being mixed.

Several of the wells sampled showed both low dissolved oxygen and high nitrate. This result is an indication of mixing of waters of different chemistries since nitrate is rapidly depleted in waters after oxygen is consumed by bacterial activity. More specific information on each well would enable confirmation of the hydraulic connection with the upgradient well, sources, and downgradient wells using the water chemistry for each well because the wells are potentially tapping different flow paths or simply mixing waters of unrelated chemistries.

Second, many of the analytical methods utilized in the study were EPA standard methods (nitrate and other nitrogen forms; trace elements; major ions, and pesticides). However, some of the analytical methods used are not EPA or equivalent standard methods, but are used primarily for research purposes (pharmaceutical and hormones). The research methods use complex instrumentation technologies and are capable of detecting trace levels of the target compounds.

As can be expected, however, variability with quality control results was observed because of matrix effects. Modifications to the procedures were implemented by the laboratories as needed to improve chromatography and detection. In addition, the combination of very low detection limits and complex matrices may yield false positives or the inability to see low concentrations despite the appropriate use of blanks, matrix spikes, surrogates and duplicates. For these reasons, despite the best efforts of the laboratories selected to conduct this work, the data generated may not be reproducible by a third party, one of the criteria required by EPA's Information Quality Guidelines.

Finally, there was limited information regarding the dairy operations. EPA had requested information on specific aspects of the dairy operations to develop a better understanding of their day-to-day operations, but that request was denied. The lack of specific information on dairy operations creates some uncertainty regarding the relationship between specific compounds detected in water wells and the dairies (for example, whether the dairy used specific pharmaceuticals for treatment of animals).

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Comment [LE35]: I think it would help to introduce them by type before plunging into the more detailed explanations. I'll give it a shot, but you can probably do better. I got them a little out of order from the descriptions that follow, though—because the first 3 were lack of info, they went together.

Comment [LE36]: Or something like that. There is probably a better way to phrase this last sentence.

Comment [LE37]: This doesn't sound like a limitation or uncertainty the way it is worded. Is it that it might not be easily replicated or what?

Comment [LE38]: Is this statement intended to apply to all the samples or some specific analyses or sample types?

Comment [LE39]: Could this one be moved up to join the other "lack of info" list?

XI. CONCLUSIONS

This report presents the results for sampling conducted from February 2010 to April 2010 by the U.S. Environmental Protection Agency (EPA) in the Lower Yakima Valley in Central Washington State. The primary purpose of this study was to investigate the contribution of various sources from nearby land uses to the high nitrate levels in drinking water wells. The study looked at three likely sources of nitrate: dairies; irrigated cropland; and residential septic systems and private residential drinking water wells for a variety of chemicals to determine if chemicals other than nitrate can be used to link the nitrate contamination in groundwater to specific sources. The analyses included chemicals that are expected to be associated with one or more of the likely sources, such as pharmaceuticals (both veterinary and human medications), personal care products, steroids and hormones, pesticides and herbicides, as well as other indicators of water quality.

The investigation also used microbial analysis to determine whether the drinking water wells were contaminated with fecal contamination. If the water wells were found to have fecal contamination, then Microbial Source Tracking (MST) was performed to identify the source (i.e., human or ruminant) of the fecal contamination. In addition, EPA performed isotopic analysis for the water wells to determine the general source, or combination of sources, of nitrates in the water wells. Finally, an age dating analysis was completed for the water wells to determine the time since infiltration of water into the water wells.

In general, the microbial and age dating data did not provide information that could be used to help identify specific sources that can contribute to the high nitrate levels detected in residential drinking water wells.

The ~~best~~ strongest evidence ~~to link~~linking specific sources to the high nitrate values was the total nitrogen and major ion data associated with the dairies. This data showed that the dairies were likely contributing to the increased trend in total nitrogen and major ion concentrations between the upgradient wells ~~to~~ and the downgradient wells. The specific contribution from the dairies is difficult to determine because of the lack of information on water wells.

> **Comment [LE40]:** Do you mean "quantify"?

Many of the organic compounds (e.g., pharmaceuticals and hormones) analyzed were detected in the dairy lagoons, manure piles, and application fields as well as the WWTP influents used as septic surrogates~~s~~. In general, the majority of these compounds were not detected in the residential water wells with several notable exceptions (WW-21 with 10 compounds detected and WW-22 with nine compounds detected).

The presence of ~~these compounds~~pharmaceuticals and hormones in ~~these sources~~at dairies and in WWTP influent indicates they are used at the dairies or by humans ~~(WWTPs)~~ but were not transported or were not transported at detectable levels to the downgradient wells during the study period. This could be the case because organic compounds are typically less mobile in water than inorganic compounds. Organic compounds tend to adsorb to organic carbon in the aquifer material and may be degraded by bacteria and either disappear entirely or may be greatly reduced

in concentrations. Even if not broken down, most organic compounds will move much slower than nitrate because they tend to adsorb to other organic matter in the aquifer. As a result, in general, they are unlikely to be transported as far or as fast as the nitrate.

The isotopic data provide evidence that the dominant source of nitrate is animal waste for four residential wells (WW-05, WW-13, WW-14, and WW-22) and the dominant source of nitrate is synthetic fertilizer for one residential water wells (WW-24). ~~The specific~~A single source of nitrate for the remainder of the residential water wells was not determined, but attributed to a combination of synthetic fertilizer and/or animal waste. Four residential water wells were determined to have a strong atmospheric contribution (WW-03, WW-15, WW-20, and WW-28).

Comment [LE41]: If that's what you mean

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XII. REFERENCES

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APPENDIX A: DATA SUMMARY TABLES (included in a separate excel spreadsheet)

APPENDIX B: DETAILS ON THE ISOTOPIC ANALYTICAL RESULTS OF THE STUDY

Samples from all the water well, dairy lagoon, and WWTP influent were submitted to the University of Nebraska, Lincoln Laboratory for isotopic analysis. The results of the isotopic analyses are presented in **Appendix A14.** The isotopic analysis is used to assist to identify the general source, or combination of sources, or dominant processes that have contributed nitrates to the drinking water wells evaluated in this study. Most of the literature on isotopic fractionation, particularly the part attributing specific samples to specific sources, makes clear that the science is still evolving and that this tool is most appropriately used to supplement other methods used to investigate the source of nitrates (Kendall and others 2007).

The sources evaluated for the isotopic analysis include nitrate formed locally in soil derived from breakdown of plant material; synthetic fertilizers; animal waste, including humans; and accumulation from atmospheric deposition from precipitation and dry deposition. It is important to note that the animal waste source does not differentiate between humans and other animal wastes.

The location of the Lower Yakima Valley at the base of the Cascade Mountain Range and in the rain shadow of those mountains has implications that lead to predictable variations is unique. This location leads the U.S. Environmental Protection Agency (EPA) to expect deviation from some of the patterns seen in other collections of data areas. For example, because of the very low rainfall in this area, it is anticipated that atmospherically deposited nitrate would accumulate in shallow soils in the caliche layer. This A caliche layer is characteristic of desert regions and forms when carbonate minerals accumulate in the shallow subsurface because insufficient rainfall occurs to wash them into the deeper groundwater. Other minerals may accumulate along with the carbonates in areas of very low rainfall. These include gypsum and, if the area is sufficiently dry, nitrates and perchlorates, a highly oxidized form of chlorine.

EPA tested for perchlorates in addition to nitrate to explore the possibility of natural buildup of nitrate in valley soils from atmospheric deposition. The reason for testing for perchlorate was to identify areas where recent addition of irrigation water could be acting to flush a reservoir of soluble compounds such as nitrate and perchlorate out of these desert soils.

EPA followed a two-step process to link a dominant process or a specific potential nitrogen source to each water well, dairy lagoon, and wastewater treatment plants (WWTPs) sampling location. First, the concentrations of nitrate in each sample were compared with values typical of systems where nitrate is locally derived from natural plant breakdown in soil. The purpose was to determine whether locally derived soil nitrate was a likely source of the nitrate.

Naturally occurring nitrate concentrations are generally expected to range from 0.3 to possibly 1.1 milligrams per liter (mg/L) (Nolan and Hitt 2003). Nitrate concentrations observed in all downgradient wells (as opposed to "supply" or upgradient well") were in excess of the value that could be expected from natural soil nitrate formation **(See Table A4 in Appendix A)**. The high

concentrations of nitrate in all of the downgradient well samples indicate that locally derived soil nitrate ~~form~~ from the breakdown of local growing plants is not a likely process to explain the data in this study.

The second step was to look for plausible sources and evaluate each sample based on those potential sources. For animal waste, data from the dairy lagoons were used to evaluate the potential ~~values~~ results that would indicate the dominant source is from animal waste **(Table B-1).**

Three dairy lagoon samples were collected from each dairy. One sample was collected at the freshest inlet end of the dairy lagoon system. For example, LG-01 was sampled at the "freshest" or influent end of the dairy lagoon system. LG-02 and LG-03 were collected at the discharge end of the system just before it was pumped onto the spray-irrigation fields. Samples LG-01, LG-04, LG-07, LG-10 and LG-13 were intended to show the youngest and least volatilized waste.

The expected trend would be for waste to increase in δ^{15}N-NH4 as the light ammonia is preferentially volatilized and the residual in the dairy lagoon system is enriched in the heavier form. This trend is ~~seen~~ evident in the data with the first of each group of three dairy lagoon samples being a smaller number (lighter) and the last two being heavier. Lagoon samples LG-10 to LG-12 differ from the other ~~later~~ dairy lagoons because they seem to lack any sign of volatilization or maturation during passage through the system. This pattern may be related to the location where EPA sampling teams collected the sample or the rate at which waste passes through this system.

The last two samples were collocated in each of the dairy lagoons, with the exception of LG-15, which is from a different dairy lagoon at the most distant portion of the system. The co-located samples (LG-02 and LG-03; LG-05 and LG-06; LG-08 and LG-09; and LG-11 and LG-12) all show similar isotopic values. Dairy lagoon sample LG-15 shows a much "heavier" signature for ^{15}N for the remaining ammonia, as is expected from its location at the distal end of the dairy lagoon system on the Bosma Dairy.

The average δ^{15}N-NH4 of the five influent streams to the dairy lagoons in this study (LG-01, LG-04, LG-07, LG-10, and LG-13) was 5.0‰. The average of the δ^{15}N-NH4 in the 10 dairy lagoon ~~values~~ samples in the older material immediately prior to ~~before~~ land application (LG-02, LG-03, LG-05, LG-06, LG-08, LG-09, LG-11, LG-12, LG-14, and LG-15) was 8.4‰.

Table B-1: Isotopic Analysis - Summary Results for Lagoons

Location	Position in System	Ammonia (mg/L)	δ^{15}N-NH4 (‰)	Assessment
LG-01: Haak	Influent	907	3.4	Fresh Animal Waste
LG-02:Haak	Discharge	923	10.1	Volatilized animal waste
LG-03: Haak	Discharge	896	9.9	Volatilized animal waste
LG-04: DeRuyter	Influent	899	6.7	Volatilization Animal Waste
LG-05:DeRuyter	Discharge	1151	10.6	Volatilization Animal Waste
LG-06: DeRuyter	Discharge	1293	10.3	Volatilization Animal Waste
LG-07:D&A	Influent	869	5.4	Fresh Animal Waste
LG-08: D&A	Discharge	696	10.3	Volatilization Animal Waste
LG-09: D&A	Discharge	658	10.1	Volatilization Animal Waste
LG-10: Cow Palace	Influent	NM	NM	NM
LG-11:Cow Palace	Discharge	274	3.1	Fresh Animal Waste
LG-12: Cow Palace	Discharge	222	2.0	Fresh Animal Waste
LG-13:Bosma	Influent	469	4.4	Fresh Animal Waste
LG-14:Bosma	Discharge	600	3.3	Fresh Animal Waste
LG-15:Bosma	Discharge	658	13.9	Volatilization Animal Waste

Based on this data, EPA decided that a δ^{15}N-NO3 value of 8.4‰ in water wells was a reasonable value to indicate that the source of nitrate was dominated by animal waste. This does not mean that all animal waste has δ^{15}N-NO3 values above 8.4‰. EPA believes it does indicate that values above this are in the range in which nitrate isotopes can be used to identify animal waste derived from nitrate with reasonable confidence. The value of 8.4‰ for δ^{15}N-NO3 is relatively consistent with information from the literature indicating a general range of δ^{15}N-NO3 values between 10‰ and 20‰ for animal waste (Kreitler 1975; Komor and Anderson 1993; and Kendall and Aravena 1999), but with some values ranging lower (Becker and others 2001 and Kendall, C. 1998).

In addition to animal waste, another potential source that the isotopic analysis can help determine is synthetic fertilizers. ~~Unfortunately the~~The study did not evaluate the isotopic values for fertilizer, however. ~~Given~~Because the lowest δ^{15}N-NH4 value from the dairy lagoons was 2.0‰, it was decided to establish a value for δ^{15}N-NO3 of 2.0‰ or less as the value in which isotopes could be used to identify synthetic fertilizer as the dominant source. The δ^{15}N-NO3 value of 2.0‰ is generally supported from literature that suggests a range δ^{15}N-NO3 values of -4.0 to +4.0‰ for synthetic fertilizers (Komor and Anderson 1993; Kendall, C.1998; and Kendall and Aravena 1999).

For δ^{15}N-NO3 values between 2.0‰ and 8.4‰, the source was identified as indeterminate, but with fertilizer and/or animal waste as potential sources of nitrate. This approach was taken because based on the data from this study, and the literature, it was not possible to determine the specific contribution from either fertilizer and/or animal waste for δ^{15}N-NO3 values between 2.0‰ and 8.4‰.

The data for δ^{18}O-NO3 was used to evaluate the degree to which an atmospheric signature was dominant in the sample. Values above δ^{18}O-NO3 of 20.0‰ were considered "strong" contributors for the atmospherically derived nitrate component. δ^{18}O-NO3 values below 20.0‰ could have an atmospheric contribution, but it was believed the contribution would be less.

Isotopic results were obtained from ammonium analyzed from the inlet to three sewer treatment plants in the Lower Yakima Valley. The plants were located in Zillah, Toppenish and Mabton and correspond to WWTP-01 through WWTP-03. The results for the analysis of δ^{15}N-NH4 from the ammonium in the influent are presented below.

Table B-2: Isotopic Analysis for WWTPs

Location	δ^{15}N-NH4 (‰)	Assessment
WWTP-01: Zillah	3.72	Very Slightly Enriched
WWTP-02: Mabton	7.43	Some NH4 Volatilization has occurred
WWTP-03: Toppenish	2.70	Very Slightly Enriched

δ^{15}N-NH4 values are expected to be lighter than the dairy wastes seen in the lagoon systems because of the limited opportunity for ammonia volatilization in the sewer system compared with the lagoon system. The value for the Toppenish system is comparable to the values seen in the dairy lagoons and may be a result of the more extensive system from this larger city. Values can be altered by other components such as materials added to the waste streams that cannot be controlled.

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APPENDIX C – QUALITY ASSURANCE AND QUALITY CONTROL

This project was implemented in three phases. In Phase 1, a GIS screening application was developed and used to identify potential sample locations and sites in the Lower Yakima Valley for Phase 2 sampling and screening. Phase 1 also developed estimates of the relative nitrogen available for application to the land from different sources. Phase 2 and Phase 3 involved extensive sampling and analysis. A discussion of the quality assurance and quality control (QA/QC) followed in Phase 2 and Phase 3 is presented below.

Approximately 330 ~~residential~~ homes in the Yakima Valley were visited and tested for nitrates, general water quality parameters, and bacteria. As stated previously, the sampling teams used nitrate colorimetric test strips as a field screening tool to provide an indication of whether the water exceeded the EPA MCL for nitrate (10 mg/L). The Hach tests strips measure nitrate concentrations in increments of 0, 1, 2, 5, 10, 20, and 50 mg/L. If the test strip indicated the water ~~may~~ might exceed the MCL, samples were collected for analysis of nitrate by EPA's Manchester Environmental Laboratory. If there was any question whether the nitrate level was close to 10 mg/L, then the sampling team collected a sample for laboratory analysis. Table C-1 provides a summary of the field and laboratory measurements collected and analyzed and the corresponding project data quality goals.

Comment [LE42]: I guess there might be non-residential homes, but I don't think so

Table C-1: Phase 2 - Field and Laboratory Measurements

	Analytical Method	Reporting Limit	Accuracy Check	Precision Check
Field Measurements				
Temperature	170.1	0.5 C	+/- 0.5 C	+/- 1.5 C
Hydrogen Ion (pH)	150.1	0.1 unit	+/- 0.1 units	+/- 0.3 units
Dissolved Oxygen	360.1	0.3 mg/L	+/- 0.3 mg/L	+/- 0.5 mg/L
Specific Conductance	120.1	1 us/cm	+/- 7%	+/- 10%
Redox Potential	SM2580B	10 mv	+/- 0.5 mv	+/- 0.5 mv
Nitrate (Hach Test Strip)	Colorimetric	0.05 mg/L	+/- 0.5%	+/- 20%
Laboratory Measurements				
Nitrates	Method 300.0	0.06 mg/L	80-120%	+/- 20%
Chloride	Method 300.0	0.06 mg/L	80-120%	+/-20%
TKN	Method 351.2	0.5 mg/L	80 -120%	+/-20%

The field sampling team followed the QAPP specifications and adhered to the QA requirements set forth by the analytical protocols (EPA 2010a). A multi-parameter water quality instrument was used in the field for measuring dissolved oxygen, oxidation/reduction (redox) potential, pH, specific conductance, and temperature. All field instruments were calibrated prior to use. For quality control, duplicate sample readings, calibration checks, and matrix spike samples (if applicable) were performed. All field testing QC samples met the frequency of analysis,

precision, and accuracy checks. Data generated are acceptable ~~and can be~~ to be used for screening purposes.

Based on the field screening test for nitrate, 102 water samples were shipped to EPA's Manchester Laboratory for analysis. Samples were confirmed for nitrates using EPA Method 300.0. Two percent of the total nitrate data points were qualified as follows: one sample (10086211) did not meet the holding time requirement and the result was qualified estimated; the nitrate concentration reported for this sample may be biased low. One sample (100866101) exceeded the highest level of the calibration curve and was qualified estimated. Data users are advised to consider the nitrate reported for this sample as biased low. All nitrates data, as reported and qualified, are acceptable for use for all purposes. All of the chloride and TKN analyses met the method required QC criteria. The data as reported are usable for all purposes.

Phase 2 was implemented following the specifications of the EPA approved "*QA Project Plan for Yakima Nitrates Study, Phase 2 – Initial Nitrate/Coliform Screening of Domestic Wells, February 2010*" (EPA 2010a). Deviations from the QAPP included changes in sample locations and modifications in the analytical method used, sampling method techniques, and additional number of samples collected. The rationale for these deviations was documented in the project team-approved Sample Alteration Form or Corrective Action Form.

In Phase 3, a new QAPP was developed and approved before Phase 3 sampling and analysis began (EPA 2010b). Based on Phase 2 screening results, samples and sub-samples were collected and shipped to the following laboratories for chemical analysis: EPA MEL, Cascade Analytical (Cascade), University of Nebraska Laboratory, USGS National Water Quality Laboratory (USGS-NWQL), USGS Laboratory in Reston (USGS-Reston) and EPA National Risk Management Laboratory RSKERC. Quality Assurance/Quality Control Summaries

~~2.~~1. **Manchester Environmental Laboratory, Port Orchard, Washington**

A Stage 4 data validation was performed by the EPA Region 10 Quality Assurance (QA) team for all the data generated by MEL **(Appendix C Table 2).**

Table C-2: Phase 3 - Summary of Chemical Analyses Conducted by MEL

Matrix	# Samples	Parameter	Analytical Method (Prep)	Analytical Method (Analysis)
Water Wells, dairy lagoons, and WWTP influent	49	TKN	AOAC 933.13	
	49	NH3	SM 10-107 (04-1-A version)	
	49	Nitrates-Nitrites	EPA Method 351.2	
	49	Total Metals	EPA Method 200.2	EPA Method 200.7
	49	Mercury	EPA Method 245.1	
	49	Alkalinity	Method 2320B	
	31	Coliforms	9221F,9221E, 9222B	

Table C-2: Phase 3 - Summary of Chemical Analyses Conducted by MEL

Matrix	# Samples	Parameter	Analytical Method (Prep)	Analytical Method (Analysis)
	13	Microbial Source Tracking	DNA PCR Techniques	
	49	Bromide, Chloride, Fluoride, and Sulfate	EPA Method 300.0	
	49	Total Phosphorous	EPA Method 365.1	
	30	Pesticides (only water wells)	Method 551.1	SW846 – Method 8270D-SIM
	30	Herbicides (only water wells)	SW846-Method 8151A	SW846-Method 8270D-SIM
Soils and Manure	16	Mercury	EPA 7471	
	16	Alkalinity	Method 2320B	
	16	Total Metals	EPA Method 200.2	EPA Method 200.7
	16	Pesticides	Method 551.1	SW846 – Method 8270D-SIM
	16	Herbicides	SW846-Method 8151A	SW846-Method 8270D-SIM

All of the chemical and microbial analyses conducted at MEL met the project data quality goals and criteria for accuracy, precision, comparability, completion, representativeness, and sensitivity, and are useable for all purposes with the following exceptions:

<u>Nitrates and Nitrogen Compounds</u>

Nitrogen compounds included ammonia, TKN, and nitrates-nitrites. Samples 10154251, 10154252, 10154253, 10154254, 10154255, 10154256, 10154257, 10154258, 10154259, 10164260, 10164261, 10164262, 10164263, 10164264 and 10164265 did not meet the required preservation when they were received at the laboratory. Nitrates/nitrites and ammonia results for these samples were qualified estimated with a possible low bias. Nineteen percent of the total data points (147) were qualified.

<u>Mercury and Alkalinity</u>

Approximately 37 percent of the total mercury data points were qualified estimated based on out of control sample spike and blank spike recoveries. Alkalinity results met all the QC criteria. The mercury and alkalinity data, as reported and qualified, are acceptable for use for all purposes.

Pesticides and Herbicides

The project data quality goals for precision and accuracy for numerous target analytes were not met for dairy lagoons and WWTPs. As stated above, all of the pesticides and herbicide results for the dairy lagoons and WWTPs could not be quantified and are considered unusable because of (1) the complexity of the sample matrices, (2) holding times that were exceeded, (3) recurring QC failures, and (4) the limitations of modified Method 8270D for detecting pesticides and herbicides at the project reporting levels,. However, the pesticides for water and soil, as qualified, are usable for all purposes.

Anions

Anions included chloride, fluoride, bromide, and sulfates. As a result of matrix interferences, the dairy lagoon and WWTP biosolids samples collected were analyzed at 50x dilutions for bromide, fluoride, and sulfate. The reporting limits for these bromide, fluroride, and sulfate were elevated and did not meet the project goals. As qualified and reported, the analytical results for water and soil are acceptable for use for all purposes.

~~3.2.~~ Cascade Analytical Laboratory, Wenatchee, Washington

Nitrate and Other Forms of Nitrogen

Cascade Analytical Laboratory is a is certified by the State of Washington to conducted drinking water analysis including analysis for nitrate. It is located in Union Gap and Wenatchee Washington, and analyzed nitrate for this study. Due to the short holding times for certain nitrates analytical methods, Cascade Analytical Laboratory was sub-contracted by Region 10 to analyze the water well, soil, and manure samples for nitrate and nitrogen compounds for Phase 3. A total of 30 water wells, 11 soil, and five manure samples were submitted.

The analytical method used for the determination of nitrates in water samples was Method 300.0. The methods used for the analysis of total nitrogen/solid, ammonia solid, and nitrate-nitrite in solid and manure samples were the Association of Analytical Communities (AOAC) Method 993.13, Standard Method 4500-NH3, and Method 4500-NO3. A Stage 4 data validation was performed by EPA Region 10 QA team for all data generated by Cascade Analytical Laboratory.

All of the QC samples and sample analysis met the technical acceptance criteria set forth by the methods. The data, as reported, are acceptable for use for all purposes.

Thirty split water samples were collected, shipped to Cascade Analytical Laboratory and MEL, and analyzed for nitrates using the EPA Method 300.0 (Cascade) and EPA Method 351.2 (MEL). Both sets of data met all the method-specified QC criteria and are acceptable for use for all purposes. The nitrates concentrations reported by both laboratories are comparable within 10 percent. The following is a list of water samples that were collected, split, and sent to these two labs:

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10154201	10154202	10154203	10154204	10154205
10154206	10154207	10154208	10154211	10154212
10154213	10154214	10154215	10154216	10154217
10154218	10154219	10154220	10154221	10154223
10154224	10154225	10154226	10154227	10154228
10154229	10164209	10164210	10164222	10164230

4.3. EPA National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, Ada, OKRSKERC

Hormone and Perchlorate Analyses

Fifteen dairy lagoon, three WWTP, and 30 water samples were analyzed for estrogens (17-α-estradiol; 17-β-estradiol;17-α-ethynyl estradiol; estriol; and estrone) by EPA's Robert S. Kerr Environmental Research Center following the in-house standard operating procedure (SOP) "*Quantitation of Estrogens in Groundwater and Animal Waste Dairy lagoon Water Using Solid Phase Extraction, Pentafluorobenzyl and Trimethylsilyl Derivatization and Gas Chromatography Negative Ion Chemical Ionization/Mass Spectrometry/Mass Spectrometry, RSKSOP-253, Revision 2, October 2010.*"

The same 30 water samples were also analyzed for perchlorate following the modified *USEPA SW846 Method 6850, "Perchlorate in Soils, Water and Wastes Using High performance Liquid Chromatography/Electrospray/Ionization (ESI) Mass Spectroscopy (MS) or Tandem Mass Spectroscopy (MS/MS).* All sample analyses were evaluated following the EPA's Stage 2B Manual Data Validation Process. The summaries of sample and QC analyses were evaluated and laboratory qualifiers were mapped to Region 10 EPA validation qualifiers following the technical acceptance criteria and method quality control specifications. All of the technical acceptance criteria for QC were met by both analyses. Target compounds detected above the Method Dection Limit (MDL) but below reporting limits were qualified estimated, "J." Data detected below the MDL were qualified non-detects, "U," and reported at the MDL level. The data, as qualified, are usable for all purposes.

5.4. USGS National Water Quality Laboratory, Denver, Colorado

Trace Organics

Fifteen dairy lagoons, three WWTP plant influent, and 30 water samples were analyzed for trace organic chemicals following the SOP for the "*Analysis of Waste Water Samples by Gas Chromatography/Mass Spectroscopy*" – USGS SOPs 1433 and 4433. All sample analyses were evaluated following EPA's Stage 2B Manual Data Validation Process (S2VM). The summaries of sample and QC analyses were evaluated and laboratory qualifiers were mapped to Region 10 EPA validation qualifiers following the technical acceptance criteria and method quality control

specifications. Samples were analyzed following the technical specifications of the analytical
method.

The data, as qualified, are usable for all purposes except for approximately 6 percent of the total
data points, which were qualified unusable based on extremely low surrogate recoveries.
Approximately 32 percent of the total data points were qualified estimated as a result of
chromatographic interference and QC results that did not meet the specified criteria.

Trace levels of 4-tert-octylphenol, diethyl phthalate, menthol, p-cresol, tri(2-
butoxyethyl)phosphate, tri(2-chloroethyl) phosphate, tri (dichloroisopropyl) phosphate, tributyl
phosphate, and triphenyl phosphate were detected in the field blank (WW29). Only the diethyl
phthalate in associated sample WW06 detected at a concentration less than 5x the value in the
blank was qualified as non-detect, "U," based on blank contamination.

6.5. University of Nebraska – Water Science Laboratory, Lincoln, Nebraska (UNL)

The University of Nebraska analyzed several different types of compounds. **Table C-3** provides
a summary of the compounds evaluated, number of samples, matrix, and analytical method.

C-3: Phase 3 - Summary of Analyses Conducted by UNL

Matrix	Compounds	No. of Samples	Analytical Method (Prep)	Analytical Method (Analysis)
Water Wells, dairy lagoons, and WWTP influent	Hormones	47	On-line SPE with C18 clean-up	SOP#LCMS_APPI_Steroids_Water-001
	Waste water contaminants	47	Off-line SPE-Modified Method 3535	LC/MS SOP-LCQ-Wastewater-001
	Pharmaceuticals	47	On-line SPE extraction with citrate buffer	SOP#LC/MS_Vet_Pharm_water-002
	Isotopic Nitrogen	47	Analyte Prep 15-002	N15 Analysis Dual Inlet IRMS
	Isotopic Oxygen	47	SOP#Analyte-O18 in Nitrate/AgNO3	SOP# Inst-Isoprime EA-18O-001
	Ammonia	47	Analyte-DISTN15-004	Titrimetric
	Nitrate	47	Analyte Prep 15-002	Titrimetric
Soil and Manure	Hormones	16	Microwave-Assisted solvent extraction (MASE) and SPE	SOP# Analyte-Steroids_Solids-001
	Waste water contaminants	16	Microwave-Assisted solvent extraction (MASE) and SPE	SOP#-Analyte-LCQ-Wastesolid-001
	Pharmaceuticals	16	On-line SPE extraction with citrate buffer	SOP#-Analyte-VetPharmSED-001

A Stage 2A data validation review was conducted by the EPA QA team on all the data. The validation included the limited evaluation of calibration, QA, and sample analytical summary results. All samples were analyzed following the technical specifications of UNL's in-house SOPs.

<u>General QA Observations for UNL Analyses</u>

UNL data sets may not meet the third-party reproducibility criterion set forth by EPA's Information Quality Guidelines (EPA /260R-02-008 October 2002) for the following reasons: (1) there is no established or standard analytical method for the analysis of the target compounds, and the analytical methods used are for research purposes only, (2) the recurrence of out-of-control QC results; (3) variability in duplicate runs; and (4) compound identification and calculations were not verified at the time of review because the instruments' raw data output was not available.

Twenty-nine water, 15 dairy lagoons, three WWTP, and 16 soil or manure samples were collected and analyzed for wastewater pharmaceuticals, veterinary pharmaceuticals, hormones and steroids, and isotopic nitrogen and isotopic oxygen. The following is a summary of the data validations for UNL:

<u>Wastewater Pharmaceuticals</u>: Approximately 10 percent of the wastewater pharmaceutical data points were qualified unusable because of extremely low spike and surrogate recoveries (less than 10 percent). The rest of the data as qualified are usable for all purposes.

<u>Veterinary Pharmaceuticals</u>: No significant problems were encountered with the analysis of soil/solid samples for veterinary pharmaceuticals. Most of the liquid samples (dairy lagoons, well water, and WWTP) underwent multiple analyses because of concentrations of some of the target compounds in the field blank and also because of matrix interferences. Approximately 9 percent of the total data points were qualified unusable and an additional 18 percent were qualified estimated concentrations with a high bias because of out of control internal standards or calibration. Five lincomycin and three monensin results in the water samples were detected above the reporting limits but were flagged non-detects based on contamination in the associated field blank, WW29. The concentrations reported were calculated using internal standard techniques. Most of the internal standards did not meet minimum area requirements when compared with the daily calibration standards. Therefore, the associated results may be biased high.

<u>Steroids/Hormones</u>: Because of the calibration results, the detected results or reporting limits for androstanedienedione, androsterone, progesterone, estrone, a-zearalanol, a-zearalenol, b-zearalanol for samples associated with the calibration run on January 18, 2011, were qualified estimated, "J/UJ." Approximately 15 percent of the total data points were flagged estimated because of calibrations. In addition, some target compounds were qualified non-detects based on contamination in the associated blank.

Isotopic Nitrogen/Isotopic Oxygen Analyses/Ammonium and Nitrate Nitrogen Analyses: Isotopic nitrogen and oxygen were determined using the amounts of ammonium and nitrate-nitrogen in water. No problems were encountered with the isotopic nitrogen, isotopic oxygen, and intermediate ammonia and nitrates nitrogen results. For QC, laoratoryb reagent blanks, duplicates, and laboratory-fortified blanks were analyzed at the required frequency. All of the results were comparable to each other. Data were not qualified and usable for all purposes.

7.6. USGS Laboratory, Reston Virginia

Recharge Age Dating

The USGS Laboratory located in Reston analyzed the recharge age of the water well samples following the SF_6 procedure.

Limitations of the Method: The recharge dating procedure is a statistical calculation derived from the SF_6 gas evolved in the sample and other existing data. It is applicable to young groundwater systems aged 1970 to present. This procedure is not applicable to areas with high anthropogenic and natural SF_6 background values such as indicated by samples WW-01, WW-11, WW-12, WW-13, WW-23, and WW-28. As a result, age could not be measured in those samples because of the high values of SF_6 as dissolved gases from the sample. These samples may indicate areas where localized anthropogenic sources of SF_6 exist. Alternatively, volcanic rocks can contain more SF_6 than the average atmospheric concentrations of SF_6 and the volcanic terrain and mineralogy of the sediments in the local aquifer may be the source of the SF_6.

> **Comment [LE43]:** Include that fact up front where this method is first described

The USGS laboratory flagged these six water wells samples with a "C" qualifier, meaning contaminated. For clarity, the validator changed the "C" qualifier with "NM," not measured. In addition, there were also some samples with recharge calculated dates before 1970. The dating technique used provides only a range, and data users should be warned that the reported recharge ages are estimates.

APPENDIX D: INFORMATION ON THE R&M Haak Dairy

The R&M Haak Dairy ("Dairy") is located in an agricultural area north of the Yakima River,
about four miles north of the city of Sunnyside.   It is in the Benton groundwater basin, which
includes the communities of Sunnyside, Grandview, Satus, Kiona, Prosser, Mabton and Richland
(Jones and others 2006). This dDairy was selected as one of the sampling locations because it is
relatively high on the landscape with very few other sources of nitrate above the dairy. The Dairy
A ditch runs from north to south through the dDairy. Cow pens, a milking parlor, and three waste
lagoons lie west of the ditch. There are several large structures where cows are kept. East of the
ditch, a center-pivot irrigation system is installed on a large sprayfield which is used by the
dDairy. The dDairy operator stated that corn and triticale were alternately grown on the
sprayfield. See Appendix D for a more detailed description of the Haak Dairy and its operations.

Within the Haak dairy property boundary, five soil units have been mapped by the U.S. National
Resource Conservation Service (NRCS , 2011). All five soil units have a silt loam texture with a
"well-drained" classification. Three of the soil units (Scooteney, Sinloc, and Warden) represent
82% of the surface area. They have a saturated hydraulic in the range of 1.1 to 4.0 feet per day,
which is characterized as "moderately high to high" in their capacity to transmit water. [3]
Likewise the other two soil units (Burke and Scoon) have a moderately high to high capacity to
transmit water to a depth of 2 to 3 feet bgs; however, below this depth a cemented layer is present
with a saturated hydraulic conductivity in the "very low to moderately low" range of 0.00 to 0.12
feet per day. The Burke and Scoon map units are located in the northwest portion of the Haak
dairy property and represent 18% of the surface area.

The NRCS information shows the surface of the Haak sprayfield, which is irrigated with
nitrogenous liquid dDairy wastewater from the lagoons, consists almost entirely of highly
permeable soils. Water from irrigation or precipitation can carry nitrogen through the surface
soils at a rate of 1.1 to 4.0 feet per day. Wastewater applied onto these highly permeable soils
increases the risk that nitrogen will be transported downward to the drinking water aquifer before
it can be taken up by plants, even if the plants have the capacity to take up more. Elevated levels
of nitrogen in soils can lead to groundwater contamination, especially if these conditions exist on
soils of relatively high permeability. The capacity of most of the surface soils within the Haak
property boundary (about 82% of the surface area) to transmit water can be characterized as
"moderately high to high".

Waste management at the Haak Dairy

Dairy inspection reports obtained from the Washington Department of Agriculture indicate the
Haak Dairy uses a lagoon system with a capacity of 9.4 million gallons. The surface area of the
first lagoon is approximately 70,000 square feet and is roughly triangular in shape. The second
lagoon is roughly rectangular and is about 37,000 square feet, and the third is roughly triangular

[3] Saturated hydraulic conductivity amounts have been converted from inches per hour to feet per day.

and is about 162,000 square feet. The lagoon system was 80 percent full at the time of the July 2008 inspection and 75 percent full at the time of the March 2010 inspection.

In addition to the lagoons, the Haak Dairy employs a solids separator and composting to treat waste. Animal corpses are composted. Waste is applied to crop fields by spreader ("honey wagon"), a sprinkler irrigation system, and a dry spreader. The inspection reports indicate the waste from the dDairy was applied to six fields at the time of the inspections.

Potential sources of Nitrogen sampled

EPA sampled several likely sources of nitrogen on the Haak Dairy. Composited samples were taken from a large manure pile, and from the dDairy sprayfield. EPA also sampled liquid effluent from the lagoon system.

A manure pile can be a source of nitrogen to the groundwater if it becomes wet. The manure pile sampled at the Haak Dairy was on bare ground just south of one of the structures where the cows were kept and not covered. The manure had high moisture content and appeared to have been recently pushed off of a concrete pad onto the ground. A composite sample was taken to provide a representative sample of the pile.

Using the seepage rate range of 0.2 to 2.4 mm/day observed by Ham and DeSutter, a lagoon system with a similar surface area to the one at Haak would be expected to have a leakage rate in the range of 482,000 gallons (roughly the volume of 0.7 Olympic-size swimming pools) to 5,783,000 gallons (roughly 8.8 pools) of liquid waste per year into the underlying soil.

EPA took a composite soil sample of a large crop field irrigated with animal waste from the lagoon system. The sample results shows a total nitrogen level of 2,760 part per million.

Other possible sources of nitrogen from the Haak Dairy

Synthetic inorganic fertilizer is a potential source of nitrogen from the Haak Dairy. Dairy inspection reports indicate that the dDairy has used commercial fertilizer in the recent years. Cow manure contains several plant nutrients including nitrogen and phosphorus. Phosphorus is often the limiting nutrient in how much manure can be applied because the amount of manure should be tailored to the nutrient needs of the type of crop being grown, and manure has a larger proportion of phosphorus relative to nitrogen for most crop needs. Applying too much phosphorus can cause surface water pollution. Growers sometimes apply manure until the phosphorus need is met and make up for the nitrogen shortfall by supplementing with inorganic nitrogen fertilizer. The report does not indicate whether the fertilizer used by the Haak Dairy contained nitrogen.

Because the area around the Haak Dairy is not served by a municipal sanitary sewer system, the dDairy presumably provides an on-site septic system for its employees. The detection of human fecal bacteria in the dDairy lagoons suggests that waste from the facility's septic system has

D-2

somehow made its way into the lagoons. Liquid leaking from the lagoons into the subsurface soils could contain nitrogen from both animal and human sources.

APPENDIX D REFERENCES

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APPENDIX E: INFORMATION ON DAIRY CLUSTER (In the process of being developed)