PRELIMINARY TECHNICAL EVALUATION OF THREE REPORTS BY U.S. ENVIRONMENTAL PROTECTION AGENCY REGION 10 ON NITRATE IN WATER WELLS, YAKIMA RIVER BASIN, YAKIMA COUNTY, WASHINGTON

Prepared for: Washington State Dairy Federation
Dairy Producers of New Mexico

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November 20, 2012

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ED_002369I_00080728-00002

INTRODUCTION

At the request of the Washington State Dairy Federation and Dairy Producers of New Mexico, Glorieta Geoscience, Inc. (GGI) conducted a preliminary technical evaluation of the following reports prepared by U.S. Environmental Protection Agency Region 10 (EPA):

1. Quality Assurance Project Plan, Yakima Basin Nitrate Study Phase 2 – Initial Nitrate/Coliform Screening of Domestic Wells February 2010 Sampling Event, Yakima County, Washington, U.S. EPA Region 10, January 27, 2010 (QAPP2)
2. Quality Assurance Project Plan For Yakima Basin Nitrate Study Phase 3 – Comprehensive Analytical Source Tracer Sampling April 2010 Sampling Event, Yakima County, Washington, U.S. EPA Region 10, April 27, 2010 (QAPP3)
3. Relation Between Nitrate in Water Wells and Potential Sources in the Lower Yakima Valley, Washington, EPA-910-R-12-003, September, 2012 (Report)

In the remainder of this report we will refer to these documents as QAPP2, QAPP3, and Report, respectively.

Access to EPA's GIS tool, field notes, water well data, reference maps and other relevant data are critical to a proper technical review of the report and its findings. Multiple requests have been made to EPA under the Freedom of Information Act; however requests for this information have not been fulfilled. Due to the unavailability of these data, GGI's technical evaluation of the three reports is preliminary only, and GGI reserves the right to revise and update this preliminary report once the EPA makes the information available.

In the following sections, we will first evaluate the overall study design/site selection as described in the QAPPs and Report documents followed by specific data collection concerns and finally the results and conclusions drawn from the data as described in the main body of the Report.

OVERALL STUDY DESIGN AND SITE SELECTION

The Report and QAPPs describe a three-phased study of nitrate in groundwater of the Yakima Valley. Phase 1 was based on compiling historic groundwater nitrate data into a GIS database. Based on these data, the Phase 2 data collection focused on areas that had shown high nitrate levels in the past. Phase 3 represents an additional subset of sites where EPA collected samples for extensive groundwater analyses together with potential source analyses for the same analytes. Thus EPA made the choice of focusing on groundwater chemistry, assuming that indicators such as pesticides and other trace organic compounds will tie the groundwater nitrate to a specific source. As we will discuss below, this strategy failed to yield clear indicators pointing to specific sources. Since EPA did not collect any data to gain a detailed understanding of aquifer properties at the Phase 3 sites, no defensible argument can be made regarding the source(s) of groundwater nitrate.

The Yakima Valley is a large agricultural area where there are multiple potential sources of nitrate in groundwater. These potential sources are intermingled, i.e., homes with septic systems are on the same properties as or immediately adjacent to farms (see aerial photo on the cover of this report). Because none of the potential sources are isolated, source tracking requires an in-depth knowledge of

aquifer properties such as thickness, flow direction and hydraulic conductivity in addition to localized effects of ditches, drains and production wells on groundwater flow. EPA did not collect any data to evaluate aquifer properties.

EPA acknowledges these shortcomings on Page 3 of the Report:

First, water well samples were collected from existing wells. No new wells were installed for this study. Information on the depths and screened intervals of the water wells is known for about a third of the wells that were sampled. In this report, designations of upgradient and downgradient are based on regional groundwater flow data from the United States Geological Survey (USGS). ***Lack of complete well information limits our ability to verify if the wells upgradient and downgradient of the sources draw water from the same water bearing zone.*** (bold highlights added)

This means that if designated upgradient and designated downgradient wells are screened into different zones, the designated upgradient well is not a valid baseline. Further, because no water levels were measured as part of the study, the identification of a well as upgradient is an unsubstantiated assumption based on the regional groundwater flow direction rather than site-specific ground water elevations calculated from surveyed well heads and measured water levels (see discussion on Report Pages 7-8). Also: "Flow directions can vary locally due to canal/lateral leakage, irrigation, drains, streams, pumpage, variations in recharge, spatially varying hydraulic characteristics, and topographic setting (USGS 2009)" (Report Page 17). Given these limitations, no definitive conclusions regarding the source of contamination can be drawn even if the designated upgradient well has lower contaminant concentrations than the designated down-gradient well.

To accurately calculate ground water flow direction(s), EPA should have sampled several upgradient wells based on measured water levels and calculated ground water elevations from professionally surveyed well heads. Further, periodic mapping of groundwater flow direction would be necessary to verify that groundwater flow is consistent through seasonal changes in farming practices and regional stream/ditch flow. The only accurate means of determining true upgradient and downgradient sampling points would require surveyed horizontal and vertical coordinates, water level measurements, well completion logs showing screened intervals, hydrogeologic cross-sections and mapping of groundwater elevations on an area map that would include all surface water, domestic and production wells and locations of all area septic tanks.

Below are specific comments GGI wishes to highlight to further address deficiencies in the overall study and QAPP 2 and QAPP3:

EPA states in QAPP2, Page 3: "*The objective of Phase 2 was to evaluate if, down gradient of potential nitrate contaminant sources, there are drinking water wells with nitrate levels over the MCL and/or elevated total coliform.*" EPA states in QAPP2, Page 4: "*Phase 3 attempts to demonstrate the potential to use low concentrations of trace organic compounds to link land use to observed nitrate contamination.*" And *"These compounds include estrogens, androgens, veterinary and human antibiotics, agricultural chemicals, personal care products and human medications and compounds such as caffeine*."

EPA states in QAPP2, Page 4: *The use of private domestic water supply wells required contacting many individual home owners and requesting access to sample their drinking water. It further involved using wells installed for another purpose as windows into what is happening in the groundwater. These wells may not be screened at horizons where they optimally intersect what we seek to monitor.*

EPA's site selection criteria include sites where "*ground-water flow can be expected to be consistent from season to season and is predictable in direction. Select sites which present as little as possible up-gradient contributing sources of nitrate.*" QAPP2, Page 5.

EPA has presented no data supporting the assumed ground water flow directions in the selected study locations, nor have they demonstrated that directions are consistent from season to season. Knowledge of upgradient nitrate sources is critical in determining potential sources. Since the direction of ground water flow was estimated and not adequately mapped for purposes of this study, all uses of 'upgradient' and 'downgradient' references should be qualified with "designated."

EPA presents no data comparing demographics from one community to another. Influent and effluent compositions at a Waste Water Treatment Facility (WWTF) can differ substantially from those for a septic system. Composition of WWTF influent and thus effluent fluctuates from weekdays to weekends, seasonally in areas of specific tourism and throughout any given day. Why did the EPA not sample directly from septic tanks or leach fields?

Well selection was based on: "*Select sites with a linear array of homes using individual domestic water supply wells along the downgradient side of...*" QAPP2, Page 5.

Because homes in the rural part of Yakima Valley all have septic systems, these need to be mapped and evaluated as sources in all investigations of groundwater nitrate. For example, ground-water contamination from on-site septic systems is a widespread problem in New Mexico (McQuillan, 2004) and septic tank effluent has contaminated more water supply wells and more acre-feet of ground water, than all other sources in the state combined (McQuillan, 2005).

Phase 3 was conducted "*to collect data to investigate the contribution of various sources from nearby land uses to the high nitrate levels in groundwater and residential drinking water wells*" (Report Page 2).

EPA used a "GIS tool" to select sites from Phase 1 for Phase 2 (Report Page 10) and from Phase 2 for Phase 3 (Report Page 13). No other information is given on how this "tool" works and why certain areas with high groundwater nitrate were chosen to be sampled and not others (see Report Figures 10 & 11). This tool has been requested from EPA via the FOIA process, but has not been provided.

While the study is supposed to identify all sources of nitrate impacting private water supply wells, a different sampling design was employed for evaluation of potential impacts from farming and septic than for dairy sources. Dairy sites were located close to the northern edge of the Valley farming area, while the other sources were sampled within a matrix of other uses (see Report Figure 11). No designated upgradient wells were sampled for potential farming and septic sources, but a designated upgradient well was included in the dairy sampling network (see Report Table 1). EPA claims "Minimal upgradient nitrate sources" (Page 18) for the non-dairy sites, but provided insufficient data to

substantiate this claim. This discredits any conclusions drawn for the latter sources due to the sampling program as implemented.

Hydrogeology

The study area is underlain by an alluvial aquifer overlying a semiconfined (does EPA mean leaky-confined?) basalt aquifer, with a possible non-continuous shallow saturated zone originating from irrigation return-flow that is situated over the true alluvial aquifer. The well network selected to be sampled for this study includes both alluvial completions and semiconfined basalt completions. No well completion data or aquifer identification data are provided within the report. A key component of the study is collecting ground water quality samples from designated upgradient and designated downgradient wells, completed into the same aquifer. Although the report assumes that ground water flow direction in both aquifers is the same, the report also states "locally, the flow direction may be modified by geologic structures and by irrigation practices, drains, ditches, canals, and other hydrologic features" (Report Page 17). Tables in the report do not provide a description of into which aquifer specific wells are completed. No measured heads or ground water elevations from sampled wells are provided in the report. Three (3) potentiometric surface maps with data based on surveyed well head data should have been constructed for: 1) alluvial aquifer; 2) basalt aquifer; 3) composite potentiometric surface for wells completed into both aquifers. These potentiometric surface maps should be constructed quarterly using quarterly ground water level measurements, and groundwater flow direction should be evaluated for a minimum of one-year before upgradient and downgradient designations are made.

Although the basalt is characterized by EPA as semiconfined, mixing of producing zones in wells completed across both aquifers can transport nitrogen downward from the alluvial aquifer into the semiconfined basalt aquifer. Well completion information is critical to assess the potential for vertical transport through the gravel pack or casing.

QUALITY ASSURANCE PROJECT PLAN – PHASE 2 SCREENING, FEBRUARY 2010

Phase 2 Property Access QAPP2, Page 5

EPA Sampling Teams will collected a GPS location from the well, and fill in an access permission form developed by the EPA team (in Spanish and English. If the homeowner is unwilling to sign the form, but is willing to have a sample taken, just note the unwillingness on the form and go ahead and collect the sample as long as verbal permission is obtained.

EPA's wording assumes that the occupants of the residences will be the owners. Did EPA research County Clerk files to determine who the owners are and specifically contact these owners? Did EPA determine if the occupants are renters or owners? How many renters consented to give access to their well without permission of the owner? EPA has provided no property access forms or notes identifying which properties are owner-occupied or which properties gave signed or verbal permission for EPA to sample onsite wells, or which properties had Spanish-speaking residents. GGI requests the opportunity to review actual access permission forms for each home EPA contacted.

Sample Collection Activities QAPP2, Page 16:

At this time, examine the well for the integrity of the sanitary seal/ surface seal. If the well is open to surface contamination (collapse around the well pad, no well pad, no seal, open seal) to the extent that material from the surface such as run-on water or organisms could fall into the well, then note that on the data form, take a photo of the installation with the Home ID number on it and plan to collect a Coliform bacteria sample at this home.

Using wells with poor surface completions skews results towards contamination from surface sources not associated with septic systems, AFOs or irrigated agriculture. Were wells with inadequate surface seals sampled, or are they eliminated from the study? GGI requests the opportunity to review all intake forms, field notes and photographs of each well EPA evaluated and sampled.

QAULITY ASSURANCE PROJECT PLAN – PHASE 3 APRIL 2010

Phase 1 Soil Sampling QAPP3, Page 25:

For sampling the agricultural field, you might plan a diagonal course through the field attempting to reach at least 1/3 of the way across. You could head for the center pivot point if the field has one. When you get to 20 of 40 subsamples, turn 90 degrees and you should re-intersect the boundary of the field at your last sample. For example – you select a direction across the field and plan on collecting a small sub-sample every 25 steps. Where ever your 25th footstep lands, take your sampler (prepared spoon or syringe) and insert it at the ball of your foot. Try to recover about 1 teaspoon or so of soil centered about 1-inch below the surface. Not too deep and not just at the surface. Place the soil into the prepared stainless steel bowl. Take 25 more steps and repeat until you have collected 40 subsamples.

Soil sampling at CAFOs nationwide is conducted in conformance with NRCS 590 Nutrient Management Standards. The 590 Standards for Washington are currently being developed and the most recent draft states: "Soil, Manure, and Tissue Sampling and Laboratory Analyses (Testing); Nutrient planning must be based on current soil, manure, and (where used as supplemental information) tissue test results developed in accordance with land-grant university guidance, or industry practice, if recognized by the university." Industry standards and NRCS 590 standards in other States recommend collection of composite soil samples at 0-12 inches, 12-24 inches and 24-36 inches.

EPA's plan provides no scientific rationale for collecting soil samples from 1 inch below the soil surface, especially when sampling for nitrates. There is no industry or land grant university standard for EPA's soil sampling methodology that suggests soil sampling only the first inch at CAFO spray fields for either environmental or agronomic purposes is valid and the soils data should be disregarded.

Lagoon Sampling:

QAPP3, Page 11 specifies *"1 sample from freshest source in the lagoon system and 2 samples from the last lagoon prior to pumping onto fields."*

QAPP3, Page 21 specifies *that Liquids from Lagoons or Sewer Plant Influent Streams (16 bottles per location). Locations are identified as LG01 to LG15 and SP01 to SP03.*

No field data on lagoon sampling procedures is currently available. It is unknown if these samples are grab samples or composite samples. If these are composite samples, how many sub-samples per composite? Anecdotally, GGI was informed that "lagoon sampling" occurred in an alley draining from the milking parlor to the lagoon. If the alley was the actual sample location, these samples should be disregarded as not representative of blended lagoon samples. Perhaps this is the reason that matrix effects precluded proper analysis of green water by EPA's Manchester Laboratory?

Page 27 of the QAPP3 specifies that *"we are attempting to integrate our sample across the accessible depth of the lagoon."*

At what depth were the samples collected? Were the lagoon samples collected from the surface, 1 foot below the surface or from deeper layers?

GGI samples more than 25 green water lagoons quarterly as required by the New Mexico Environment Department Ground Water Discharge Permits. Appendix A presents GGI's SOP for green water lagoon sampling.

REPORT ON RELATION BETWEEN NITRATE IN WATER WELLS AND POTENTIAL SOURCES IN THE LOWER YAKIMA VALLEY, WASHINGTON

Site-specific study design

As mentioned above, EPA has not demonstrated that the designated upgradient and downgradient wells are valid reference points for determining sources of nitrate in domestic wells. In addition, we have the following concerns with respect of the specific sampling sites in Phase 3.

Haak Dairy Site: The selected designated upgradient well is not upgradient from the potential dairy sources given the groundwater flow direction indicated (Report Figure 12), thus (see also comments under Study Design), conclusions based on the designated upgradient and designated down-gradient comparisons are not valid.

Dairy Cluster Site: Given the indicated groundwater flow direction, the designated upgradient well is at best upgradient from Cow Palace and Liberty/Bosma dairies. Thus (see also comments under Study Design), conclusions based on the designated upgradient and designated down-gradient comparisons are not valid for DeRuyter and D&A Dairies. Conclusions based on a designated upgradient and designated down-gradient comparisons may or may not be valid for Cow Palace and Liberty/Bosma Dairies.

Crop and septic sites: No detailed maps are provided showing the locations of the wells and associated fields/septic systems and presumed groundwater flow directions. Also no designated upgradient wells were sampled. Therefore, the validity of the results/conclusions cannot be evaluated.

Volume of Manure and Green Water

EPA highlights under the Report Analytical Results and Discussion section (Report Page 30 onward) how much manure and green water is produced by the Phase 3 dairies and compare volumes to people and

swimming pools. These statistics are irrelevant as long as a dairy uses these nutrients in accordance with its nutrient management plan and crop needs.

Age Dates

Reported age dating results indicate a mixing of older and younger waters. It is likely that production wells completed into the lower basalt aquifer are pumping water that is older than water in the overlying shallow alluvial aquifer throughout the valley. Surface water supplies younger water for irrigation. Some irrigation water percolates downward and recharges the shallow alluvial aquifer, thus mixing waters from 3 sources: 1) surface water, 2) the alluvial aquifer, and 3) the basalt aquifer. Mixing of waters of different ages precludes use of the age dating data for definitive source identification. Again, without specific information on well completion, samples cannot be legitimately evaluated for the objectives of the study.

Further, aging of the groundwater at best gives a maximum age of nitrate – old groundwater could have a nitrogen contribution from years ago or yesterday.

Soils

As discussed above, EPA's soil sampling plan for nitrate, consisting of pacing off sample points and collecting only the top one-inch of soil, is not found in any agriculture, industry or land grant university standard. To obtain valid data deeper samples need to be composited. For this reason the soils data should be disregarded.

Nutrient Management

EPA provides a generalized picture of cropping patterns and crop nitrogen requirements in the valley. The dairies being evaluated are all operating under NMPs which require nitrogen and phosphorus to be applied to crops at agronomic rates. EPA provided no nutrient application, soils, tissue samples or crop production data to indicate dairies have over applied manures or green water to land application fields.

General Chemistry

Results from major ions and trace inorganic elements show a range of concentrations in these elements that does not allow source tracking (Report Table C6). For example, in the discussion for Haak Dairy, EPA contends that elevated concentrations of Barium and Zinc in the designated downgradient wells is indicative of dairy groundwater contamination, yet the designated upgradient Dairy Cluster well (WW-06) has the highest Zinc concentration of all wells analyzed. Barium is found at concentrations similar or higher in the residential wells (WW-18, WW-22) compared to the wells designated downgradient of the Dairy Cluster.

Given that the dairies are located in a matrix of farming and septic systems and the shortcomings in the study design, none of the major ions and trace inorganic elements provide conclusive evidence regarding the source of nitrate in the wells designated downgradient from the dairies.

Isotopes

$\delta^{18}O$ values for nitrate derived from the reduced sources (ammonium, urea) can be estimated using a 1:2 mix of atmospheric oxygen to water oxygen during nitrification (Böttcher et al. 1990). Shallow groundwater in the Yakima valley has a $\delta^{18}O$ of -13 to -14.5‰ (McCarthy & Johnson 2009), while air has a $\delta^{18}O$ of 23.8‰. This should result in a $\delta^{18}O$ near 0‰, although Xue et al. (2009) note that $\delta^{18}O$ values up to 5‰ higher than the upper limit for nitrate produced by this mechanism can occur due to microbial processes and evaporation in the soil column. Analyzed perchlorate data do not correlate with $\delta^{18}O$ (see Figure A, below), thus casting doubt that atmospheric deposition is a likely cause for the high $\delta^{18}O$ values reported. Nitrate fertilizer can have a $\delta^{18}O$ signature of $\delta^{15}N$ = 0 to 5.6‰ and $\delta^{18}O$ = 18-26‰ (e.g., Mengis et al., 2001; Roadcap et al., 2002; Vitòria et al., 2004, Deutsch et al., 2005, Rock and Ellert, 2007, Xue et al., 2009). This means that the high values of $\delta^{18}O$ in the EPA study, which are well outside the range of a previous USGS study in the valley ($\delta^{18}O$ of nitrate: -8 to +10‰, McCarthy & Johnson 2009), cannot be readily explained.

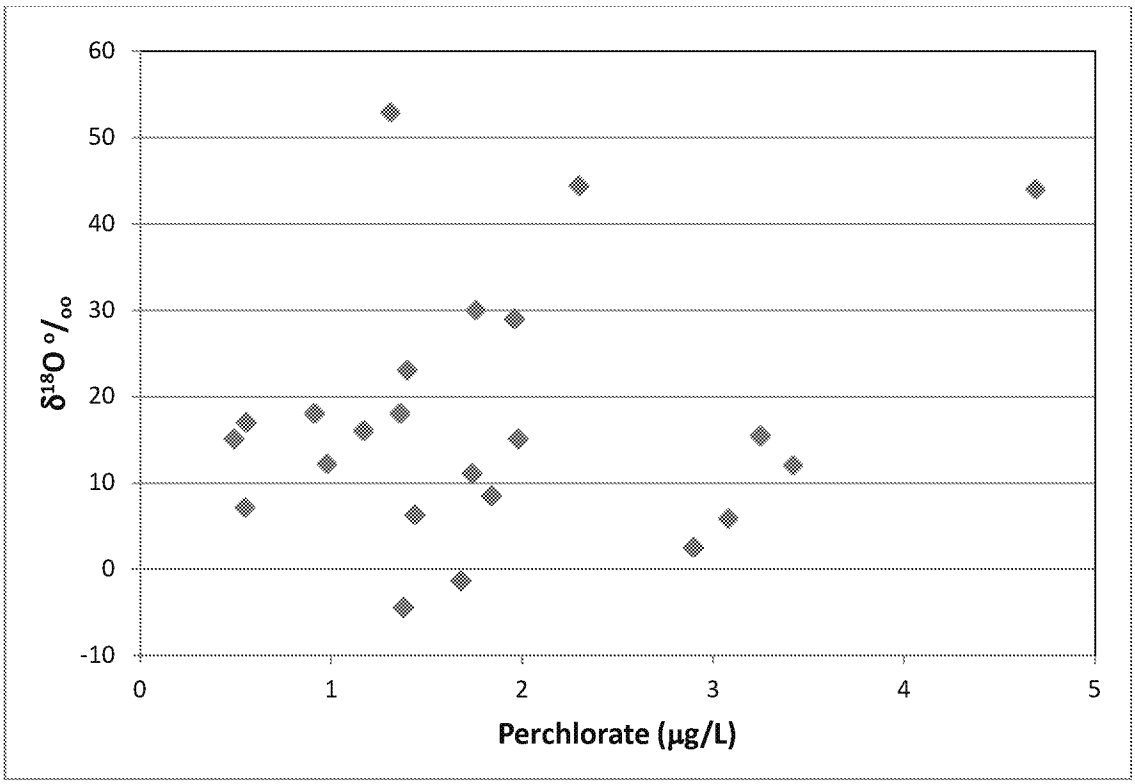

Figure A: Relationship between perchlorate and $\delta^{18}O$ in Phase 3 wells based on data in Report Tables C7 and C15.

$\delta^{15}N$ values in the human and dairy sources examined show a wide range of values (2-14‰), with both sources overlapping, but being distinct from ammonium and urea based fertilizers (-1.5 to -0.4‰, Wassenaar, 1995; Vitòria et al., 2004; Xue et al., 2009).

Overall, the isotope data provide no ability to distinguish between human and dairy sources. It must be noted that domestic wells were sampled in an area where human wastes are disposed of by septic systems in the vicinity of the domestic wells, i.e. homes that have their own wells also have septic

systems on the property. As stated already, without detailed knowledge of all potential contributors and groundwater flow direction, the isotope data are meaningless for distinguishing human vs. dairy sources. Only nitrate from synthetic fertilizer that has undergone no nitrification (which would be an assumption) can be distinguished based on $\delta^{15}N$.

Organic Compounds

EPA highlights the results of Atrazine (pesticide) in the Haak Dairy section (Report Table 11), yet all values are either non-detects or estimates. Similarly, all values for the Dairy Cluster well are also estimates. This does not allow for any conclusions, especially since both upgradient wells were already contaminated (Report Table C9). Other pesticides were detected in isolated wells without any clear pattern.

As detailed in the Report, trace organics, hormones, and microbiology also did not yield any patterns. However, it is worth mentioning that the designated upgradient well at the Dairy Cluster was the only well that had detectable levels of total coliform, suggesting that the aquifer in which it is screened is receiving bacteria from non-dairy sources.

Pharmaceuticals were detected in both designated upgradient wells at the dairy study sites indicating non-dairy sources. Specifically, at Haak Dairy, Monesin was detected in the designated upgradient well in the same concentrations as in the designated downgradient wells. The same was true for Tetracycline at the Dairy Cluster site. It is difficult to address conclusions regarding pharmaceuticals since the EPA's lab (see discussion in QA/QC section) does not stand by its results. Even if we analyze these poor quality pharmaceutical sample results, no consistent trend was observed using pharmaceuticals, thus these compounds, even if used at the dairies and detected in lagoons, manure or soils, do not help identify the source(s) of nitrate in downgradient wells.

Miscellaneous

On page 29 the Report states: "The ^{18}O values are reported as ^{18}O-NO3 (for nitrate)." GGI assumes that values are reported as $\delta^{18}O$ as indicated in the Report tables.

On page 48 the Report states: "A difference lies in the fact that human waste is treated before discharge into the environment, but animal waste is either not treated at all or minimally treated before discharge into the environment (EPA 2004)." This is incorrect, human waste is only treated in waste water treatment plants, septic systems are little more than settling systems with leach fields that are designed to leach untreated septic waste into the soil. In contrast, dairy lagoons have been constructed according to National Resources Conservation Service standards with clay liners (Jay Gordon, pers. comm., Nov 2012).

Appendix E Quality Assurance and Quality Control

There are numerous instances where the participating analytical laboratories state that their results do not meet the level of the QAPP and may also have problems meeting third-party review. However, the EPA report still utilizes these data for comparison and development of conclusions. Our comments

correlate to the summary analysis by the laboratories presented in Appendix E. Additionally, GGI reviewed the Corrective Action Forms.

EPA's Manchester Environmental Laboratory, Port Orchard, Washington

Nitrate and Nitrogen Compounds

Report Exception: *Nitrogen compounds included ammonia, TKN, and nitrate 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. Nitrate/nitrites, TKN, and ammonia results for these samples were qualified estimated with a possible low bias. Thirty one (31 percent) of the data points (147) were qualified estimated.*

All of these samples (10154251 through 10154529 and 10164260 through 10164265) are "LG" or lagoon samples. These samples contained pH preservation levels above the stipulated pH value of 2 when measured at the laboratory. This indicates an increase of pH during shipment to the laboratory. Based on GGI field experiences and the recommendation of NMSU research (Ulery et al., 2004), the amount of sulfuric acid added to the lagoon samples should have been doubled to insure proper preservation. Additionally, there are concerns regarding protocols for the lagoon samples that do not address stratification within the lagoons and the homogeny of the final sample volume that is distributed among the numerous sample kits.

The precision of the results is suspect due the failure to obtain a triplicate (duplicate sample) from one the lagoons as determined in the QAPP and noted in the Corrective Action Form dated August 1, 2012. All of these factors impact the quality of the analytical results producing a lower level of confidence for their use in assessing impacts to land application areas and shallow ground water.

Mercury and Alkalinity

Report Exception: *Thirty nine percent (39 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.*

The Data Validation Report for the Inorganic Analyses of the Water Samples Collected from the Yakima Basin Nitrate Study Phase 3 (USGS Memorandum dated February 10, 2011) by this laboratory notes: 1) the laboratory fortified blank (LFB) associated with at least 12 mercury results were outside the recovery acceptance criteria; and 2) The matrix spike and/or matric spike duplicate were outside the recovery requirements. As a result, the mercury data is qualified as acceptable for identification (a determination of presence) but the value is an estimate and cannot be used for quantitative assessments. Again, most of the samples are used to characterize lagoons and land application areas.

Pesticides and Herbicides

Report Exception: *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.*

As identified in prior methods, the green water/lagoon samples continue to be the most difficult to analyze and are undependable for correlation. The status of the pesticides results are presented, but the herbicide results for water and soil are not clarified.

Anions

Report Exception: *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, fluoride, 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.*

See prior comments regarding the waste samples. It is apparent that the sampling protocols as presented in the QAPP have resulted in poor results for characterization of the lagoon chemistry. This impacts the quality objective goal for showing correlations in application of lagoon waters on land applications areas.

Cascade Analytical Laboratory, Wenatchee, Washington

Nitrate and Other Forms of Nitrogen

The identification of analytical methods for nitrogen species in the QAPP did not include methods commonly used to quantify wastewater, namely those found in *Standard Methods for the Examination of Water and Wastewater*. The QAPP should have identified this potential (with information provided by the participating laboratory) and provided the necessary information to sustain quality control for the sampling program (i.e. providing proper holding times, appropriate container and preservation).

Bacteria

Report Exception: *For bacterial analyses, a holding time of 30 hours must be met for drinking water samples and a holding time of 6 hours must be met for wastewater samples. All samples met these requirements, except for the following dairy lagoon and wastewater treatment plant samples: 10154251, 10154252, 10154253, 10154271, 10164263 and 10164264. The fecal coliform results for these samples were qualified estimated based on holding time exceeded.*

For bacteria samples, 20 percent (or 6 of 30) samples, all wastewater samples, exceeded holding time. Without knowing the number of fecal coliform colonies in the original sample, estimates of fecal coliform concentrations in samples that exceeded holding times are meaningless. See previous comments regarding wastewater sample qualifications.

USGS National Water Quality Laboratory, Denver, Colorado

Trace Organics

Report Exemption: *Data users are advised to consider the values reported as a screen. For full usability, data need further confirmation for the following reasons: (1) data were not thoroughly verified by the validator because of the absence of the instrument raw data output at the time of review, and (2) the laboratory followed their in house SOP and the recurrence of results out of SOP QC control limits indicates that the data may not be reproducible by a third party. The data reported can only be used for information purposes and a good starting point in determining sample locations for confirmatory analyses.*

The trace organics results should be considered as not qualified for use in the report for any quantifying applications based on the unresolved quality control issues presented in the exemption.

University of Nebraska Lincoln – Lincoln Water Science Laboratory (UNL)

General QA Observations and Wastewater Pharmaceuticals

Report Exemption: *UNL data sets may not meet the third party reproducibility criterion set forth by EPA's information Quality Guidelines (EPA /260R02008 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.*

The exemption continues to identify that 55 percent of the total data points were assigned as being estimates. The use of this data as a correlation tool to determine source is suspect since concentrations of these species are used as the basis of the correlation.

Veterinary Pharmaceuticals

See prior discussion regarding wastewater pharmaceuticals.

USGS Laboratory, Reston, Virginia

Recharge Age Dating

The selected method for age dating followed the SF_6 procedure. The dependency on the single procedure to determine groundwater recharge age does not provide for any comparative test. An additional method such as the CFC (chlorofluorocarbons) procedure should have been considered to provide a comparative result.

CONCLUSIONS

EPA States the following objectives for the study:

- *EPA hopes to assess which activities on the landscape are contributing excess nitrate to shallow ground water.* QAPP2, page 3
- *In addition, the sampling from this project will provide enforcement-quality data that could be used in later enforcement actions.* QAPP2, page 3

EPA did not achieve these objectives because the aquifer properties such as groundwater flow direction were not evaluated, not all potential sources at each study site were evaluated and mapped and trace organic compound analyses did not yield reliable data or were inconclusive. As a consequence, EPA did not produce a study with reproducible results that supports its conclusions that specific sources of nitrate in domestic wells the Yakima Valley can be identified. Specifically:

1. Overall the Report provides a significant lack of supporting technical information for EPA to arrive at the conclusions presented in the report.
2. Locally the ground water flow direction may be modified by geologic structures and by irrigation practices, drains, ditches, canals, and other hydrologic features.
3. Very limited data on well completion, screened intervals, pump setting, casing diameter, presence or absence of surface/sanitary seals is presented.
4. Lack of well completion information severely limits EPA's ability to verify if the wells identified as upgradient and downgradient of potential sources produce water from the same water bearing zone.
5. No water levels were measured and converted to ground water elevations with which to construct seasonal potentiometric surface maps in each aquifer to determine temporal changes in both localized and valley-wide ground water flow directions.
6. The dairies and other sites are located in a matrix of farming and septic systems, which makes source tracking impossible without detailed knowledge of aquifer and well properties.
7. The selected upgradient well at Haak Dairy is not upgradient from potential dairy sources given the groundwater flow direction indicated in Report Figure 12, and conclusions based on upgradient and down-gradient comparisons are therefore not valid.
8. Given the indicated groundwater flow direction, conclusions based on an upgradient and down-gradient comparisons are not valid for DeRuyter and D&A Dairies because no upgradient well was sampled for these dairies.
9. The designated upgradient well at the Dairy Cluster was the only well that had detectable levels of total coliform, indicating that the aquifer in which it is screened is receiving bacteria from non-dairy sources.
10. No upgradient wells were sampled at septic sites or farm fields, and therefore the validity of the results/conclusions cannot be evaluated against data for dairies.
11. Since EPA did not collect any data to gain a detailed understanding of aquifer properties at the Phase 3 sites, EPA has no defensible argument regarding the source(s) of groundwater nitrate.
12. Mixing of waters of different ages precludes use of the age dating data for definitive source identification.
13. EPA's soil sampling methodology does not follow any accepted NRCS or land grant university soil sampling standard for either agronomic or environmental investigations. All soils data should be disregarded.
14. EPA has provided no historical land-use, nutrient application, soils, tissue samples or crop production data to indicate dairies have over-applied nutrients to land application fields.

15. The EPA states it selected WWTF effluent samples as "representative" of septic system effluent, however this claim cannot be supported by available studies. The effluent composition of WWTF is not necessarily representative of septic system effluent.
16. None of the major ions and trace inorganic elements provides conclusive evidence regarding the source of nitrate in the wells downgradient from the dairies.
17. High values of $\delta^{18}O$ in the EPA study, which are significantly outside the range of a previous USGS study in the valley, cannot be readily explained.
18. The isotopic data provide no basis by which to distinguish between human and dairy sources.
19. The quality of much of the laboratory data indicates many of these data will not pass the third party reproducibility criterion set forth by EPA's Information Quality Guidelines.
20. A full 20% (6 of 30) of samples for fecal coliform bacteria exceeded holding time at Cascade Analytics.
21. EPA's Manchester Laboratory reported 15 nitrogen samples out of 49 (31 percent) were not properly preserved and did not achieve required holding times.
22. EPA's Manchester Laboratory reported that project data quality goals for precision and accuracy for numerous target analytes were not met for dairy lagoons and WWTPs.
23. EPA's Manchester laboratory reported that all of the pesticide and herbicide results for the dairy lagoons and WWTPs could not be quantified and are considered unusable.
24. The reporting limits for bromide, fluoride, and sulfate were elevated due to matrix effects and did not meet the project goals.
25. The USGS laboratory followed their in house SOP for trace organics and the recurrence of results out of SOP QC control limits indicates that the data may not be reproducible by a third party.
26. UNL data sets may not meet the third party reproducibility criterion set forth by EPA's information Quality Guidelines (EPA /260R02008 October 2002) for hormones, wastewater pharmaceuticals, veterinary pharmaceuticals, isotopic nitrogen, isotopic oxygen, ammonia, and nitrate; soil and manure for hormones, wastewater pharmaceuticals, and veterinary pharmaceuticals.
27. EPA did not produce enforcement-quality data from this study.

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Appendix A

Lagoon Sampling Protocol

Collect a composite sample from each lagoon using a sample dipper. A composite sample shall consist of six sub-samples taken from eight different locations distributed evenly throughout the lagoon.

Collect the sub-samples in a clean bucket thoroughly mix and take a composite sample from the bucket to fill in the sampling bottles.

Make sure you collect each sub-sample from 1 foot below the water line by dipping the sample dipper.

A sample "dipper" can be constructed by attaching a clean, plastic container with a wide opening to a length of light-weight wooden pole or pipe, such as PVC. This dipper must either be a one-use sampling device that is disposed of after each sample location or must be decontaminated between each lagoon with a solution of Alconox (or equivalent non-phosphate cleaning product) and clean water. The Alconox solution should be prepared as directed on the label.

Precautions

Special care should be used regarding personal safety when obtaining samples directly from the edge of lagoons, as the footing in these areas can be dangerous and could cause falls into the lagoon.

Samples should be obtained with a container that will provide a composite or mixed representative sample of the lagoon water.

Do not collect a sample from the top layer, make sure you dip the sample dipper to 1 foot below the water line before you collect the sample.

Sample Handling and Shipping

Samples should be examined for accurate labeling for both the individual sample bottles and the Chain-of- Custody Document supplied by the analytical laboratory. The preservation of the sample includes the refrigeration with either clean ice in sealed bags or freezer packs such as Blue Ice. The laboratory may provide freezer packs with a prepared sample kit. The laboratory will provide directions regarding shipping companies (FedEx or bus lines), and notify the laboratory of the shipment of the samples.

Packaging of the samples in a cooler must be completed so that the cooler will not be opened (such as wrapping with shipping tape and some tamper-proof tape). The samples have to be packed such that the bottles will not leak or break if the container is bumped during transit. Generally, it is recommended to seal sample bottles in Zip-lock (or similar) bags and pack clean newspaper or bubble-wrap around bottles and ice packs to prevent them from moving during transit.

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