INTERTOX

600 Stewart St.
Suite 1101
Seattle, WA 98101 Tel 206.443.2115
U.S.A. Fax 206.443.2117

TECHNICAL MEMORANDUM

To: U.S. EPA, Region 10

From: Richard Pleus and Gretchen Bruce, Intertox, Inc.

Re: Comments on *Relation Between Nitrate in Water Wells and Potential Sources in the Lower Yakima Valley, Washington*, released by U.S. EPA, September, 2012

Date: November 27, 2012

EXECUTIVE SUMMARY

U.S. EPA released its document, *Relation Between Nitrate in Water Wells and Potential Sources in the Lower Yakima Valley, Washington* in September, 2012 (U.S. EPA, 2012a). The document summarizes results of sampling conducted by the Agency to

> …investigate the contribution from various land uses to the high nitrate levels in groundwater and residential drinking water wells, which is the predominant source of drinking water for many residents in the Lower Yakima Valley (U.S. EPA, 2012a, p. ES-1).

These sampling results represent Phase 3 of U.S. EPA's assessment of nitrate sources in the Lower Yakima Valley. In this phase, U.S. EPA sampled drinking water wells and potential sources of nitrate contamination in the Lower Yakima Valley from February to April 2010. U.S. EPA conducted multi-parameter sampling on 29 water wells (26 residential drinking water and 3 dairy supply wells), 12 dairy lagoons, 11 soil samples, 5 dairy manure pile samples, and 3 wastewater treatment plant (WWTP) influent samples.

Considering that U.S. EPA's document contains influential information[1], we reviewed the report to assess whether it adequately meets a minimum level of scientific reliability to support valid conclusions. We examine a number of components of U.S. EPA's work presented in the document, including sampling and analytical program design and data quality issues, data presented for specific sample types and locations, the U.S. EPA-commissioned peer review of the Phase 3 report, and U.S. EPA's conclusions.

We find that a number of issues with the design of the sampling and analytical program result in data that are of insufficient quality to support a scientifically reliable assessment of the potential source of contaminants. Specifically:

- Well sampling locations were selected in a biased manner, such that only those with the highest nitrate concentrations measured during the Phase 2 investigation were

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[1] "Influential," when used in the phrase "influential scientific, financial, or statistical information," means that the Agency can reasonably determine that dissemination of the information will have or does have a clear and substantial impact (i.e., potential change or effect) on important public policies or private sector decisions (U.S. EPA, 2002; p. 19)

selected for sampling in Phase 3. This bias towards higher concentrations can result in invalid conclusions about the extent of contamination.

- Only two well water samples were collected upgradient of the dairy sources, one upgradient of each area, providing inadequate information on background conditions and making it impossible to determine whether concentrations measured downgradient are statistically similar to or different from background.
- U.S. EPA relied on existing residential wells as the source of sampled groundwater, and did not establish that upgradient and downgradient wells sampled the same aquifers.
- Review of nearby land use suggests there are other uncharacterized sources of contamination upgradient of the dairy areas, including livestock activities, cropland, and septic systems.
- Water samples were grab samples that reflect concentrations at a single point in time, and it is unknown how measured results reflect longer term conditions.
- Cropland sampling was limited to sampling of corn, hop, and mint fields, and contributions from other types of crops (e.g., alfalfa, wheat, hay, tree fruit, grapes) were not assessed.
- A substantial percentage of the analytical data are “J qualified”—i.e., reported concentrations are estimated. These concentrations can be biased low or high such that direct quantitative comparison of samples is not appropriate without case-by-case evaluation.
- U.S. EPA had difficulty analyzing both trace organics and wastewater pharmaceuticals, and indicated that results of these analyses should be considered screening level and not fully usable for quantitative evaluations.
- U.S. EPA’s Water Science Lab reported that monensin and lincomycin were detected in the well water field blank sample, such that any detects of these analytes in well water samples should be qualified.
- U.S. EPA did not meet preservation requirements for about one-third of the nitrate analyses, which could bias sample results.
- U.S. EPA did not collect field duplicate samples for well water or lagoon samples due to an oversight and so cannot establish the reproducibility (precision) of sampling and analytical methods applied to these samples.
- Detection limits for some analytes, especially wastewater pharmaceuticals, appear elevated.
- Differential movement of contaminants through soil and groundwater, due to different fate and transport properties, makes it impossible to establish “fingerprints” for these compounds and determine the source of contaminants.
- Nitrate isotopic ratios for synthetic fertilizer and animal waste sources can vary beyond the ranges assumed to by U.S. EPA, and their methodology cannot distinguish between human and other animal sources.

Given the data do not meet a minimum level of reliability, the assessments of Haak Dairy and the Dairy Cluster as well as the assessments of irrigated cropland, wells downgradient of residential septic systems, and WWTP influent cannot be used to make reliable determinations about the source of contaminants. Specifically:

- None of the detected pesticides, trace organics, wastewater pharmaceuticals, or hormones can be reliably attributed to the dairies because of detection in upgradient sources and/or WWTP samples, or data quality issues.
- Veterinary pharmaceuticals can have multiple sources including other agricultural sources and human use, such that downgradient detections cannot be attributed to dairies. In addition, the detection of monensin in the field blank samples indicates that it cannot validly be reported as detected in downgradient samples.
- At the Dairy Cluster, some downgradient concentrations of barium are lower than the upgradient concentration, and some directly adjacent downgradient wells have very different concentrations. In addition, U.S. EPA does not support its assertion that barium is used at the dairies and therefore that the dairies are a potential source.

Regarding the peer review process for the Phase 3 document, U.S. EPA did not conduct an appropriately rigorous peer review in accordance with the spirit of the peer review process as described in U.S .EPA's own guidance. Specifically,

- U.S. EPA's selection of peer reviewers was not transparent, and all four peer reviewers were drawn from federal agencies, potentially limiting the perspectives of provided comments.
- Aside from one peer reviewer, most of the peer review comments received were extremely brief and not adequately rigorous to provide U.S. EPA with sufficient information on the quality of the science presented in the Phase 3 document.
- Of the more rigorous comments received, concerns presented were similar to those we discuss, including the lack of appropriate characterization of contributions from mixed land use, absence of evidence that wells sampled the same aquifers, and misrepresentation of the overlapping ranges of isotopic ratios contributed by different nitrate sources.

In summary, because of the numerous sampling design and analysis issues in the Phase 3 program as well as the potential impact of highly mixed local land uses, we conclude there is insufficient information to determine with scientific certainty whether and how much any of the sources could have contributed to contamination in downgradient wells. In particular, because of the numerous issues highlighted above, no particular location can be implicated as a source of any of the contaminants measured.

1.0 BACKGROUND

U.S. EPA released its document, *Relation Between Nitrate in Water Wells and Potential Sources in the Lower Yakima Valley*, Washington in September, 2012 (U.S. EPA, 2012a). The document summarizes results of sampling conducted by U.S. EPA to

> …investigate the contribution from various land uses to the high nitrate levels in groundwater and residential drinking water wells, which is the predominant source of drinking water for many residents in the Lower Yakima Valley (U.S. EPA, 2012a, p. ES-1).

Nitrate is both natural and a product of human activities. For human related activities, particularly in this area of Washington, the potential sources of contamination the U.S. EPA evaluated include dairies, irrigated cropland, and residential septic systems. Media sampled include water from drinking water wells and dairy sources, dairy lagoons, soils from dairy application fields and irrigated croplands, and wastewater treatment plant (WWTP) influent. Analytes include various forms of nitrogen, major ions, isotopes of nitrogen, pharmaceuticals (veterinary and human), steroids and hormones, pesticides, and microbes.

The study was conducted in three phases. The goal of Phase 1 was to identify major sources of nitrogen in the study area, based on historical records and available information. The goal of Phase 2 was to evaluate nitrate contamination of groundwater downgradient of dairies, irrigated cropland, and residential septic systems, and identify sampling locations for Phase 3. The goal of Phase 3 was to further evaluate nitrate contamination and evaluate whether chemicals other than nitrate are associated with specific sources and can be used to link nitrate contamination in groundwater and drinking water wells to those sources. The U.S. EPA (2012a) report focuses primarily on the Phase 3 sampling.

In Phase 3, U.S. EPA sampled drinking water wells and potential sources of nitrate contamination in the Lower Yakima Valley from February to April 2010. U.S. EPA collected 331 samples from residential drinking water wells for nitrate and bacteria, and conducted multi-parameter sampling on 29 water well samples (26 residential drinking water and 3 dairy supply wells), 12 dairy lagoon samples, 11 soil samples, 5 dairy manure pile samples, and 3 WWTP influent samples. U.S. EPA published a Quality Assurance Project Plan (QAPP) in April 2010, which describes the objectives of the sampling and analytical program and the methods to be followed (U.S. EPA, 2010).

The Agency released its report describing the results of the Phase 3 sampling in the fall of 2012.

2.0 INTERTOX'S REVIEW

Intertox reviewed the scientific reliability of the work conducted by U.S. EPA, focusing on the Phase 3 results including the U.S. EPA (2012a) report and supporting documents [e.g., the Phase 3 QAPP (U.S. EPA, 2010); QAPP deviations Corrective Action Form (CAFs) and Sample Alteration Forms (SAFs)[2]; Quality Assurance Validation Memos[3]; and Phase 3 data[4]]. Based on our review, we have prepared these comments.

In reviewing this work, Intertox considered the fundamental tenets of scientific investigation. Specifically, we considered the experimental design of Phase 3, the measurement methods, the quality of the data, and the conclusions reached based on these data. To support our evaluation, we considered a number of relevant guidance documents.

Overall, in our assessment of the U.S. EPA (2012a) document, we have found that a number of experimental design and data quality issues, including selection of biased sample locations, lack of proper background (upgradient) samples, and analytical problems resulting in a large percentage of unusable or qualified sampling data, result in data that cannot be used to draw scientifically valid conclusions about the source of nitrate or other contaminants measured downgradient of dairies. In addition, while U.S. EPA has issued guidance for designing and conducting sampling and analytical studies of this type, it does not follow its own guidance in many cases.

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[2] QAPP deviations Corrective Action Form (CAFs) and Sample Alteration Forms (SAFs) available at ftp://ftp.epa.gov/reg10ftp/sites/yakima/QAPP_Deviations_SAFs_and_CAFs/

[3] Quality Assurance Validation Memos available at ftp://ftp.epa.gov/reg10ftp/sites/yakima/YV_Validation_Memos/

[4] Phase 3 data available at ftp://ftp.epa.gov/reg10ftp/sites/yakima/groundwater_data/

The following sections summarize our comments on (1) the sampling and analytical program design and data quality issues, (2) results for specific sample types and locations, (3) the U.S. EPA-commissioned peer review of the Phase 3 report, and (4) U.S. EPA's conclusions.

3.0 REQUIREMENTS FOR INTEGRITY OF INFLUENTIAL SCIENTIFIC DATA

In the case of the Phase 3 sampling and analytical program, U.S. EPA is both a collector and generator of scientific data, and a user of this information to support decisions about sources and implications of nitrate contamination in the Lower Yakima Valley. In this capacity, U.S. EPA has stated that "EPA must rely upon information of appropriate quality for each decision we make" and that it is "…dedicated to the collection, generation, and dissemination of high quality information" (U.S. EPA, 2002).

To maximize the quality of information they disseminate, U.S. EPA has published policy and procedural guidance. This policy and guidance is found in a number of different documents, but one of the foundational documents is entitled *Guidelines for Ensuring and Maximizing the Quality, Objectivity, Utility, and Integrity of Information Disseminated by EPA* (U.S. EPA, 2002). [5]

In regards to the quality of information it uses to make decisions, the Agency states that it issues these guidelines to:

> …ensure and maximize the quality, including objectivity, utility and integrity, of disseminated information… "Objectivity" focuses on whether the disseminated information is being presented in an accurate, clear, complete, and unbiased manner, and as a matter of substance, is accurate, reliable, and unbiased. "Integrity" refers to security, such as the protection of information from unauthorized access or revision, to ensure that the information is not compromised through corruption or falsification. "Utility" refers to the usefulness of the information to the intended users (U.S. EPA, 2002).

Regarding the situations to which these guidelines apply, U.S. EPA (2002) states:

> These Guidelines apply to "information" EPA disseminates to the public. "Information," for purposes of these Guidelines, generally includes any communication or representation of knowledge such as facts or data, in any medium or form.

Thus, U.S. EPA's guidelines for data quality would apply to information collected in the Phase 3 program.

U.S. EPA emphasizes the particular importance of ensuring the quality of "influential" information, indicating that such information "should meet a higher standard of quality" (U.S. EPA, 2002). U.S. EPA defines "influential information" as follows:

> "Influential," when used in the phrase "influential scientific, financial, or statistical information," means that the Agency can reasonably determine that dissemination of the information will have or does have a clear and substantial impact (i.e., potential change or effect) on important public policies or private sector decisions (U.S. EPA, 2002; p. 19);

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[5] U.S. EPA developed this guidance in response to guidelines issued by the Office of Management and Budget (OMB)1 under Section 515(a) of the Treasury and General Government Appropriations Act for Fiscal Year 2001 (Public Law 106-554; H.R. 5658).

and:

> For disseminated influential original and supporting data, EPA intends to ensure reproducibility according to commonly accepted scientific, financial, or statistical standards. It is important that analytic results for influential information have a higher degree of transparency regarding (1) the source of the data used, (2) the various assumptions employed, (3) the analytic methods applied, and (4) the statistical procedures employed (U.S. EPA, 2002; p. 21).

U.S. EPA has also emphasized the importance of peer review in ensuring the quality of its scientific data, stating in its *Peer Review Handbook* (U.S. EPA, 2012c) that:

> Science is the foundation that supports all of our work here at EPA. Strong, independent science is of paramount importance to our environmental policies. The quality of science that underlies our regulations is vital to the credibility of EPA's decisions and ultimately the Agency's effectiveness in protecting human health and the environment. One important way to ensure decisions are based on defensible science is to have an open and transparent peer review process.

Regarding the peer review process, U.S. EPA states:

> Peer review is a documented critical review of a specific Agency scientific and/or technical work product. Peer review is conducted by qualified individuals (or organizations) who are independent of those who performed the work, and who are collectively equivalent in technical expertise (i.e., peers) to those who performed the original work. Peer review is conducted to ensure that activities are technically supportable, competently performed, properly documented, and consistent with established quality criteria. Peer review is an in-depth assessment of the assumptions, calculations, extrapolations, alternate interpretations, methodology, acceptance criteria, and conclusions pertaining to the specific major scientific and/or technical work product and of the documentation that supports them. Peer review may provide an evaluation of a subject where quantitative methods of analysis or measures of success are unavailable or undefined such as research and development… Regardless of the timing of peer review, the goal is ensuring that the final product is technically sound (U.S. EPA, 2012c; p. 12).

Using U.S. EPA's guidelines as well as other standard scientific guidelines, we assessed whether the work, data, process, and procedures of U.S. EPA's Phase 3 assessment meet accepted data quality standards.

4.0 COMMENTS ON U.S. EPA'S PHASE 3 SAMPLING AND ANALYTICAL PROGRAM

4.1 General Concerns about Sampling and Analytical Program Design and Data Quality Issues

The following summarizes our comments related to the sampling and analytical program design and data quality issues.

In their Quality Assurance Project Plan (QAPP) for Phase 3, U.S. EPA (2010) stated their goal for the sampling program as follows (p. 6-7):

> With this study, EPA proposes an even-handed assessment of potential sources of nitrate by working to analytically detect trace concentrations of compounds released with the nitrate. We will also look at other chemical changes which have been used to

> link up-gradient land use to effects in drinking water wells. EPA hopes to assess which activities on the landscape are contributing excess nitrate to shallow ground water. In this way we can determine which practices or activities are protective of continuing ground-water quality, and which activities are threats to the ground-water resource. In addition, the sampling from this project will provide enforcement-quality data for nitrates and bacteria that could be used in later enforcement actions…
>
> In order to develop a linkage between the high nitrate observed in a private drinking water well and the land use which is adversely affecting ground-water quality it will be necessary to look beyond nitrate. Analytical methods are available to detect a wide range of organic compounds which originate with the nitrate and which may provide a linkage back to the source. By looking at the agricultural chemicals, the hormones or the personal care products traveling with nitrate, we hope to link and identify the farming practice, the confined animal feeding operation or the rural residential septic system which is the source of the nitrate, respectively. Many of these trace organics can be detected at exquisitely low concentrations – some as low as single digit parts per trillion.

However, because of numerous deficiencies with the program design as well as analytical problems that resulted in unusable or estimated data, the resulting data set was insufficient to support scientifically valid conclusions about the sources of contaminants to downgradient wells. General issues with the dataset are discussed below.

4.1.1 U.S. EPA selected groundwater well sampling locations in a biased manner

In Phase 3, groundwater well sampling locations were chosen from those locations expected to have the highest nitrate concentrations. This has at least two implications: (1) wells with lower concentrations that might provide a more complete picture of contaminant presence and behavior were not sampled, and (2) reported concentrations likely overestimate average concentrations at downgradient sites. Thus, sampling bias may lead to invalid conclusions about the nature and extent of contamination.

Specifically, U.S. EPA selected the wells that had the highest nitrate concentrations in Phase 2 for more extensive sampling and analysis in Phase 3 (U.S. EPA, 2012a; p. 14). U.S. EPA (2010) stated this intention in its Phase 3 QAPP, indicating, "Phase 3 will include revisiting the domestic wells which tested highest for nitrate in Phase 2" (p. 8).

In addition, the Phase 2 sampling results were themselves biased high: U.S. EPA (2012a) states with regard to the Phase 2 sampling (p. 13), "The sampling team also used nitrate colorimetric test strips (Hach® test strips) as a field screening tool to provide an indication of whether the water exceeded the MCL [maximum contaminant limit] 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 Hach® test strip indicated the water may exceed the MCL (10 mg/L), samples were collected for analysis by EPA's Manchester Environmental Laboratory…" In total, in Phase 2, 331 homes were screened (between February 22−March 6, 2010), and the lab received 189 samples for analysis of which 102 were analyzed for nitrate and chloride, 2 for nitrate and nitrite, and 123 for total Kjeldahl nitrogen (TKN) (p. 13). Samples for 67 of those homes, or about 20%, were found to exceed the MCL of 10 mg/L for nitrate.

U.S. EPA (2012a) acknowledges the sampling bias, stating (p. 14), "The percentage of homes with nitrate levels in wells above the MCL in this study were higher than the 12 percent from earlier studies because the homes sampled in Phase 2 were selected based on their proximity to likely sources. This method of selection would be expected to bias the results compared with a study where the sampling locations were selected randomly." Thus, sampling results obtained during Phase 3 cannot be interpreted as giving a scientifically valid picture of the nature and extent of contamination in the sampled areas.

4.1.2 U.S. EPA collected insufficient upgradient samples to discern measured downgradient levels from background

In Phase 3, U.S. EPA (2012a) states that they collected and analyzed samples from "representative" residential drinking water wells upgradient of the dairies (p. ES-3, p. 14), i.e., at locations not expected to be impacted by dairy activities. However, they do not specify what makes these wells "representative," and they only collected samples from two upgradient locations, one upgradient of each dairy sampling area (WW-01 upgradient of Haak Dairy, sampled April 13, 2010, and WW-06 upgradient of the Dairy Cluster, sampled April 15, 2010).

Two additional wells upgradient of the Dairy Cluster were sampled during Phase 2 but not Phase 3 (U.S. EPA, 2012a, footnote, p. 16). Table C1 (U.S. EPA, 2012a) indicates that "nitrate as N" was measured in each of these wells and concentrations at both were 5 mg/L (in wells WW-22085 and WW-22103). U.S. EPA does not indicate why these wells weren't evaluated further in Phase 3. Evaluating only one upgradient well from each site results in a dataset that is inadequate to conduct statistically valid comparisons of upgradient and downgradient concentrations.

In any experiment conducted to determine the nature and source of environmental contamination, collection of sufficient background samples is critical. Per U.S. EPA (1989a), "Background sampling is conducted to distinguish site-related contamination from naturally occurring or other non-site-related levels of chemicals." Specifically, when sampling groundwater, the intent of collecting samples from upgradient wells is to provide information on background conditions hydraulically upgradient of a site, for comparison to wells suspected of being impacted by site-related activities. For example, non-point sources such as agricultural practices as well as industrial or commercial activities may influence background water quality and should be distinguished from site-related contamination (Aller et al, 1991).

U.S. EPA's *RCRA Ground-Water Monitoring Technical Enforcement Guidance Document* (U.S. EPA, 1986) elaborates on principles for appropriate design of sampling programs to characterize background in groundwater monitoring programs. U.S. EPA (1986) states (p. 67):

> There are at least three main questions that the technical reviewer should ask when reviewing the decisions the owner/operator has made regarding the placement of the background monitoring wells:
>
> - Are the background wells far enough away from waste management areas to prevent contamination from the hazardous waste management units?
> - Are enough wells installed and screened at appropriate depths to adequately account for spatial variability in background water quality?
> - Are well clusters used at sampling locations to permit comparisons of background ground-water data with downgradient ground-water data obtained from the same hydrologic unit?

They further state that, by regulation, "the owner/operator must install as a minimum one background well." Indeed, 40 CFR 265.91 (Interim Status Standards for Owners and Operators of Hazardous Waste Treatment, Storage, and Disposal Facilities, Subpart F: Ground-Water Monitoring, 265.01− Ground-water monitoring system) states that a groundwater monitoring program to support investigations to meet the goals of the Resource Conservation and Recovery Act (RCRA) must consist of at least four wells: one upgradient from the unit and three hydraulically downgradient. The upgradient wells are intended to collect samples that are representative of background ground-water quality in the uppermost aquifer near the facility and that are not affected by the facility. The "number, locations, and depths must ensure that they immediately detect any statistically significant amounts of hazardous waste or hazardous waste constituents that migrate from the waste management area to the uppermost aquifer." However, while the regulations state that one upgradient well is sufficient, they are clear that monitoring at the upgradient well(s) must take place quarterly for a full year to establish background parameters indicating the suitability of the ground water as a source of drinking water (40 CFR 265.92(c)(1))—in other words, sampling once at a single upgradient well is insufficient.

With regard to numbers of wells, U.S. EPA (1986) (p. 67) further cautions that one background well may be insufficient:

> …a facility that uses only one well for sampling background water quality may not be able to account for spatial variability. It is, in fact, a very unusual circumstance in which only one background well will fully characterize background ground-water quality…In most cases, the owner/operator should install multiple background monitoring wells in the uppermost aquifer to account for spatial variability in background water quality data.

They elaborate (p. 132):

> The inclusion and exclusion of various components of variability in background ground-water data have a substantial impact on the performance of the statistical test. When a background sampling program includes data from only one upgradient well, there is no component of spatial variability in the background data.

Because only one upgradient sample was collected for comparison to samples collected downgradient of each dairy sampling area, there is insufficient statistical power to determine whether concentrations measured downgradient are similar to or different from background. As such, there is no scientific certainty about any conclusions drawn in this regard. Because of the deficiency in upgradient/background data, the following assertion by U.S. EPA (2012a), for example, is not valid (p. 21), "...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 a well upgradient of the dairy lagoon, it indicates the dairy lagoon is a likely source of chloride to the downgradient well."

In addition to the insufficient number of upgradient samples near the dairies, U.S. EPA collected *no* well water samples upgradient of the other types of potential contaminant sources evaluated in the program, including residential septic systems and irrigated crop lands. Consequently, U.S. EPA cannot draw valid conclusions about the type and extent of contamination contributed from these sources as opposed to other potentially confounding sources.

Finally, U.S. EPA collected no background soil samples from any location, to characterize concentrations of constituents in soil in the Lower Yakima Valley from such sources as atmospheric deposition, or from other nonpoint residential or urban/industrial sources.

4.1.3 U.S. EPA does not demonstrate that the upgradient and downgradient wells sampled the same hydrologic units

When assessing whether a potential source could have impacted a drinking water aquifer, it is critical to confirm that sampling data intended to characterize upgradient and downgradient conditions are drawn from the same hydrologic unit. Water collected from different units would be expected to have different characteristics and concentrations. Without confirmation of this, U.S. EPA cannot support conclusions based on comparisons between these wells—differences in measured upgradient and downgradient concentrations could be due to sampling of different aquifers rather than the introduction of a contaminant source between the upgradient and downgradient wells.

For example, U.S. EPA (1986) cites RCRA requirements for groundwater sampling that state with regard to sampled aquifers (p. 66):

> The upgradient wells must be located and constructed to provide representative samples of groundwater in the same portion of the aquifer monitored by the downgradient wells to permit a comparison of groundwater quality (40 CFR 265, Subpart F, 265.92(a)(1)).

They further elaborate (p. 67):

> The owner/operator should also install enough background monitoring wells to allow for depth-discrete comparisons of water quality. This means simply that for downgradient wells completed in a particular geologic formation, the owner/operator should install upgradient well(s) in the same portion of the aquifer, so that the data can be compared on a depth-discrete basis…

In its QAPP for Phase 3, U.S. EPA (2010) acknowledged that sampling from domestic drinking water wells might result in collection of samples from different water horizons, but determined that time and resource limitations outweighed this concern (p. 8):

> The use of private domestic water supply wells requires contacting individual home owners and requesting access to sample their drinking water. It further involves using wells installed for another purpose for use as groundwater monitoring wells. These wells may not be screened at horizons where they optimally intersect the water we seek to monitor. However, the alternative of either direct-push geoprobe style investigatory soil borings or dedicated well installations is not feasible given our interest in timely collection of this data and the resources available.

Despite their lack of knowledge about the horizon monitored, U.S. EPA proceeded to collect samples from these wells and attempted to draw conclusions based on these data without verifying that samples from locations of interest were collected from the same aquifers.

U.S. EPA (2012a) makes a number of statements that demonstrate, post sampling, they still lacked critical information about the aquifers that were sampled. For example:

- When U.S. EPA collected samples from drinking water wells, they "sampled residential drinking water from a tap and depth to water was not measured" (p. 17).

- U.S. EPA (2012a) acknowledges (p. ES-3, p. 3) that “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.”
- With regard to Haak Dairy, U.S. EPA (2012a) states (p. ES-5), “Information on the construction and depth of the upgradient and one downgradient well would be helpful to provide additional certainty regarding the likely sources.” They further state (p. 36), “Available information about the construction and depth of WW-03 and WW-04, the downgradient wells, suggest they are completed in the alluvial aquifer at depths of 95 feet and 88 feet. Information about the upgradient well, WW-01, is limited.”
- With regard to the Diary Cluster, U.S. EPA (2012a) states (p. ES-6), “As with the Haak Dairy, information on the construction and depth of the upgradient well and five of the downgradient water wells sampled during Phase 3 would be helpful to clarify the contribution of sources to the increased concentrations measured in the downgradient wells.”
- U.S. EPA (2012a) suggests that the dairy supply wells may draw from a different aquifer than downgradient residential wells, stating (p. 85), “The water in the dairy supply wells that are known to be screened in the deeper basaltic aquifer is older than in the downgradient residential wells which are commonly screened in the shallower alluvial aquifer.”

Regarding the complex groundwater flow in the Lower Yakima Valley, U.S. EPA (2012a) acknowledges that without more complete information, they cannot draw definitive conclusions about the basis of concentration differences reported in upgradient vs. downgradient study wells. For example, they state (p. 8):

> The Lower Yakima Valley is filled with sediments shed by the ridges at the margins of the study area and those deposited in the valley bottom by the Yakima River. These sediments 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 groundwater velocities among aquifer materials of such contrasting grain size (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 nitrate could produce different downgradient effects in groundwater (such as nitrate in water wells), even in wells from neighboring homes.

Without confirming that upgradient and downgradient samples are drawn from the same aquifers, U.S. EPA cannot make valid conclusions that differences in upgradient and downgradient concentrations are due to the contribution of an intervening source. An example of a conclusion drawn by U.S. EPA (2012a) that cannot be reliably and scientifically supported without more complete hydrologic information is as follows (p. 38):

> Based on the observed concentrations, chloride and other ions are being introduced to the aquifer between the upgradient and downgradient wells at the Haak Dairy. One explanation for the observed increase in these major ions is that the dairy lagoons are

> introducing these ions to the groundwater. As with total nitrogen, this indicates that the Haak Dairy is a likely source of the major ions in the three downgradient residential drinking water wells at the Haak Dairy.

Likewise, U.S. EPA's conclusions with regard to the Dairy Cluster can also not be supported, for example where they state (U.S. EPA, 2012a; p. 54):

> The figures show a similar pattern to that observed at the Haak Dairy, with elevated concentrations in the downgradient wells (WW-10 to WW-17) compared with the upgradient wells (WW-06) and the supply wells (WW-07 to WW-09), with the highest concentrations in the lagoons. Alkalinity also showed a similar pattern. The increase in the concentrations ranges from up to: seven-fold for sodium; nine-fold for magnesium; 10-fold for calcium; and more than 30-fold for chloride. Potassium showed a slight increase. As with the Haak Dairy, sulfate showed the largest increase in concentration between the upgradient and downgradient wells. As with the Haak Dairy, the dairy sources are a likely source of major ions in the downgradient water wells.

4.1.4 U.S. EPA does not acknowledge other land uses that could contribute contamination upgradient of dairy, cropland, and residential septic sources

Overall, because of the large number of potential sources to groundwater contamination in the Lower Yakima Valley, without a more carefully controlled sampling program, it is impossible to assign measured contamination to a given source. Multiple potential groundwater contaminant sources exist in the Lower Yakima Valley, including agricultural, industrial, and human wastewater sources.

For example, U.S. EPA (2012a) states that sampled dairies were selected in part because of "minimal upgradient nitrate sources to the extent possible" (p. 17). However, examination of the Haak Dairy and Dairy Cluster locations, including the information provided in Figure 7 (Lower Yakima Valley Dairy Locations), Figure 8 (Lower Yakima Valley Crop Inventory), and Figure 9 (Lower Yakima Valley Septic System Distribution) suggests that additional uncharacterized sources could contribute to concentrations measured in these wells. Specifically:

- Figure 8 juxtaposed with Figure 7 suggests that some other types of crops (including tree fruit and corn) are grown north of Haak Dairy, some croplands are north and northeast of the Dairy Cluster, and some septic systems are north and northeast of Haak Dairy and the Dairy Cluster.
- A large livestock facility and what appears to be an adjacent application field are located to the northeast of Haak Dairy (not shown in Figure 7, but visible on Google Earth).

In addition, based on Figure 12 and the illustrated groundwater flow direction, WW-01 does not appear to be truly upgradient of wells WW-03, WW-04, and WW-05 at Haak Dairy—the "upgradient" well appears to be further to the west of the other wells. The impact of this discrepancy on comparisons between upgradient and downgradient concentrations is uncharacterized.

The sampling locations intended to reflect irrigated cropland and septic sources may also be impacted by additional sources. U.S. EPA (2012a) indicated that the irrigated cropland sampling locations were selected in part because of "minimal upgradient nitrate sources" (p.

18), and that residential septic system sampling locations were selected in part because of "minimal upgradient nitrate sources other than septic" (p. 18). However, the cropland locations near Mabton are located downgradient of populated areas where septic systems would be expected (some are indicated in Figure 9), and examination of satellite views (e.g., Google Earth) as well as Figure 7 shows a number of dairies or other livestock facilities in this area including upgradient. In fact, regarding these locations, U.S. EPA acknowledges (p. 84), "the irrigated crop fields are surrounded by similar agricultural uses, and many are situated downgradient of dairies, making more difficult EPA's ability to discern the source of nitrate in drinking water wells downgradient of the irrigated crop fields." The impact of these uncharacterized sources on conclusions about irrigated cropland and septic system sources is unknown, particularly given that background groundwater or soil samples are not collected upgradient of the "irrigated cropland" and "septic system" locations, as discussed in Section 4.1.2. Because of inadequate control of these sampling programs, no scientific conclusions can be drawn about the nature or contribution of any of these sources to contamination of soil or groundwater in the Lower Yakima Valley.

4.1.5 U.S. EPA collected grab samples, which are insufficient to characterize long term conditions

All of the samples collected by U.S. EPA (2012a) were grab samples, i.e., single samples that represent conditions at a discrete location and time. However, it is recognized that groundwater concentrations, in particular, can fluctuate over time. The relationship between concentrations measured in the groundwater samples (collected between February through April 2010) and average or longer term conditions is not known, i.e., whether measured concentrations are higher or lower than average.

Barcelona et al. (1989) describe a number of factors that can cause temporal variability in measured groundwater concentrations, including "'natural' causes, physical-chemical transport properties or sampling-related variables:"

> Examples of natural causes are inhomogenous spatial distributions of the constituents superimposed on the local and regional ground-water flow field, temporal variability in recharge, and inhomogeneities in aquifer properties (e.g., transmissivities). Physical-chemical transport properties may include dispersitivities, sorptive interactions or chemical reactions. Sampling-related variables are well design, sampling devices, and field sampling and laboratory analysis protocols. Other sources of temporal variability in water-quality data which are often attributed to natural effects include hydrologic transience, the time and space variations in contaminant source, strength and composition, and the interactions between reactive chemical, biochemical and mineral constituents in recharge or flowing ground water.

Regarding the design of sampling programs to capture the variability of groundwater concentrations, it is concerning that U.S. EPA (2012a) does not conform to its own recommendations. A U.S. EPA research document, *Sampling Frequency for Ground-Water Quality Monitoring* (U.S. EPA, 1989b), suggests that "quarterly sampling frequency is a good initial starting point for ground-water quality monitoring network design, though bimonthly frequency may be preferred for reactive chemical constituents."

Concentrations of some of the analytes included in the U.S. EPA (2012a) program are expected to show seasonal variations. For example, concentrations of fertilizers and pesticides in soil are expected to be higher immediately following application; without more careful sampling, it is not known how these temporal variations affect groundwater concentrations. In addition, time of irrigation or precipitation could impact surface soil concentrations and rates of movement of compounds through soil.

U.S. EPA (2012a) acknowledges the potential effect of temporal factors on pesticide levels, stating (p. 23), “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 before the time of sample collection and may not have been detected in the soil samples collected by EPA.” However, U.S. EPA (2012a) does not provide any information on the time of application of pesticides or fertilizers compared to the dates of soil sampling that might allow an assessment of whether sampled results are biased low or high relative to average.

Several of the well sampling locations appear to be in close proximity to one another; one would expect similar concentrations to be measured in samples from these wells. For example, collocated samples were collected at a lagoon at D and A Dairy (samples LG-08 and LG-09) and at a lagoon at Cow Palace (samples LG-11 and LG-12) (U.S. EPA, 2012a; p. 53). However, there were wide variations in some parameters from LG-08 and LG-09, particularly concentrations of trace organics, wastewater pharmaceuticals, and veterinary pharmaceuticals (e.g., in these samples, reported trace organic concentrations varied by about four to five fold between the two samples, and two wastewater pharmaceuticals were reported detected in LG-08 at concentrations about 10-fold higher than their detection limits, but were nondetect in LG-09). The range of concentrations reported for samples collected at nearly the same location and time illustrate the heterogeneous nature of the sampled media and the potential variability in repeated sample measurements. Without further experimentation and investigation to quantify this variability, the potential for erroneous conclusions about similarities and differences in contaminant concentrations based on very small sample sizes is significant.

4.1.6 U.S. EPA did not demonstrate that “irrigated crop” samples are representative of contributions from cropland in the Lower Yakima Valley

U.S. EPA collected samples at and near six irrigated crop locations, including two fields each of corn, hops, and mint, to assess the potential contribution of cropland to nitrate and other constituents in well water. They selected these types of crops because “they require significant quantities of nitrogen to produce the large amounts of plant biomass for yield in contrast with other crops such as tree fruit” (U.S. EPA, 2012a; p. 17). In the Phase 3 QAPP, they stated (U.S. EPA, 2010), “For crop land, three crops were selected based on fertilizer application rates and pesticide usage. Corn fields, hop yards and mint fields were selected based on the amount of fertilizer used in their culture” (p. 16).

However, numerous other types of crops grown in the Lower Yakima Valley were not sampled to determine their contribution to nitrate and other constituents in groundwater. Thus, while a key objective of the sampling program was “attempting to use linking or tracer compounds to evaluate linkage between up-gradient land uses to nitrate in down-gradient drinking water wells” (U.S. EPA, 2010; p. 15), U.S. EPA did not attempt to comprehensively determine the sources of these “linking or tracer” compounds in the Lower Yakima Valley. Lack of data on these contributions reduces scientific certainty about possible sources of contaminants to groundwater.

U.S. EPA (2012a) stated that they initially considered irrigated cropland to be a potential source of nitrate to groundwater due to synthetic fertilizer application (which they assumed they could distinguish from fertilizers of animal waste origin using isotopic analysis), but admit that “through this study, it became clear that several of the irrigated crop fields sampled had also received manure applications” (p. 2). Consequently, U.S. EPA has demonstrated that potential cropland and livestock operation sources of nitrate cannot be reliably distinguished.

In addition to nitrate, the Phase 3 sampling program included numerous other analytes “to evaluate whether chemicals other than nitrate can be used to identify likely sources of the nitrate contamination in the groundwater and drinking water wells.” However, other crop types can contribute to these contaminant types and may influence conclusions based on these analytes. For example, numerous pesticides are applied to tree fruits (Table 1) and grapes (Table 2) in Washington State. Other crops grown on significant acreage in Yakima County that were not considered in the U.S. EPA sampling program include alfalfa, winter wheat, and hay (U.S. EPA, 2012a; Appendix G).

Further, soil samples collected at each crop field were collected from 30 shallow (1 inch) soil samples per field that were composted to give a “representative” soil sample (U.S. EPA, 2012a; p. 17). Thus, soil data cannot be used to discern variations in concentrations across the crop fields; compositing makes it impossible to determine whether contamination was relatively homogeneous or whether localized hot spots biased average concentrations upward.

Table 1. Examples of Tree Fruit Pesticides Used in Washington State

Fungicides/Bactericides	Herbicides	Insectides and Miticides	
A-506 pseudomonas	2,4-d	Abamectin	Hydrochloride
Fluorescens	Carfentrazone-ethyl	Acequinocyl	Imidacloprid
Azoxystrobin	Clopyralid	Acetamiprid	Indoxacarb
Bacillus pumilus	Dichlobenil	Azadirachtin	Kaolin clay
Bacillus subtilis	Diuron	Azinphos methyl	Lambda-cyhalothrin
Boscalid	Fluazifop	Bacillus thuringiensis	Lime sulfur/calcium
Captan	Fluroxypyr	Bifenazate	Malathion
Chlorothalonil	Glufosinate-ammonium	Buprofezin	Methidathion
Copper hydroxide	Glyphosate	Carbaryl	Methomyl
Cyprodinil	Isoxaben	Chlorantraniliprole	Methoxyfenozide
Dodine	Isoxaben	Chlorpyrifos	Novaluron
Fenarimol	Napropamide	Clofentezine	Oxamyl
Fenbuconazole	Norflurazon	Clothianidin	Permethrin
Fish oil	Oryzalin	Deltamethrin	Petroleum oil
Fixed copper	Oxyfluorfen	Diazinon	Pheromone
Flutriafol	Paraquat	Dicofol	Phosmet
Iprodione	Pendimethalin	Diflubenzuron	Polysulfide
Kaolin clay	Pronamide	Dimethoate	Potassium salts of fatty acids
Kresoxim-methyl	Pyraflufen-ethyl	Emamectin benzoate	Propargite
Lime sulfur/calcium polysulfide	Rimsulfuron	Endosulfan	Pyrethrins
Mancozeb	Sethoxydim	Esfenvalerate	Pyridaben
Metconazole	Simazine	Etoxazole	Pyriproxyfen
Metiram	Terbacil	Fenbutatin oxide	Rosemary/peppermint oil
Myclobutanil	Trifluralin	Fenpropathrin	Spinetoram
Oxytetracycline		Fenpyroximate	Spinosad
Petroleum oil		Fish oil	Spirodiclofen
Potassium bicarbonate		Flonicamid	Spirotetramat
Potassium salts of fatty acids		Flubendiamide	Sulfur
Propiconazole		Formetanate	Tebufenozide
Pyraclostrobin		Gamma-cyhalothrin	Thiacloprid
Quinoxyfen		Granulosis virus	Thiamethoxam
Streptomycin sulfate		Hexythiazox	
Sulfur			
Tebuconazole			
Thiophanate-methyl			
Thiram			
Trifloxystrobin			
Triflumizole			
Ziram			

Source: WSU Extension (2011).

Table 2. Examples of Grape Pesticides Used in Washington State

Fungicides	Herbicides	Insectides and Miticides	
Azoxystrobin Boscalid Captan Cyprodinil Difenconazole Fenarimol Fenhexamid Iprodione Kresoxim-methyl Metrafenone Micronized flowable sulfur Myclobutanil Paraffinic oil Potassium bicarbonate Pyraclostrobin Pyrimethanil Quinoxyfen Sulfur Sulfur dust Tebuconazole Tetraconazole Trifloxystrobin Triflumizole	2,4-D Carfentrazone-ethyl Clethodim Dichlobenil Diuron Flumioxazin Fluazifop Glufosinate Glyphosate Napropamide Nonionic surfactant Norflurazon Oryzalin Oxyfluorfen Paraquat Pendimethalin Pronamide Pyraflufen ethyl Rimsulfuron Sethoxadim Simazine Trifluralin	Acetamiprid 1,3-dichloropropene Beta-cyfluthrin Bifenthrin Buprofezin Carbaryl Chlorantraniliprole Cyfluthrin Dinotefuran DiTera Dormant oil Fenpropathrin Imidacloprid Malathion Metham sodium Potassium salts Promax Spineoram Spinetoram Spinosad Sodium tetrathiocarbonate Thiamethoxam Zeta-cypermethrin	Abamectin Bifenizate Fenpyroximate Propargite

Source: WSU Extension (2012)

4.1.7 U.S EPA's Phase 3 results for a large percentage of analyte types and matrices are unusable or qualified due to analytical difficulties

U.S. EPA (2012a) reported problems with conducting analyses for a number of the analyte groups and media. As a result, some data were identified as unusable whereas other analyses were not conducted. In addition, a large percentage of the remaining data was characterized as qualified. The lack of complete and high quality data sets for all compound types in all media diminishes the ability to draw reliable scientific conclusions about possible sources of these contaminants.

As a result, for many of the parameters, U.S. EPA does not meet its Completeness criterion specified in its Phase 3 QAPP (U.S. EPA, 2010), specifically, "Completeness is the percentage of valid results obtained compared to the total number of samples taken for a parameter. Since sampling from inspections are usually grab and limited in number of samples, the number of valid results obtained from the analyses are expected to be equal or better than 85%" (p. 14).

Specific data quality problems are described below.

First, a large proportion of the analytical results in all media are "J qualified." For example, approximately 64% of the pesticides measurements in well water are J qualified, as are 47% of the wastewater pharmaceuticals measurements in well water. A large proportion of other sample types are also J qualified (e.g., 52% of trace organics and 20% of wastewater pharmaceuticals measurements in lagoons; 21% of pesticides measurements in soils; and 52% of trace organics, 26% of wastewater pharmaceuticals, and 37% of veterinary pharmaceuticals measurements in WWTP samples). Per U.S. EPA (1996), the J qualifier indicates,

> …the analyte was positively identified- the associated numerical value is the approximate concentration of the analyte in the sample. The "J" qualifier indicates

> that one or more QA/QC requirements have not met contact required acceptance criteria but the instrumentation was functioning properly during the analysis. For example, a "J" qualifier may indicate that the sample was difficult to analyze or that the value may lay near the low end of the linear range of the instrument. "J" data are considered biased, but provide definitive analyte identification.

While a J qualifier does indicate positive identification of an analyte, U.S. EPA (1996) emphasizes that "All qualified data should be carefully evaluated to determine if the data are biased…qualified data should always be carefully reviewed on a case-by-case basis prior to use…" They further elaborate,

> It is important to understand the direction of bias associated with "J" qualified data before using the data to document an observed release. Qualified data may have high, low, or unknown bias. A low bias means that the reported concentration is likely an underestimate of the true concentration. For example, data may be biased low when sample holding times for volatile organic compounds (VOCs) are moderately exceeded or when recovery of QA/QC compounds is significantly less than the amount introduced into the sample. Low surrogate recovery would also indicate a low bias. A high bias means the reported concentration, is likely an overestimate of the true concentration. For example, data may be biased high when recovery of QA/QC compounds is significantly higher than the amount in the sample. A bias is unknown when it is impossible to ascertain whether the concentration is an overestimate or an underestimate. For example, an unknown bias could result when surrogate recoveries exceed method recovery criteria and matrix spike/matrix spike duplicate compounds below method recovery criteria fail the relative percent difference (RPD) criteria in the same sample.

Thus, the uncertainty associated with J qualified data limits the validity of any quantitative comparisons between samples that have this qualifier. In our review of U.S. EPA's Phase 3 assessment, all J qualified data appear to be evaluated as if reported concentrations represent true concentration values, without considering the potential bias in the data on a case-by-case basis.

Second, U.S. EPA indicates that pesticide results from dairy lagoon and WWTP samples are unusable. Specifically, U.S. EPA (2012a) states (p. 23),

> 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 sample matrix; however, a procedure to resolve the matrix interference could not be developed within the maximum holding time specified for these samples. The maximum sample holding times would have been exceeded by the time the laboratory could have developed and tested an effective and reliable procedure. Therefore, the pesticide results for the dairy lagoon and WWTP samples are considered unusable for all purposes.

Regarding these pesticide data, U.S. EPA (2012a) summarized (p. E-8),

> 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.

This limits the size of the dataset that U.S. EPA can use in their efforts to trace contaminant sources.

Third, due to quality control issues, U.S. EPA advises data users to consider trace organics results as a "screen," i.e., to be used "only for information purposes" and requiring "confirmatory analyses." Regarding the trace organics measurements, U.S.EPA (2012a) (p. 23) states that they

> …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.

However, regarding these data, U.S. EPA (2012a) states (p. E-10):

> USGS NWQ Laboratory analyzed fifteen dairy lagoons, three WWTP plant influent, and 30 water samples for trace organic chemicals following the SOP for the "Analysis of Waste Water Samples by Gas Chromatography/Mass Spectroscopy" – USGS SOPs 1433 and 4433. …
>
> 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 inhouse 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.
>
> Samples were analyzed following the technical specifications of the analytical method. Approximately 6 percent of the total data points were qualified unusable based on extremely low surrogate recoveries. Approximately 32 percent of the total data points were qualified estimated due to chromatographic interference and QC results that did not meet the specified criteria.

Thus, because the trace organics results are considered to be screening-level only, U.S. EPA cannot validly use any of these data to support conclusions about potential sources of contaminants in drinking water wells.

Fourth, U.S. EPA (2012a) indicates that the wastewater pharmaceuticals data from the University of Nebraska—Lincoln Water Science Laboratory (UNL) should also be considered a "screen." In addition, all reported well water results for two wastewater pharmaceutical compounds (naproxen and triclosan) are rejected ("R qualified") as are all reported dairy lagoon results for two compounds (amphetamine and methamphetamine).

Specifically, regarding the wastewater pharmaceuticals data, U.S. EPA (2012a) states (p. E-12):

> Data users are advised to consider the values reported as a screen. For full usability, data needs 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) there is no established standard analytical method for the analysis of the target compounds and the recurrence of out of control QC results and big variability in the duplicate runs indicated that the data may not be reproducible by a third party. The data reported can only be used for informational purposes only and a good starting point in determining sample locations for confirmatory analyses.

Yet even within U.S. EPA's own report, they do not fully acknowledge these data qualifications. On the same page, U.S. EPA (2012a) states regarding the wastewater pharmaceutical results (p. E-12), "Approximately 10 percent of the wastewater pharmaceutical data points were qualified unusable because of extremely low spike and surrogate recoveries (less than 10 percent). An additional 55% of the total data points were qualified estimated due to out of control recoveries in the associated QC runs. The rest of the data as qualified are usable for all purposes." U.S. EPA does not reconcile how they can characterize 35% of the wastewater pharmaceutical data as "usable for all purposes" when they clearly state that sample results should only be considered a "screen." These inconsistencies in U.S. EPA's qualifications of the data further erode confidence in the overall data usability.

Fifth, a significant portion of the veterinary pharmaceuticals data are either qualified as unusable or estimated. For example, all detected concentrations for the dairy lagoons are either rejected as unusable ("R qualified"), or estimated ("J qualified") (U.S. EPA, 2012a; Table C12).

Regarding the limitations of the veterinary pharmaceuticals data, U.S. EPA (2012a) states (p. E-12),

> 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 nondetects 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.

In addition, U.S. EPA's Water Science Lab (U.S. EPA, 2011) warned that much of the veterinary pharmaceutical data are biased and should be used with caution, stating,

> Due to the complexity of the liquid matrices (water, lagoon and WWTP) and chromatographic interferences, internal standards used for calculating the concentrations of the target compounds were affected resulting in a potentially high biased associated data. Data users are warned to use the reported values with caution

> as the concentrations of the compounds in the samples maybe lower than what were reported.
>
> Approximately 9% of the total data points were qualified unusable and additional 18% were qualified estimated concentration with a high bias due to out of control internal standards and or calibration. Five Lincomycin and 3 monensin results in the water samples were detected above the reporting limits but were flagged non-detects due to contamination in the associated field blank, WW29.

U.S. EPA's interpretation of the detected veterinary pharmaceutical in the field blank introduces additional uncertainties: U.S. EPA's Water Science Lab (U.S. EPA, 2011) indicates that three monensin detects in well water samples were flagged as non-detect due to contamination of the field blank WW29 by monensin (although Table C12 of U.S. EPA, 2012a does not indicate that monensin was detected in the field blank—this discrepancy must be addressed). Since sample WW29 was the only field blank collected and analyzed for veterinary pharmaceuticals in water, all compounds detected in the field blank should be labeled as qualified when detected elsewhere. However, as discussed in Sections 4.3.2 and 4.3.3, below, U.S. EPA reported positive detections of monensin in several other well water samples: they report that monensin was detected in the sample upgradient of the Haak Dairy and all three of the wells downgradient of the Haak Dairy, and in two of eight wells downgradient of the Dairy Cluster. It is not apparent why all these reported detects weren't also qualified as nondetects, since the single field blank sample WW29 should be applicable to all of the well water samples.

Sixth, U.S. EPA did not meet preservation requirements for many of the nitrate samples. U.S. EPA (2012a) indicates that 31% of the 147 samples for nitrate/nitrites, TKN, and ammonia were qualified estimated with a possible low bias because the samples did not meet the preservation requirements when they were received at the laboratory (p. E-8). It is not known if or how not meeting the preservation requirement may have differentially affected measured concentrations in upgradient and downgradient samples, but this preservation issue further erodes confidence in the data.

Thus, because of numerous data quality issues, it is invalid to use much of the pesticides and veterinary pharmaceuticals well water data or any of the trace organics or wastewater pharmaceuticals well water data in quantitative comparisons or to assess potential sources of contaminants to downgradient wells.

4.1.8 U.S. EPA did not collect field duplicate samples

In addition to the analytical and data quality issues described above, U.S. EPA (2012a) did not collect field duplicate or triplicate samples for water wells or lagoons "due to an oversight" (p. E-5). This discrepancy is noted in the U.S. EPA laboratory corrective action form.[6] Per the Phase 3 QAPP, the rate of field duplicate collection was to be 1 in 10 samples (U.S. EPA, 2010; p. 35). U.S. EPA indicates that the measure taken to correct this issue is, "Laboratory analytical duplicate quality control samples were analyzed." However, field and laboratory duplicates are not equivalent.

Field duplicates are independent samples collected as close as possible to the same point in space and time. They represent separate samples taken from the same source and analyzed

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[6] F Corrective Action form for the Phase 3 Yakima Valley Nitrate Study, dated August 1, 2012. ftp://ftp.epa.gov/reg10ftp/sites/yakima/QAPP_Deviations_SAFs_and_CAFs/YV_CAF_no_field_duplicates.pdf

independently. They are useful in documenting the reproducibility (precision) of the sampling and analytical process. In general, U.S. EPA recommends that field duplicates be included at a frequency ranging from one per day per matrix to 10% of all field samples per matrix (U.S. EPA, 1992; U.S. EPA, 2007). If field duplicate results are highly variable and fall outside of quality objectives established in the project Sampling and Analytical Plan (SAP) or QAPP, then potential sources of the variability (e.g., sampling or analytical issues, or heterogeneity of the sampled matrix) can be investigated to determine the overall impact on data quality.

In contrast, a laboratory duplicate is typically an interlaboratory split of one sample; it is used to document the precision of the analytical method (U.S. EPA, 1992). It does not capture any influences introduced by the sampling protocol (e.g., sample collection, sample storage/transfer) or the in-field heterogeneity of the sampled matrix.

U.S. EPA's failure to collect field duplicates further reduces confidence in the quality of the collected data.

4.1.9 U.S. EPA's detection limits for some analyses are high

In general, a detection limit is the lowest amount of a chemical that can be "seen" above the normal, random noise of an analytical instrument or method. A chemical present below that level cannot reliably be distinguished from noise (U.S. EPA, 1989a). However, in some cases, the detection limits reported by U.S. EPA (2012a) for certain compound types in well water are higher than typically achieved. Consequently, lack of detection of these compounds can lead to erroneous conclusions about whether particular sources are contributing to groundwater concentrations.

For example, U.S. EPA's detection limit for wastewater pharmaceuticals in well water (0.2 µg/L) is higher than typically achieved for drinking water sources. USGS (2009) cites much lower reporting levels in drinking water for a number of the same compounds, including:

- Acetaminophen: 0.036 µg/L
- Azithromycin: 0.004 µg/L
- Cotinine: 0.014 µg/L
- Diphenhydramine: 0.015 µg/L
- Ibuprofen: 0.042 µg/L
- Thiabendazole: 0.011 µg/L

U.S. EPA (2012a) interprets the wastewater pharmaceutical data as follows, "Detection of these compounds in water wells may provide evidence that septic systems are a likely source of nitrate…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" (p. 24). Conversely, if these compounds are not detected, U.S. EPA may erroneously conclude that septic systems are not contributing to well contamination when in fact the detection limits are simply too high to detect the contribution.

4.1.10 U.S. EPA cannot validly apply chemical fingerprinting techniques because, in addition to other issues, fate and transport properties of the analyzed compounds differ

A primary purpose of U.S. EPA's Phase 3 investigation was to analyze wells "for a variety of chemicals to evaluate whether chemicals other than nitrate can be used to identify likely sources of the nitrate contamination in the groundwater and drinking water wells" (U.S. EPA, 2012a; p. ES-1).   U.S. EPA described this objective in more detail in the QAPP for Phase 3 (U.S. EPA, 2010), stating:

> Phase 3… will analyze for a wide range of potential tracing or linking compounds which may be traveling with the nitrate. These compounds would then potentially identify, or link back to, the land use from which the nitrate came. These compounds include estrogens, androgens, veterinary and human antibiotics, agricultural chemicals, personal care products and human medications and compounds such as caffeine or ibuprofin. (p.8)

One technique that is sometimes used to characterize the source of a contaminant plume or to monitor the migration of a leachate in the environment is "chemical fingerprinting" (Plumb, 2004). However, detection of contaminants in groundwater can be influenced by the analytical and sampling program design (discussed elsewhere in this Section) as well as chemical-specific factors that affect their fate and transport through soil and other subsurface media. For fingerprinting to be most effective, chemicals should be similar and behave in a similar manner (e.g., fingerprinting has been effectively applied to dioxins/furans and polychlorinated biphenyl compounds (PCBs)). Compounds that are dissimilar may behave in different ways; e.g., some may be relatively immobile, while others may volatilize and others move readily through the subsurface. However, because of the widely different chemical types evaluated in the U.S. EPA (2012a) program, it is impossible to establish a relationship between patterns of detection downgradient and in source (e.g., dairy, septic system, or cropland) samples.

U.S. EPA (2012a) acknowledges the potential impact of differences in chemical properties and behavior on interpreting the sampling and analytical data to determine source allocation, stating for example (p. 8-9):

> In addition to the variability caused by the physical characteristics of the aquifer, many compounds react with the silts, sands, and gravels of the aquifer in a way that slows their transport. Some compounds, such as nitrate and ions like chloride, tend to minimally adsorb and are transported nearly as fast as the water flows in the aquifer. Nitrate does not break down unless it encounters denitrifying bacteria and organic carbon, resulting in a low oxygen or anoxic environment. Other compounds, such as iron or manganese, often participate in chemical reactions and can create relatively immobile minerals, which can change their concentrations as measured in water wells (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 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);

and (p. 22):

> Organic compounds are subject to a number of factors that affect their fate and transport properties and would cause them to travel differently from nitrate in

> groundwater. Organic molecules are much more likely to sorb to materials in the aquifer, which could retard their migration compared to nitrate. In addition, organic compounds are subject to microbial degradation, which would reduce their concentration in groundwater over time.

Yet, U.S. EPA analyzes certain compound types that are unlikely to be detected in groundwater and will contribute little to understanding of contaminant sources. For example, U.S. EPA (2012a) analyzes synthetic hormones, stating (p. 28):

> Some of the synthetic hormones analyzed could be indicative of specific animal sources. For example, 17-α-ethynyl-estradiol is a synthetic analogue of 17-α-estradiol and is used in hormonal contraception exclusively in humans. This compound would not be expected to be found in dairy lagoons, unless the lagoons also receive human waste, but could be found in WWTP influent and septic systems.

However, estrogenic compounds and other hormones (including estrone, 17 β-estradiol, 17α-ethynlestradiol, and testosterone) tend to strongly sorb to soil (Snow et al., 2007) and studies have demonstrated that endocrine disrupting compounds tend to biodegrade in the environment (Snow et al., 2007). In fact, 17-α-ethynyl-estradiol was not detected in any of the U.S. EPA (2012a) drinking water wells. However, lack of detection of these compounds does not necessarily mean that human (e.g., septic) waste sources did not contribute other contamination to these wells.

U.S. EPA recognized that analyses for many of the compound types it included in the sampling program would result in data unlikely to be useful for tracing chemical movement, stating in the Phase 3 QAPP (U.S. EPA, 2010; p. 8):

> Phase 3 is attempting to demonstrate the potential to use low concentrations of trace organic compounds to link land use to observed nitrate contamination. These organic compounds are subject to microbial degradation. Further, they tend to sorb to the organic carbon in the porous media of the aquifer matrix. This can significantly retard the movement of the organic molecules with respect to the movement of groundwater or nitrate. The specification of very low detection limits for many of the organic analyses in this project are hoped to overcome these limitations. Phase 3 will also provide enforcement-quality data.

Nonetheless, they proceeded to collect these data, which were subsequently plagued by data quality issues and were largely unusable for conducting a valid scientific assessment.

4.2 Validity of Location- and Compound-Specific Results

Section 4.1 provides comments on general study design and data quality issues. The following sections consider location- and compound-specific results and conclusions presented in the U.S .EPA (2012a) report. The study design issues noted above (e.g,. insufficient upgradient samples to allow statistical comparisons to background, insufficient time points to assess temporal variability, unusable and qualified data) apply to the results discussed here such that these data cannot be used to draw scientifically valid conclusions about the contribution of dairies or other sources to measured contamination.

4.2.1 Isotopic analyses

In addition to analysis of inorganic and organic compounds, hormones, and pathogens, U.S. EPA submitted samples from well water to the UNL Laboratory for isotopic analysis of nitrate (NO_3), and samples from the lagoons for isotopic analysis of ammonium (NH_4). As described by U.S. EPA (2012a; p. 28), "Stable isotopes of the various nitrogen species that make up dissolved inorganic nitrogen (nitrate, nitrite, and ammonium) in water can indicate the general source, or combination of sources, or dominant processes acting on nitrogen in groundwater." For nitrogen, the most common isotope is ^{14}N (the "light" isotope) which comprises 99.636% of total nitrogen in the atmosphere, and ^{15}N (the "heavy" isotope) makes up the rest of total nitrogen in the atmosphere, or about 0.364%. The ratio of the heavy isotope to the light isotope can provide an indication of the source of the nitrogen.

U.S. EPA applied isotopic analysis of nitrogen to identify the possible origin of nitrate (NO_3) in water wells and lagoons, i.e., whether it is from synthetic fertilizer, animal sources, the atmosphere, or a combination of sources. U.S. EPA did isotopic analysis of samples from 24 wells as follows: 3 dairy supply wells (1 at Haak Dairy and 2 at the Dairy Cluster), 10 downgradient of dairy wells (3 at Haak Dairy and 7 at the Dairy Cluster), 1 background residential well, 4 downgradient of septic wells, and 6 downgradient of crop field wells. They did not do isotopic analysis of the two upgradient wells. U.S. EPA also did isotopic analysis of ammonium (NH_4) in the 15 lagoon samples.

U.S. EPA (2012a) summarized its methodology and assumptions in Appendix D, and the isotopic signatures and interpreted dominant source of nitrogen in Table D2. They assert that $\delta^{15}N\text{-}NO_3$ well water values below 2% indicate a synthetic fertilizer source, values greater than 8.4% indicate an animal waste source, and intermediate values (≥2% and ≤ 8.4%) indicate a synthetic fertilizer and/or animal waste source. Based on these analyses and assumptions, U.S. EPA identified seven of the residential wells as having one dominant source: six with "animal waste" and one with "fertilizer" identified as the only source. They list 14 other wells for which a less definitive declaration is made (the source indicated is a combination of fertilizer and/or animal waste and/or atmospheric).[7] U.S. EPA also asserted that $^{18}O\text{-}NO_3$ values greater than 20% reflect an atmospheric source.

However, our review of U.S. EPA's assumptions about isotopic ratios associated with specific sources indicates that $\delta^{15}N\text{-}NO3$ values attributable to synthetic fertilizer and animal waste sources can vary beyond the ranges assumed to by U.S. EPA, and that rain water can also influence $\delta^{15}N\text{-}NO3$ values. Further, $\delta^{18}O\text{-}NO^3$ ratios reflecting atmospheric contributions can also vary outside the range U.S. EPA assumed. Additionally, U.S. EPA's methodology cannot distinguish between human and other "animal" sources. Overall this approach is inadequate to conclude that the animal wastes are the predominant source of nitrate in the downgradient wells or residential wells.

Fertilizer sources

With regard to assignment of specific isotope measurements to certain sources, U.S. EPA (2012a) suggests that $\delta^{15}N\text{-}NO_3$ well water values below 2% should signify that "synthetic fertilizers are the likely dominant source of nitrate in water wells" since "the lowest $\delta^{15}N\text{-}NH_4$ value from the dairy lagoons was 2.0%" (p. D-6). In other words, they assume that since dairy lagoons reflect animal waste, the range of isotope values for nitrogen (in

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[7] Regarding the isotopic data, U.S. EPA states (p. 84) "The isotopic data provide some indication of the likely nitrate sources for seven of the 25 residential wells tested (six animal waste and one synthetic fertilizer). Although the isotopic analysis identified animal waste as the source of the nitrate in six wells, this analytical technique cannot differentiate between human and nonhuman waste." However, U.S. EPA only did isotopic analysis of 21 "residential" wells.

ammonium) measured here reflects possible nitrogen isotopic values associated with animal wastes.

However, the U.S. EPA study "did not directly evaluate the isotopic values for [synthetic] fertilizer used in the study area" (p. D-6) and it therefore is unknown what the actual synthetic fertilizer δ^{15}N-NO$_3$ values are in the study area. U.S. EPA states that the "ratios for synthetic fertilizers are often within a range of -4.0 to +4.0%," and provides several references. Table 3 lists the ranges of δ^{15}N-NO$_3$ values reported from analyses of a number of fertilizer types, including the references cited in the report. δ^{15}N-NO$_3$ values for fertilizers vary based on fertilizer type (Kendall 1998). In general, for fertilizers not explicitly identified as organic fertilizers (i.e., synthetic fertilizers), these data show that δ^{15}N-NO$_3$ values range from about -8 to 8%.

TABLE 3. Ranges of δ^{15}N-NO$_3$ values obtained from various fertilizers

Reference	Low end of range (%)	High end of range (%)	Comments
Report-Appendix D		<2	
Kreitler, Ragone et al. (1978)	-8	6.2	90% of samples ranging from -3‰ to 2‰
Heaton (1986)	-5	7	Fertilizers from: US, France, Germany, Australia, South Africa
Komor and Anderson (1993)	-4	4	Commercial fertilizers
Aravena, Evans et al. (1993)	-2	4	Commercial fertilizers
Herbei and Spalding (1993)		1.5[b]	Single fertilizer analyzed
Macko and Ostrom (1994)	-3	2	Chemical fertilizers
Battaglin, Kendall et al. (1997)	-5	5[a]	Values based on combined references
Battaglin, Kendall et al. (1997)	-5	0[b]	Values based on combined references
Kendall (1998)	-4	4	Values based on combined references
Kendall (1998)	2	30[c]	Organic
Becker, Peter et al. (2002)	-4 (mean=2.75)	4	Synthetic fertilizers
Townsend, Young et al. (2002)	-5	8[a]	Unspecified commercial fertilizer
Townsend, Young et al. (2002)	2	8[b]	Anhydrous ammonia
Townsend and Macko (2007)	-2	2	Values based on combined references
Kendall, Elliott et al. (2007)	-8	7	Values based on combined references

[a] Nitrate based fertilizers; [b] Ammonia based fertilizers; [c] Organic fertilizers

U.S. EPA acknowledges that reported local δ^{15}N-NO$_3$ ranges can differ from world-wide reported values, stating (p. D-3):

> local end-members specific to a particular study region often have a smaller isotopic range in comparison to worldwide reported values, and therefore measuring the isotopic compositions of local end-members can sometimes help better constrain and interpret nitrate isotope values within a specific data set.

Since local fertilizer samples were not analyzed in this study, it is uncertain how these values compare to reported world-wide $\delta^{15}N-NO_3$ values. In general, nitrate based fertilizers have slightly higher $\delta^{15}N-NO_3$ values than ammonia-based types, with even higher values reported for organic fertilizers (Kendall 1998). Nonetheless, based on reported $\delta^{15}N-NO_3$ values for inorganic fertilizers, the highest reported value was 8% and the average high end of the range was approximately 5% (Table 3). Thus, $\delta^{15}N-NO_3$ values up to 8% could be associated with synthetic fertilizers (U.S. EPA assumes values between 2 and 8% could reflect a mixed synthetic fertilizer and animal waste source).

Figure 1 illustrates the range of comparative $\delta^{15}N$ values that have been reported for fertilizer as well as rain, animal waste, and soils (Kendall 1998). These data are a compilation of various data sources and portray other $\delta^{15}N$ sources in addition to fertilizers and animal waste that may contribute to nitrate compositions in surface and ground waters. This figure suggests that for fertilizer, $\delta^{15}N-NO_3$ values may range up to about 6.5% and $\delta^{15}N-NH_4$ values may range up to 4% (in other words, $\delta^{15}N-NO_3$ values are slightly higher). "Soil" (fertilized and natural) and rain water are additional sources of $\delta^{15}N$ (with values up to about 14% for natural soil and 25% for fertilized soil, and up to about 18% for rain water) that can influence $\delta^{15}N-NO_3$ values in surface and ground water. Indeed, U.S. EPA states that "for $\delta^{15}N-NO_3$ values between 2.0% and 8.4% the source of nitrate in the water wells cannot be confidently attributed to a single source" as "atmospheric contribution, other sources could be solely animal waste, solely synthetic fertilizer, or a mixture of all three with an atmospheric contribution" (p. D-6). The authors of the Report did not question if $\delta^{15}N-NO_3$ values <2% or >8.4% were also influenced by other contributions including soil and rain water and with that uncertainty it is not apparent whether their $\delta^{15}N-NO_3$ cutoff values accurately reflect actual source contributions.

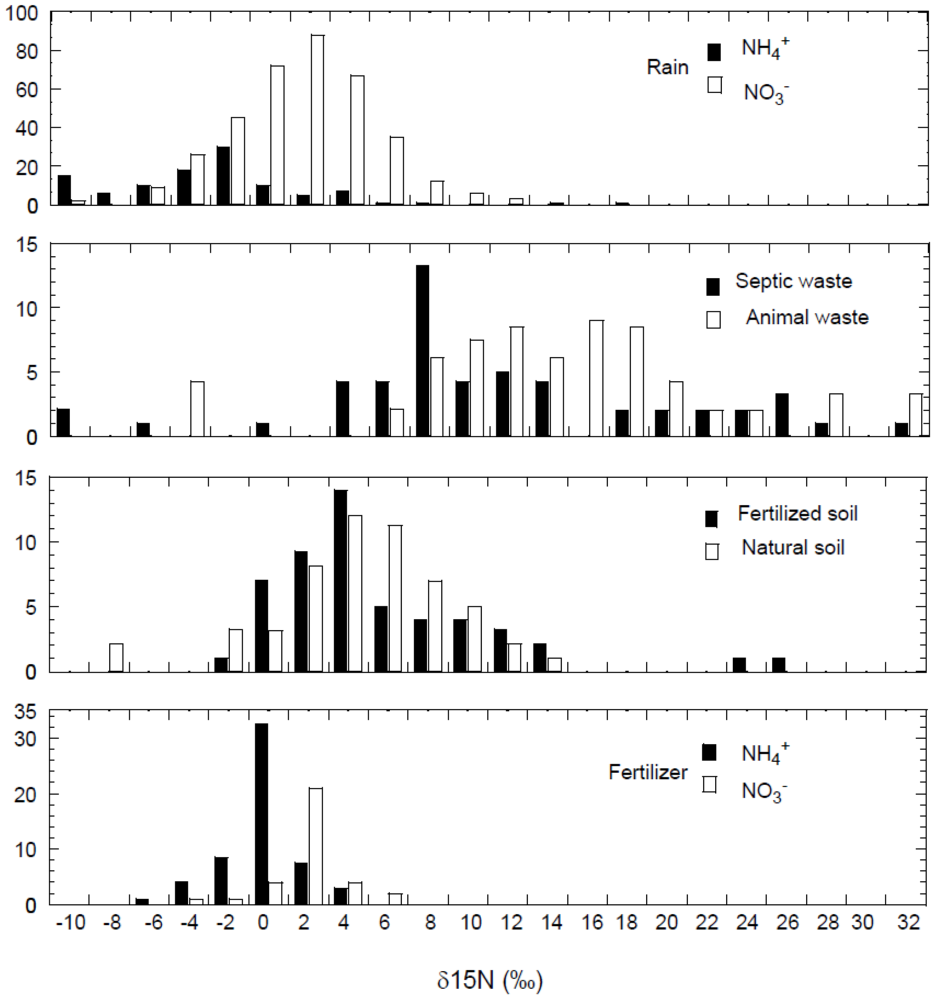

Figure 1. $\delta^{15}N$ Values Obtained from Major Sources of Nitrogen in the Hydrosphere (from Kendall, 1998)

Applications used to determine the source of nitrates based on $\delta^{15}N\text{-}NO_3$ values can be complicated by biogeochemical reactions such as ammonia volatilization, nitrification and denitrification (Kendall 1998). The Report notes that "denitrification will result in a coupled linear increase of both $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ values" and "this combined isotope and concentration pattern was not observed in the water wells, which indicates that the nitrate isotope compositions measured in the water wells are primarily controlled by mixing of one or more nitrate sources." Results from groundwater studies using $\delta^{15}N\text{-}NO_3$ values to identify relative contributions by fertilizers and or/animal wastes are difficult to interpret in clayey soils when denitrification cannot be ruled out or if the nitrate level in the soil organic matter is significant (Gormly and Spalding 1979; Kendall 1998). The Report does not provide data regarding the nitrate level in the soil organic matter or evidence that it may leach out under certain conditions.

<u>Animal waste sources</u>

The Report states that "a $\delta^{15}N\text{-}NO_3$ ratio above 8.4% was used to indicate that the likely dominant source of the nitrate in the water wells was animal waste" (p. D-5). This value was chosen because "the average δ^{15}N-NH_4 ratio at the discharge end of the lagoons was 8.4% and this ratio forms the lower end of the expected range for the weights of nitrogen that, after microbial conversion to nitrate, would be transported in groundwater to drinking water wells" (p. D-5). However, based on a review of the literature, the lower range limit for δ^{15}N-NO_3 values that suggest an animal waste source of nitrate by most authors or studies is 10% (Table 4).

Table 4. Ranges of δ^{15}N-NO_3 Values from Animal Waste

Reference	Low end of range (‰)	High end of range (‰)	Comment
Report- Appendix D	>8.4		
Kreitler and Jones (1975)	10	22	Barnyard waste soil
Heaton (1986)	8	23	Manure, barnyards soils, sewage-contaminated soil
Komor and Anderson (1993)	10	22	Reference: Heaton 1986
Aravena, Evans et al. (1993)	10	20	Values based on combined references
Herbei and Spalding (1993)		>10	
Kendall (1998)	10	25	Reference: Kreitler 1975
Becker, Peter et al. (2002)	10	20	Values based on combined references
Townsend, Young et al. (2002)	10	20	Values based on combined references
Townsend and Macko (2007)		>10	Values based on combined references
Kendall, Elliott et al. (2007)	10	20	Reference: Kreitler 1975

U.S. EPA also states that "values of δ^{15}N-NO_3 below 8.4% do not rule out animal waste as a source" and that "the tendency for the δ^{15}N-NH_4 value to continue to increase is why 8.4% is considered a lower bound for identifying animal waste as a source of nitrate in the water wells" (p. D-5).

Only one author (Heaton, 1986) sets the low end of the range below 10% (8%) for a δ^{15}N-NO_3 value that is representative of animal waste while the rest of the authors use 10% as the lower bound. The cutoff value of 8.4% for δ^{15}N-NO_3 used in the study is not consistent with the 10% that is widely used in the literature—U.S. EPA indicates that the 8.4% value is actually the average δ^{15}N-NH_4 ratio at the discharge end of the lagoons. The δ^{15}N-NH_4 values at the discharge ends reported in Table D1 range from 2.0% to 13.9%. However, the data presented in Tables 3 and 4 and Figure 1, above, suggest that the lower end of this range may reflect contributions from synthetic fertilizer sources. The spread in the data suggests that the isotopic analyses provide no definitive evidence regarding the source of nitrate in the wells.

Further, U.S. EPA (2012a) does not acknowledge that "animal" sources can include human, e.g., septic sources—i.e., even if the measured δ^{15}N-NO_3 value is suggestive of animal waste, the measurement cannot distinguish between an animal (i.e., cattle) or human source. U.S. EPA did not measure δ^{15}N-NO_3 values in septic systems, thus they did not determine local septic system values for this parameter. Thus, rather than assigning any δ^{15}N-NO_3 measurement to an "animal waste" source, it would be more valid to assign it to an "animal and/or human" waste source.

Atmospheric contribution

U.S. EPA states that "ratios above 20.0% for $\delta^{18}O-NO_3$ were considered to have some contribution from atmospherically derived nitrate" based on the literature which states "that $\delta^{18}O-NO_3$ ratios from synthetic fertilizer, soil cycling, and animal wastes are typically below 15.0%" (p. D-6). Table 5 lists the range of $\delta^{18}O-NO_3$values (18-75%) that suggest a contribution from atmospheric sources.

Table 5. Ranges of $\delta^{18}O-NO_3$ Values from Atmospheric Sources

Reference	Low end of range (%)	High end of range (%)	Comment
Appendix D		>20	
Kendall (1998)	55	75	Precipitation (Bavaria, Germany)
Kendall (1998)	18	70	Precipitation (Colorado, New York, Vermont)
Kendall (1998)	23	58	Precipitation (Muensterland, Germany)
Kendall (1998)	28	51	Precipitation (East-Central Canada)
Battaglin, Kendall et al. (1997)	23	75	Values based on combined references

Figure 2 shows a histogram of the frequency of data distribution and the world-wide ranges of $\delta^{18}O-NO_3$ measured in precipitation from all the data sources referred to in Kendall (1998).

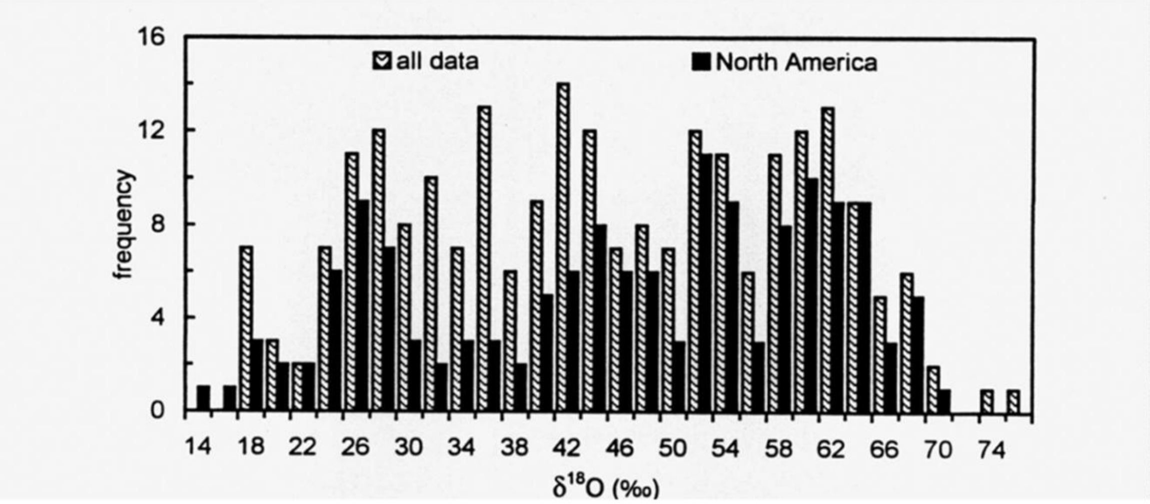

Figure 2. Histogram illustraing the range of values and the frequency of observations of δ18O-NO3 in nitrate from precipitation samples collected world-wide as compiled and presented in Kendall, 1998. Data are from numerous sources with North American values presented with solid bars.

U.S. EPA states "values of $\delta^{18}O-NO_3$ below 20.0% could have an atmospheric contribution, but it becomes indistinguishable from other sources" (p. D-6). They did not explain why water in one well would be influenced by atmospheric contribution while another is not. Given that U.S. EPA assumes that atmospheric contribution (rain) could increase $\delta^{18}O-NO_3$

in well water, rain could also increase the percentage of δ^{15}N-NO_3 in the same sample, as suggested in Figure 1. However, U.S. EPA states, "If the nitrate in any given water sample has a significant component of atmospheric nitrate, then the δ^{18}O-NO_3 value will be higher than the δ^{18}O-NO_3 values reported for other sources such as fertilizers and animal waste" (p. D-6).

U.S. EPA acknowledges "since the major nitrate sources have ranges of δ^{18}O-NO_3 values, the exact contribution of each end-member cannot be determined, but a qualitative evaluation can be made" (p. D-6). As with δ^{15}N-NO_3, the fertilizers used in the area were not analyzed for δ^{18}O-NO_3 therefore it is unclear what the potential contribution to the δ^{18}O-NO_3 value is from fertilizers compared to atmospheric sources. U.S. EPA states, "Ratios above 20.0% for δ^{18}O-NO_3 were considered to have some contribution from atmospherically derived nitrate. This ratio was selected because the literature based on multiple studies of various nitrate sources suggests that δ^{18}O-NO_3 ratios from synthetic fertilizer, soil cycling, and animal wastes are typically below 15.0% (Kendall et al. 2007)" (p. D-6).

However, review of the literature indicates that the range of δ^{18}O-NO_3 values that have been reported for fertilizers ranges from -5 to 58%, and varies considerably based on their composition (Table 6). The high end of these reported δ^{18}O-NO_3 ranges for synthetic (25%) and natural (58%) fertilizers are above the 15.0% stated by U.S. EPA as the upper level for δ^{18}O-NO^3 ratios. Since actual δ^{18}O-NO_3 value for fertilizers used in this area was not obtained makes the source determination identification based on δ^{18}O-NO_3 values difficult.

Table 6. Ranges of δ^{18}O-NO_3 Values for Different Fertilizer Types

Reference	Low end of range (%)	High end of range (%)
Aravena, Evans et al. (1993)	18	22[a]
Kendall, Elliott et al. (2007)	17	25[a]
Kendall, Elliott et al. (2007)	-5	15[b]
Kendall, Elliott et al. (2007)	46	58[c]

[a]Synthetic fertilizer; [b] Nitrate from ammonia-based fertilizer; [c] Natural fertilizer

Summary of Isotopic Analysis Review

Overall, δ^{15}N-NO_3 values attributable to synthetic fertilizer and animal waste sources can vary beyond the ranges assumed to by U.S. EPA, and that rain water can also influence δ^{15}N-NO_3 values. Further, δ^{18}O-NO^3 ratios reflecting atmospheric contributions can also vary outside the range U.S. EPA assumed. Also, even if the assumptions U.S. EPA used to derive the source signature ranges are accurate, this methodology cannot distinguish between human and other "animal" sources. Finally, if one compares the "supply" well results to downgradient results, they are generally similar (although statistical analysis is not possible due to the small number of samples, and results for downgradient samples are highly variable). Overall this approach cannot be used conclude that the dairy farm wastes are the predominant source of nitrate in the downgradient wells or residential wells.

4.2.2 Assessment of samples collected at and near Haak Dairy

In Table 16 (p. 44-45), U.S. EPA (2012a) summarizes detections in wells downgradient of Haak Dairy, and also identifies which of these were detected in "dairy sources" on the dairy site. However, this summary is misleading in that it does not present other important data that puts these results in perspective, including concentrations and detection limits, detections in WWTP influent, and statements made by U.S. EPA indicating that certain analytical results should be considered qualified or "screen" values.

Specific results and U.S. EPA's conclusions are discussed below.

Pesticides Table 16 (U.S. EPA, 2012a) reports that atrazine (the only pesticide detected) was detected in two of three wells downgradient of the Haak Dairy and in the upgradient well. In addition, atrazine was detected in "dairy sources" (one dairy application field sample). Regarding these results, U.S. EPA (2012a) states (p. 39), "The detection of atrazine at a higher concentration in one of the downgradient wells compared with the upgradient well indicates that there likely is a source from a crop field associated with the Haak Dairy; however, the presence of atrazine in the upgradient well indicates that the Haak Dairy is not the only source."

Some missing information puts these results in context:

- While atrazine was detected at a slightly higher concentration in one downgradient well (0.11 µg/L) compared to the upgradient well (0.015 µg/L), in the other two downgradient wells, atrazine was not detected in one sample [Table 16 mistakenly identifies atrazine as detected in WW-03 when it was not detected in this well] and was detected at 0.015 µg/L in the other. Thus concentrations are variable across the aquifer, and only one of three downgradient wells was in excess of the upgradient concentration. Further, "background" detection of atrazine is expected since it is widespread in the environment in agricultural areas (U.S. EPA, 2012b).
- Atrazine was also detected in the well upgradient of the Dairy Cluster at 0.051 µg/L (J qualified; see Section 4.2.3).
- The atrazine quantitation limit ranges from 0.095 to 0.1 µg/L— two of the three detected concentrations are below this range, and the other only slightly exceeds it. Further, all detected concentrations are reported as "estimated" (J qualified).

In addition, as discussed in Section 4.1.2, a single upgradient sample is insufficient to determine whether there is a statistical difference in upgradient and downgradient concentrations. Thus, one cannot conclude that the concentrations of atrazine measured in the upgradient and downgradient wells are different, and U.S. EPA can draw no valid conclusions about the possible contribution of Haak Dairy to these concentrations in well water.

Trace organics Table 16 (U.S. EPA, 2012a) reports that one trace organic (DEHP) was detected downgradient of Haak Dairy. It was detected in one downgradient well at 5.26 µg/L, but was also detected in the upgradient well at 2.66 µg/L. It was also detected upgradient of the Dairy Cluster (at 1.74 µg/L, J qualified) and in 2/10 wells downgradient of the Dairy Cluster (at 2.77 (J qualified) and 1.03 µg/L). In addition, DEHP was also detected in 3/3 WWTP samples and, in general, was not detected in dairy lagoons (it was detected in only 1/15 lagoon samples, at 4.58 µg/L in LG-10). Further U.S. EPA reported that the trace organic concentrations should be interpreted as "screen" values (see Section 4.1.7).

DEHP is commonly detected in treatment plant influent. For example, ATSDR (2002) reported that "DEHP was present in 48% of the influent and 12% of the effluent samples taken from New York City sewage treatment plants during 1989–1993" (p. 188). It is "a widely used chemical that enters the environment both through disposal of industrial and municipal wastes in landfills and by leaching into consumer products stored in plastics." Regarding this compound, U.S. EPA states (p. 58) that "DEHP is a common plasticizer and could come from a variety of sources." Together, these data suggest that dairies were not a source of DEHP to groundwater, but that human waste water is a possible source.

Veterinary Pharmaceuticals Table 16 reports that three veterinary pharmaceuticals were detected in water wells downgradient of Haak Dairy: chlortetracycline, monensin, and tetracycline.

Monensin was detected in the upgradient well (at 0.027 µg/L) and all three of the downgradient wells (at 0.022, 0.023, and 0.028 µg/L). However, monesin was detected in only one downgradient well at a concentration that exceeded the upgradient concentration. Thus, while monensin was also detected in the Haak Dairy lagoons, manure sample, and application field sample, there is no evidence that the dairy is contributing to increased levels of monensin in the well water. According to U.S. EPA (2012a; p. 49),

> The detection of monensin in the upgradient well indicates there is an upgradient source of this compound. The high concentrations of monensin seen in the Haak Dairy lagoon samples, manure pile, and application field sample indicate that it is used at the Haak Dairy. The data indicate that the Haak Dairy is a possible source of monensin in the three downgradient residential drinking water wells. Given the presence of monensin in the upgradient well, another source of monensin is likely.

Further, as discussed in Section 4.1.7, U.S. EPA states that monensin was detected in the field blank for the well water samples and, as such, monensin should have been qualified as nondetect in other well water samples.

Chlortetracycline was detected in one downgradient well (at 0.049 µg/L), but not in the upgradient well (detection limit 0.02 µg/L). Tetracycline was detected in two of the downgradient wells (at 0.041 and 0.075 µg/L) but not in the upgradient well (detection limit 0.02 µg/L), and in the dairy lagoon, dairy manure pile, and dairy application field samples. According to U.S. EPA (p. 40), "The detections in all the dairy supply sources provides a good indication that tetracycline is used at the Haak Dairy. These data indicate that the Haak Dairy is a likely source of tetracycline in the two downgradient residential water wells." However, tetracycline is also used as a human pharmaceutical (Drugs@FDA.com, 2012), and was also detected in one of three WWTP influent samples. Further, tetracycline compounds (oxytetracycline) are used as a fungicide and bactericide on tree fruit in Washington State for the control of fire blight on apples and pears (WSU Extension, 2011). Thus, other sources of tetracycline to groundwater cannot be ruled out. Further, because of a number of issues discussed in Section 4.1 (including small number of samples, lack of evidence that aquifers are connected), these data cannot be used to conclude that Haak Dairy is the source of tetracycline to the downgradient wells.

Hormones Testosterone was detected in all three downgradient drinking water wells downgradient of Haak Dairy (at 0.007, 0.009, and 0.012 µg/L) and in dairy sources. However, it was also detected in the upgradient well, at a higher concentration then downgradient (at 0.021 µg/L). In addition, though not shown in Table 16 (U.S. EPA, 2012a), testosterone was detected in 3/3 WWTP influent samples. Regarding these results, U.S. EPA (2012a; p. 61) states, "The dairies are a possible source of the testosterone in the downgradient wells; however, given the concentration in the upgradient well, another source for the testosterone is likely." Based on these observations, there are clearly other contributions to contaminant concentrations in the downgradient wells. Overall, none of the organics or hormone sampling results demonstrate that the dairy is contributing to contaminant concentrations in the drinking water wells.

Isotopic analysis Regarding the isotopic data, U.S. EPA (2012a) states (p. 85), "The isotopic data provide strong evidence that animal waste (human or non-human) is the likely dominant source of the nitrate contamination in at least one of the residential water wells (WW-05) downgradient of the Haak Dairy. However, since isotopic analysis cannot differentiate between human and non-human waste, both could be sources of the nitrate in the downgradient well. Isotopic data for the other two residential drinking water wells downgradient of the Haak Dairy indicate that the source of the nitrate could be animal waste, fertilizer, derived from the atmosphere, or some combination of these sources." However, as discussed in Section 4.2.1, isotopic ratio signatures are broader than assumed by U.S. EPA, and this methodology cannot reliably assign nitrate detected in wells to any given source.

4.2.3 Assessment of samples collected at and near the Dairy Cluster

In Table 25 (p. 65-67), U.S. EPA (2012a) summarizes detections in wells downgradient of the Dairy Cluster, and also identifies which of these were detected in "dairy sources" on the dairy site. However, as with the results presented for Haak Dairy, this summary is misleading in that it does not present other important data that put these results in perspective, including concentrations and detection limits, detections in WWTP influent, and statements made by U.S. EPA that indicate certain analytical results should be considered "screen" values.

Specific results and U.S. EPA's conclusions are discussed below.

Pesticides Regarding pesticides, Table 25 (U.S. EPA, 2012a) reports:

- Three pesticides (atrazine, alachlor, and ioxynil) were detected in the upgradient or downgradient water wells associated with the Dairy Cluster. The three pesticides detected in the water wells were not detected in the dairy manure pile or dairy application field samples.
- One of these (atrazine) was detected upgradient (at 0.051 µg/L) and in six of eight downgradient wells (at concentrations ranging from 0.011 to 0.19 µg/L). However, atrazine is widespread in the environment in agricultural areas (U.S. EPA, 2012b) and background detection is expected, as indicated by the detection in the upgradient well. Further, all detected concentrations were J qualified (i.e., estimated), and all but two of the reported concentrations were below the quantitation limit of 0.1 µg/L.
- Alachlor was only detected in two of eight downgradient wells (at 0.011 and 0.057 µg/L). It was not detected upgradient or in any other well (quantitation limit 0.1 µg/L). Both reported concentrations were below the quantitation limit and were J qualified (estimated).
- Ioxynil was detected in only one of eight downgradient wells (at 0.0063 µg/L). The reported concentration was well below the quantitation limit (0.1 µg/L) and was J qualified (estimated).

Further, as discussed in Section 4.1.2, only one upgradient sample was collected. This is insufficient to determine whether there is a statistical difference in concentrations. Nonetheless, regarding the pesticide concentrations, U.S. EPA (2012a) states (p. 57), "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 agriculture, which could include application by the dairies on the associated fields." U.S. EPA provides no evidence to support this assertion. Based on the data, U.S. EPA can draw no valid conclusions about the possible contribution of the Dairy Cluster to pesticide concentrations in well water.

Trace organics Table 25 (U.S. EPA, 2012a) reports that one trace organic (DEHP) was detected downgradient of the Dairy Cluster, in two of eight wells (at 1.03 and 2.77 µg/L; both J qualified). In all of the other wells it was not detected (<2 µg/L). It was detected in eight lagoons in the Dairy Cluster. It was also detected in 3/3 WWTP samples. Further, per U.S. EPA, the trace organic concentrations should be interpreted as "screen" values (see Section 4.1.7).

As discussed in Section 4.2.2, DEHP is commonly detected in treatment plant influent. For example, ATSDR (2002) reported that "DEHP was present in 48% of the influent and 12% of the effluent samples taken from New York City sewage treatment plants during 1989–1993" (p. 188). It is "a widely used chemical that enters the environment both through disposal of industrial and municipal wastes in landfills and by leaching into consumer products stored in plastics." Regarding this compound, U.S. EPA states (p. 58) that "DEHP is a common plasticizer and could come from a variety of sources." Together, these data suggest that dairies were not a source of DEHP to groundwater, but that human waste water is a possible source.

Wastewater pharmaceuticals Table 25 (U.S. EPA, 2012a) reports that one wastewater pharmaceutical was detected in water wells downgradient of the Dairy Cluster: DEET, in one of eight wells (at 0.67 µg/L). In all other drinking water wells, DEET was not detected (quantitation limit = 0.2 µg/L). DEET was detected in 8/12 lagoons at the Dairy Cluster. DEET can be used to protect livestock form biting flies (Blume et al., 1971). However, it is also used by humans and was detected in 3/3 WWTP samples. Further, U.S. EPA specifies that wastewater pharmaceutical results are only to be considered as screening level values and therefore should not be used in quantitative comparisons.

Veterinary pharmaceuticals Table 25 (U.S. EPA, 2012a) reports that five veterinary pharmaceuticals were detected in water wells downgradient of the Dairy Cluster: monensin, chlortetracycline, tetracycline, tylosin, and virginiamycin.

Monensin was detected in two of eight downgradient wells (at 0.033 and 0.0499 µg/L); in all other wells including the upgradient well, it was nondetect (at <0.02 µg/L). It was also detected in two dairy supply wells, dairy lagoons, manure piles, and application fields. Per U.S. EPA (2012a; p. ES-7, p. 86), "The Dairy Cluster is a likely source of monensin because this antibiotic is used in dairy cows but not people. Monensin was not detected in samples from the WWTP influent samples that were collected as surrogates for residential septic systems, providing further support that the dairies are a likely source." However, as discussed in Section 4.2.2, monensin was also detected in the well upgradient of Haak Dairy (at 0.027 µg/L). With regard to the detection upgradient of Haak Dairy, U.S. EPA (2012a) concluded (p. 49), "Given the presence of monensin in the upgradient well, another source of monensin is likely." Because the number of background samples upgradient of the Dairy Cluster was so severely limited (i.e., one sample, collected at a single location and point in time), it is impossible to definitely conclude that monensin was not present upgradient of the Dairy Cluster as well. Further, as discussed in Section 4.1.7, U.S. EPA states that monensin was detected in the field blank for the well water samples and, as such, monensin should have been qualified as nondetect in other well water samples.

Chlortetracycline was detected in one downgradient well (at 0.119 µg/L), but not in the upgradient well (detection limit 0.02 µg/L). Tetracycline was detected in the upgradient well (at 0.051 µg/L, J qualified) and in two of eight downgradient wells (at 0.038 and 0.049 µg/L), which had lower concentrations than the upgradient well. Tetracycline was detected in all of the dairy lagoon samples, dairy manure pile samples, and dairy application field samples, which according to U.S. EPA (2012a; p. 60), indicates that "…tetracycline is used at the dairies. It is possible that the dairy sources are one of the sources of the tetracycline in the downgradient wells. However, given that the concentrations in the upgradient well are higher than the downgradient wells, another source for the tetracycline is likely" (p. 60). Further, as discussed in Section 4.2.2, tetracycline is used as a human pharmaceutical, and was detected in one of three WWTP influent samples. In addition, tetracycline compounds (oxytetracycline) are used as a fungicide and bactericide on tree fruit in Washington State for the control of fire blight on apples and pears (WSU Extension, 2011). Thus, other sources of tetracycline to groundwater cannot be ruled out. Because of a number of sampling plan design and data quality issues discussed in Section 4.1, these data cannot be used to conclude that the Dairy Cluster is a source of tetracycline to the downgradient wells.

Tylosin was detected in one of eight downgradient wells at a concentration of 0.029 µg/L. All other concentrations were below the quantitation limit of 0.02 µg/L. It was also detected in five lagoons, two manure piles, and one application field sample. Virginiamycin was detected in one of eight downgradient wells at a concentration of 0.023 J µg/L, just slightly above the quantitation limit of 0.02 µg/L. It was also detected in six lagoons. However, for the reasons stated previously (i.e., insufficient upgradient samples, samples collected at only one point in time, lack of confirmation that samples were collected in the same aquifer), these data are insufficient to conclude that the Dairy Cluster is the source of these detected compounds.

Hormones Three hormones were detected in downgradient wells: androsterone, androstadienedione, and testosterone. Of these:

- Androsterone was detected in three of eight downgradient wells (at 0.008, 0.018 , and 0.019 µg/L; all J qualified). It was not detected in any of the other wells (detection limit 0.002 µg/L) or in any of the dairy source samples. It was detected in 3/3 WWTP influent samples.
- Androstadienedione was detected in one of eight downgradient wells (at 0.004 µg/L; J qualified). It was not detected in any of the other wells (detection limit 0.002 µg/L) but was detected in three lagoons and four manure samples. It was also detected in 3/3 WWTP influent samples.
- Testosterone was detected in one of eight downgradient wells (at 0.004 µg/L) and in the upgradient well (at 0.005 µg/L). It was also detected in one residential well (at 0.003 µg/L, in well WW-18, west of Mabton, not located near the dairies), in one of four wells downgradient of septic systems (at 0.001 µg/L), and in one of the wells downgradient of the hops field (at 0.004 µg/L), as well as in 3/3 WWTP influent samples.

Because these hormones were detected in all of the WWTP samples and at other locations not near the dairies but in only some of the dairy source samples, these data do not demonstrate dairies as a source of hormones to the wells.

Isotopic analysis Regarding the isotopic data, U.S. EPA states (p. 86), "The isotopic data provide strong evidence that animal waste (human or non-human) is the likely dominant source of the nitrate in at least two of the residential water wells downgradient of the Dairy Cluster. Because isotopic analysis cannot differentiate between human and non-human waste, both could be sources of the nitrate in these downgradient wells. Isotopic data for the other residential drinking water wells downgradient of the Dairy Cluster indicate that the source of the nitrate could be animal waste, fertilizer, or derived from the atmosphere, or some combination of these sources." However, as discussed in Section 4.2.1, isotopic ratio signatures are more ambiguous than assumed by U.S. EPA, and this methodology cannot reliably assign nitrate detected in wells to any given source.

Trace inorganics Overall, regarding the trace inorganics data downgradient of the Dairy Cluster, U.S. EPA states (p. 56): "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. Barium was the only trace inorganic element that increased between the upgradient well and the downgradient wells, with the highest concentrations in the lagoons." Possible reasons why barium was the only element that increased are not discussed. Some reasons could be differences in fate and transport behavior and the lack of other sources between the upgradient and downgradient wells. Also, it is interesting to note that barium concentrations downgradient are not consistent: wells WW-13 and WW-14, downgradient of the Liberty/Bosma dairy and close to a lagoon (sampled as LG-15) appear to be directly adjacent to each other. However, the concentration of barium in WW-13 is 8.7 µg/L, and the concentration in WW-14 is 35.9 µg/L. By comparison, the concentration of barium in the upgradient well is 11.2 µg/L, greater than the concentration in WW-13.

These comparisons show that comparison a single upgradient measurement to the downgradient measurements is scientifically invalid and produces no meaningful information, and that concentrations downgradient are highly variable. Note also that while U.S. EPA (2012a) assumes that dairies are a source of barium, stating for example (with regard to Haak Dairy, p. 38), "Two metals, barium and zinc, which may be used at dairies, were detected in both the water wells and dairy lagoons," they provide no supporting data in this regard, such as a discussion of how barium is used at dairies. Barium can be found in fertilizers and soil amendments (ATSDR, 2007); however, the barium seems to be found in those fertilizers originating from natural rocks and salt deposits (Senesi et al., 1983).

4.2.4 Assessment of samples collected at and near irrigated cropland

In Table 32 (p. 75), U.S. EPA (2012a) summarizes detections in the six wells downgradient of irrigated croplands and also identifies which of the detected compounds were detected in the composited soil samples at each of the six fields. Again, additional detail on reported concentrations and detections at other locations relative to those measured at and near the croplands would help put the results in perspective. Further, detection of many of the same contaminants in soil and downgradient wells near the croplands demonstrates the difficulty in assigning contaminants detected in wells at any location to any particular source type due to the highly mixed land use.

Specifically:

- U.S. EPA (2012a) states (p. 87), "Nitrogen-rich fertilizers, such as inorganic synthetic fertilizer and manure, are applied to irrigated crop fields and are a possible source of nitrate in drinking water wells…The six water wells downgradient from the irrigated crop fields and sampled by EPA during Phase 3 all had nitrate levels greater than the MCL."

- U.S. EPA (2012a) states (p. 87), "The isotopic data provide strong evidence that synthetic fertilizer is a dominant source in one residential drinking water well downgradient of a mint field [WW-24] and that animal waste (human and non-human) is a dominant source of the nitrate in one well downgradient of a hops field [WW-27]. Isotopic analysis cannot differentiate between human and non-human waste. Isotopic data for the other residential drinking water wells downgradient of the crop fields indicate that the source of the nitrate could be animal waste or fertilizer, with some contribution from the atmosphere." However, as discussed in Section 4.2.1, isotopic ratio signatures are more ambiguous than assumed by U.S. EPA, and this methodology cannot reliably assign nitrate detected in wells to any given source.
- Two pesticides were detected in the downgradient wells: atrazine and bentazon. Atrazine was detected in 1/2 samples downgradient of the mint field (at 0.017 µg/L, J qualified) and 1/2 samples downgradient of the hops field (at 0.025 µg/L, J qualified). Atrazine was not detected in the associated soil samples, and as discussed in Sections 4.2.2 and 4.2.3, it was detected in wells upgradient of the dairies and is ubiquitous in agricultural environments. Bentazon was detected in two wells at 0.028 and 0.033 µg/L (both J qualified), downgradient of the mint field. It was also detected in the soil sample at the mint field.
- Several veterinary pharmaceuticals (erythromycin, lincomycin, monensin, ractopamine, sulfamethazine, sulfathiozole, tiamulin, and virginiamycin) were detected in one well downgradient of the hops field. Only monensin was detected in the associated soil sample. It is not clear why these compounds were detected here; however, the well is located in an area with heavy agricultural use, and these results illustrate the difficulty in parsing out sources of groundwater contaminants based on limited sampling data. Per U.S. EPA (2012a; p. 74), "Possible manure application to the hop field could account for the monensin detected in the downgradient residential well." Note that one of these (sulfamethazine) was also detected in WWTP influent samples.
- Bentazon was detected in two water wells and the associated mint field soil samples. These results indicate that bentazon was applied to the crop field and is likely migrating to the groundwater and water wells.

Overall, regarding these data, U.S. EPA (2012a) states (p. 87), "Given the historic and current application of nitrogen-rich fertilizers in the Lower Yakima Valley, it is expected that irrigated crop fields would be a likely source of high nitrate levels in downgradient drinking water wells. The data collected in this study provide some corroboration that irrigated crop fields are a likely a source of nitrate in groundwater. The data supporting this conclusion is not as strong for the crop fields as it is for the dairies. The reasons for this include: lack of upgradient well data; the irrigated crop fields sampled are situated amongst other agricultural uses, including upgradient dairy operations; fewer analytes detected in both the crop field samples and the corresponding downgradient wells; more limited information about crop field operations; and the crop fields' positions on the landscape relative to other potential sources."

Of note, however, the arguments U.S. EPA (2012a) makes to support its assertion that data linking irrigated croplands to nitrate in well water is "not …strong" would also apply to the data associated with the dairies, specifically:

- There is also a "lack of upgradient well data" for the dairies (only one upgradient well at each location).
- Dairies are also "situated amongst other agricultural uses."
- Few analytes were "detected in both" the dairy samples and corresponding downgradient wells.
- Conclusions about the dairies are also influenced by their "positions on the landscape relative to the other potential sources."

Nonetheless, using the data that were collected, direct statistical comparison of levels of nitrogen measured in soil and water at and near the irrigated croplands to levels measured at and near the dairies shows there is no significant difference in the concentrations for irrigated cropland vs. dairy samples (Tables 7 and 8).

Table 7. T-test Results (two independent samples t-test) Comparing Nitrogen Measurements in Soil Samples Collected at Dairy vs. Irrigated Cropland Locations

Nitrogen Measurement	General Location and Sample Count	Mean (SD) (mg/kg)	T-test Result
Total Nitrogen/Solid	Dairy (n = 5) Crop (n = 6)	2,492 (1,009) 2,195 (915)	No difference (p = 0.621)
Nitrate-N/Nitrite	Dairy (n = 5) Crop (n = 6)	117.5 (80.0) 96.1 (99.4)	No difference (p = 0.707)
Ammonium-N	Dairy (n = 5) Crop (n = 6)	5.74 (1.9) 44.4 (81.3)	No difference (p = 0.320)

Table 8. T-test Results (two independent samples t-test) Comparing Nitrogen Measurements in Water Samples Collected at Locations Downgradient of Dairies vs. Downgradient of Irrigated Croplands

Nitrogen Measurement	General Location and Sample Count	Mean (SD) (mg/L)	T-test Result
Nitrite-N (Cascade Analytical Laboratories)	Dairy-Downgradient Well (n = 11) Crop-Downgradient Well (n = 6)	29.2 (15.3) 28.3 (22.2)	No difference (p = 0.921)
Nitrate+Nitrite as N (Manchester Environmental Laboratory)	Dairy-Downgradient Well (n = 11) Crop-Downgradient Well (n = 6)	30.7 (16.2) 30.4 (23.6)	No difference (p = 0.974)

Soil samples were collected from sixteen locations: 10 associated with dairies (two at Haak dairy, consisting of one manure and one soil sample; and eight at the Dairy Cluster, consisting of four manure and four soil samples), and six associated with irrigated crop land (two soil samples from each of mint, corn, and hops fields). No background soil samples were collected; therefore, measured concentrations cannot be compared to local background conditions and the contribution from other sources (e.g., atmosphere) cannot be assessed.

Each soil sample was analyzed for nitrogen species using three methods; however, a total of six different methods were used so that the methods/results are not directly comparable across all samples. Specifically:

- "Kjedahl Nitrogen/Solid" was measured in only one sample (SO-01, Haak Dairy manure sample) so the results were not comparable to any other data.
- "Ammonia Solid" and "NO3N/Total Solid" were only measured at the dairies (in manure samples) so the results are not comparable to irrigated crop soil samples.
- The other three nitrogen types ("Total Nitrogen/Solid", "Nitrate-N/Nitrite", and "Ammonium-N") were measured at each general location (Haak Dairy, Dairy Cluster, and the three irrigated cropland types), so the results are comparable.

Independent samples t-tests were conducted to compare nitrogen soil sampling results for samples collected at dairies and the irrigated crop fields, for each of the three types. Based on these analyses, there was no significant difference in the concentrations for dairies and irrigated crop samples, for any of the three nitrogen measurements (Table 7).

Likewise, independent samples t-tests were conducted to compare nitrogen water sample results for samples collected downgradient of the dairies vs. downgradient of the irrigated crop fields. Based on these analyses, there was no significant difference between the concentrations measured downgradient of the dairies vs. downgradient of the croplands, for either nitrite-N or nitrate+nitrite as N (Table 8).

4.2.5 Assessment of samples collected downgradient of residential septic systems

U.S. EPA (2012a) reports that "As of 2009, there were about 22,000 septic systems registered with Yakima County" (p. 12). To assess the potential contribution of nitrate and other contaminants from septic systems, U.S. EPA sampled four residential wells downgradient of domestic septic systems in Mabton (well WW-21), Harrah (well WW-19), and Sunnyside (wells WW-20 and WW-22). Chemicals detected in these wells were compared to chemicals detected in samples collected from the influent to three wastewater treatment plants (WWTPs) located in Toppenish, Mabton, and Zillah.

Regarding the sampling of WWTP influent and downgradient of septic system wells, the Phase 3 QAPP stated (U.S. EPA 2010, p. 16):

> For rural residential septic characterization, samples will be taken from the influent stream to 3 different small sewer treatment plants in the lower valley. These plants will be selected so as to have a similar demographic in the contributing area as the adjacent non-sewer area. In this way it is not necessary to sample from a specific drain field and a wider range of potential linking organic compounds will be encountered. Four home locations down-gradient of significant concentration of septic systems and which provided high nitrate samples in Phase 2 will be re-sampled in Phase 3 for the same wide range of trace organic compounds, age dating gases and general chemical analytes to provide the strongest basis for comparison with the AFO [animal feeding operation] and crop-land associated wells.

The objective of this sampling was to "help differentiate water wells affected by septic systems (humans) from water wells influenced by other sources such as dairy lagoons or irrigated cropland" (U.S. EPA, 2012a; p. 23). That is "Detection of these compounds in water wells may provide evidence that septic systems are a likely source of nitrate. 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" (p. 24). U.S. EPA further elaborated (p. 76),

> The treatment plant influent samples were collected to serve as surrogates for septic systems by providing a characterization and quantification of compounds that are found in rural septage. EPA recognizes that these WWTPs may receive substances that are not found in residential septic systems (for example they may also receive commercial and industrial waste streams). The WWTPs sampled serve rural communities and are sufficiently similar to residential septic systems for the purposes of this study. This approach was used to determine whether the compounds detected in wells with high nitrate concentrations in areas with a high density of septic systems are similar to the compounds detected in WWTP influent or whether these wells are affected by other sources.

In Table 37 (p. 82), U.S. EPA (2012a) summarizes detections in the four wells downgradient of septic systems. Table 37 reports detections of two pesticides (atrazine and bentazon), 10 veterinary pharmaceuticals (erythromycin, lincomycin, monensin, ractopamine, sulfamethazine, sulfamethoxazole, sulfathiazole, tetracycline, tiamulin, and virginiamycin), and 8 hormones (11-keto testosterone, 17β-estradiol, 17α-estradiol, androstadienedione, β-zearalanol, estrone, testosterone, and epitestosterone).

Samples collected downgradient of the septic systems suffer from many of the same problems as the samples collected downgradient of the dairies, specifically that inadequate (in this case, no) samples were collected upgradient of the septic systems to assess area background exclusive of the contribution from the putative source, samples were grab samples collected at a single point in time and do not reflect potential temporal/seasonal variability or the possibility of a heterogeneous matrix, and many of the analytical results were qualified. Further, U.S. EPA reported no efforts to confirm that these "downgradient of septic system" samples were in fact relevantly located to capture the contribution from septic systems—e.g., did the sampled aquifers intersect the septic systems? Were they truly downgradient?

While U.S. EPA collected three samples of WWTP wastewater influent in Zillah, Mabton, and Toppenish, they did not confirm that these samples are representative of what might be found in septic systems upgradient of the residential "septic system" wells or in septic systems located near the dairies, though U.S. EPA (2012a) did state (p. ES-8) "The WWTP influent had no actual or potential hydrogeological connection with the residential wells." Further, in attempting to analyze these samples, U.S. EPA encountered numerous matrix interference issues such that results for some chemical classes (pesticides) were declared unusable. Overall, the data collected in these wells and the WWTP influent do not contribute scientifically valid information to this assessment. Nonetheless, these data show that diverse agricultural and human sources, exclusive of dairy sources, contribute to contaminant concentrations in groundwater in the Lower Yakima Valley.

Independent samples t-tests were conducted to compare nitrogen water sample results for samples collected downgradient of the dairies vs. downgradient of the septic systems. Based on these analyses, there was no significant difference between the concentrations measured downgradient of the dairies vs. downgradient of the septic systems, for either nitrite-N or nitrate+nitrite as N (Table 9).

Table 9. T-test Results (two independent samples t-test) Comparing Nitrogen Measurements in Water Samples Collected at Locations Downgradient of Dairies vs. Downgradient of Septic Locations

Nitrogen Measurement	General Location and Sample Count	Mean (SD) (mg/L)	T-test Result
Nitrite-N (Cascade Analytical Laboratories)	Dairy-Downgradient Well (n = 11) Septic-Downgradient Well (n = 4)	29.2 (15.3) 26.9 (12.9)	No difference (p = 0.797)
Nitrate+Nitrite as N (Manchester Environmental Laboratory)	Dairy-Downgradient Well (n = 11) Septic-Downgradient Well (n = 4)	30.7 (16.2) 28.7 (14.0)	No difference (p = 0.836)

4.3 Review of the U.S. EPA's Peer Review Process for the Phase 3 Assessment

As part of its evaluation, U.S. EPA solicited a peer review of the Phase 3 document. U.S. EPA provides a discussion of the intent of peer review in its *Peer Review Handbook* (U.S. EPA, 2012c):

> Peer review is intended to uncover any technical problems or unresolved issues in a preliminary (or draft) work product through the use of independent experts. This information is then used to revise that draft product so that the final work product will reflect sound technical information and analyses. Peer review is a process for enhancing a scientific or technical work product so that the decision or position taken by the Agency, based on that product, has a sound, credible basis…

> Peer review is intended to uncover any technical problems or unresolved issues in a preliminary (or draft) work product through the use of independent experts. This information is then used to revise that draft product so that the final work product will reflect sound technical information and analyses. Peer review is a process for enhancing a scientific or technical work product so that the decision or position taken by the Agency, based on that product, has a sound, credible basis.

U.S. EPA developed a Peer Review Plan for the Phase 3 project prior to October 2012 (U.S. EPA, 2012d). In terms of its potential impact on public policy or the private sector, the project was characterized by an Office of Management and Budget (OMB) Category of "influential." However, in our review of the Peer Review Plan, the charge to the peer reviewers, and the submitted comments from the peer reviewers[8], we find that the peer review did not achieve the level of transparency and rigorous analysis necessary to adequately inform U.S. EPA of the limitations of the Phase 3 document.

First, while the peer review request was for "independent experts" in the area of chemical-biogeochemistry, public nominations were not solicited, nor does it appear that public, scientific societies were asked to nominate peer reviewers. Per U.S. EPA's *Peer Review Handbook* (U.S. EPA, 2012c):

> An independent peer reviewer is an expert who was not associated with the generation of the specific work product either directly by substantial contribution to its development or indirectly by significant consultation during the development of the specific product….Independence is freedom from institutional or ideological bias

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[8] U.S. EPA presents the Peer Review Plan, the identity of the Peer Review Panel, the Charge to the Third Party Reviewers, and the submitted Peer Reviewer comments on their website at: http://cfpub.epa.gov/si/si_public_pra_view.cfm?dirEntryID=242089

> regarding the issues under review and is necessary for objective, fair, and responsible evaluation of the work product. If a selected reviewer has a particular scientific or technical perspective, it may be desirable to balance the review with peer reviewers with other perspectives. In addition to being independent, ideally, peer reviewers should be free of real or perceived conflicts-of-interest.

However, U.S. EPA was not transparent about the process they used to select the peer reviewers (e.g., no information in this regard is presented on their website) nor do they present information demonstrating the independence of the peer reviewers from conflicts-of-interest.

Second, the peer review group was small in number (4)[9], which limits the breadth of technical capability offered by the group. Only three peer review response reports were found on U.S. EPA's website.[10] While it can be argued that all of the peer reviewers are independent, in that they are drawn from outside the U.S. EPA office that conducted the Phase 3 work, all are either U.S. EPA, USGS, or USDA employees.[11] While U.S. EPA's *Peer Review Handbook* (U.S. EPA, 2012c) states, "Peer reviewers can come from EPA, another Federal agency, or from outside of the Federal government," one might wonder how the inclusion of nonfederal employees might have broadened the perspective of the provided comments. It is also not clear when the peer reviewers were convened and how much time was provided to them to conduct their review. If the allotted time was brief, the peer reviewers might not have had sufficient time to conduct a thorough assessment.

Third, the comments by a majority of the peer reviewers were short and lacking in rigor. While Dr. Young provided nine pages of detailed comments, the other response documents are no more than two pages long and some responses are a single word (e.g., Q. "Are the uncertainties adequately addressed and clearly articulated?" A. "Yes."). Given the length of the Phase 3 document and the size of the sampling and analytical program, it is surprising that the reviewers did not have more extensive observations about the program.

Fourth, some of the comments provided are consistent with what we observed. For example, Dr. Young comments on the uncertainties in determining contaminant sources introduced by the mixed land use:

> (p. 1) I don't see anything within the data that could more strongly link the nitrate contamination to specific sources. Based on the age dating results, isotope results, and fairly widespread occurrence of atrazine and a few other compounds, the nitrate in many of the wells is most likely from a mix of sources which would be challenging to tease apart, probably requiring a much more extensive sampling campaign and more knowledge of well depth and screen lengths;
>
> (p. 3) Approximately how long have the dairies been in operation? The age dating results suggest that many of the wells are probably sampling mixed older and younger water, so I'm still unsure about whether the upgradient vs. downgradient wells can be used to directly identify dairy-related impacts. I think this is addressed well in Section X, but I think the uncertainties associated with mixed land use need to be mentioned throughout the report;

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[9] While there are five separate names listed on U.S. EPA's website, Dr. Lorraine Edmond's report was not provided on the website as of date of these comments.

[10] Stephen Kraemer, Ph.D and Roger Burke, Ph.D., are co-authors of a single report.

[11] Lorrain Edmonds, Stephen Kramer, and Roger Burke are affiliated with the U.S. EPA, Megan Young is affiliated with the USGS, and David Turkalson is affiliated with the USDA.

> (p. 4) Pg 15. How certain is it that the dairy areas only contain dairy-related sources? The aerial photos seem to show surrounding fields- are these all dairy fields? Maybe state that within the mixed septic & irrigated cropland areas, these sources were all within X kilometers of the sampled wells, while in the dairy areas, only dairy-related fields were located within X kilometers of the sampled wells;
>
> (p. 5) Pg 17: In the criteria for selection of septic systems, there needs to be further explanation about how well the selected wells met the criteria of "minimal upgradient nitrate sources other than septic." Maybe an approximate distance away from any irrigated and fertilized fields? On page 15, it is mentioned that the three other areas contain both septic systems and irrigated cropland sources.

She also comments on the possibility that wells sampled different aquifers:

> (p. 4) Pg 9 Study Area- what is the possibility that some/ any of the wells sampled in this study are within the deeper aquifer? This section goes into detail about the uncertainties, but in the sections on the different well results, the report makes it sound like there is reasonable certainty that the upgradient and downgradient wells are tapped into an aquifer with a known and somewhat rapid flow direction. Since approximate depth to the confined aquifer isn't mentioned in the Study Area section, I can't evaluate the likelihood that any of the wells might be in a deeper aquifer with an unknown flow direction.

She also comments on the overlapping isotopic compositions contributed by different nitrate sources:

> (p. 5) Pg 26. Second paragraph in Isotopic Analysis. I would suggest changing the phrasing of this paragraph to state that multiple studies have shown that various dominant nitrate sources can have overlapping isotopic compositions, and that unless the range of isotopic values for nitrate source end-members within the local study area has been well measured (and have distinct isotope values), nitrate which falls into the isotopic range in which the sources overlap cannot be distinguished based on isotopes alone.

She also comments on the contribution of other land uses to some of the specific detected contaminants:

> (p. 6) Pg 33-34. Since atrazine was found in the upgradient well and the downgradient wells, it seems like you should mention that the atrazine could also be from other surrounding land uses, the occurrence of atrazine in the application fields doesn't provide a very strong link to the downgradient wells, particularly since it seems to have been found in wells with different land uses as well;
>
> (p. 8) Pg 67. I think the complications associated with mixed land uses should also be mentioned here, particularly because the detections of some compounds in the various upgradient wells indicates the presence of different sources of various compounds within the study areas. You can emphasize that sites were selected to try and minimize mixed land use, but it will always be close to impossible to find areas with only a single land use.

Overall, we find that U.S. EPA did not conduct an appropriately rigorous peer review that embraces the spirit of the peer review process as described in U.S .EPA's own guidance (U.S. EPA, 2012c).

5.0 CONCLUSIONS

U.S. EPA (2012a) emphasizes a number of results in order to support its conclusion that dairies are contributing significantly to well water contamination. However, it downplays results that both suggest other sources also contribute significantly and that demonstrate the difficulty in allotting contamination to any source without a more detailed and careful sampling and analysis program. U.S. EPA also does not adequately emphasize the numerous data quality concerns.

A number of issues with the design of the sampling and analytical program are apparent, resulting in data that are insufficient to conduct scientifically reliable assessments of the potential source of contaminants. Specifically:

- Well sampling locations were selected in a biased manner, such that only those with the highest nitrate concentrations measured during the Phase 2 investigation were selected for sampling in Phase 3. This bias towards higher concentrations can result in invalid conclusions about the extent of contamination.
- Only two upgradient well water samples were collected, one upgradient of each dairy sampling area. As a result, there is little information on "background" conditions (i.e., conditions unimpacted by the sites), and it is impossible to determine whether concentrations measured downgradient are statistically similar to or different from background. Consequently, there is no scientific certainty about any conclusions drawn with regard to these data. Further, U.S. EPA did not collect well water samples upgradient of the other types of sources it evaluated, including septic systems and irrigated crop lands, such that conditions unimpacted by these sites are not known.
- U.S. EPA did not collect background soil samples to assess concentrations of contaminants in soil in the lower Yakima Valley from such sources as residential, urban, or industrial sources. Thus, the contribution from these sources is not known.
- U.S. EPA does not demonstrate that upgradient and downgradient wells are measuring the same aquifer, since U.S. EPA relied on existing residential wells and had limited information on the depth of many wells. Regarding this, U.S. EPA states, "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."
- U.S. EPA had little information on groundwater flow and acknowledges that "Very frequently, there are 10- to 100-fold differences in groundwater velocities among aquifer materials of such contrasting grain size…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 nitrate could produce different downgradient effects in groundwater (such as nitrate in water wells), even in wells from neighboring homes."
- Review of nearby land use suggests there are other uncharacterized sources of contamination upgradient of the dairy areas, including livestock activities, cropland, and septic systems.
- Water samples are grab samples reflecting concentrations at a single point in time. Groundwater conditions and water conditions can fluctuate seasonally and it is not known how measured results reflect longer term conditions. In addition,

concentrations of some of the analytes such as soil fertilizer and pesticides are also expected to show seasonal variations in concentrations depending on application time.

- Cropland sampling was very limited. Contributions from other types of crops (e.g., alfalfa, wheat, hay, tree fruit, grapes) were not assessed. Interpretation of crop field data is also complicated by the fact that some are located near other possible source areas (e.g., near septic systems) and crop fields were treated with both synthetic and animal fertilizers.
- A substantial percentage of the analytical data are “J qualified”—i.e., reported concentrations are estimated. These concentrations can be biased low or high such that direct quantitative comparison of samples is not be appropriate without case-by-case evaluation.
- U.S. EPA had difficulty analyzing both trace organics and wastewater pharmaceuticals, and indicated that results of these analyses should be considered screening level and not fully usable for quantitative evaluations. However, these two analyte types would be most useful in supporting efforts to assess whether human wastewater sources contribute to concentrations detected in downgradient wells. The lack of quality data for these parameters limits the usefulness of this investigation.
- U.S. EPA’s Water Science Lab reported that monensin and lincomycin were detected in the well water field blank sample, such that any detects of these analytes in well water samples should be qualified.
- U.S. EPA did not meet preservation requirements for about one-third of the nitrate analyses, which could bias sample results.
- U.S. EPA did not collect field duplicate samples for well water or lagoon samples due to an oversight and so cannot document the reproducibility (precision) of the sampling and analytical methods applied to these samples, reducing confidence in the quality of the well water data.
- Detection limits for some analytes, especially wastewater pharmaceuticals, appear elevated. Consequently, it is inappropriate to conclude that human waste did not contribute to concentrations in corresponding wells, since lack of detection could be due simply to elevated detection limits.
- Differential movement of contaminants through soil and groundwater due to different fate and transport properties makes it impossible to establish “fingerprints” for these compounds and determine the source of contaminants.
- Nitrate isotopic ratios for synthetic fertilizer and animal waste sources can vary beyond the ranges assumed to by U.S. EPA, and their methodology cannot distinguish between human and other animal sources.

Given the data do not meet a minimum level of reliability, the assessments of Haak Dairy and the Dairy Cluster as well as the assessments of irrigated cropland, wells downgradient of residential septic systems, and WWTP influent cannot be used to make reliable determinations about the source of contaminants. Specifically:

- None of the detected pesticides can be reliably attributed to the dairies. Atrazine was detected in both upgradient wells and at variable concentrations downgradient. All reported concentrations are “J qualified” (estimated), and atrazine is largely ubiquitous in agricultural areas. Alachlor was only detected in two downgradient wells, and reported concentrations are J qualified. Ioxynil was detected in only one downgradient well at a concentration well below the quantitation limit and reported concentrations were J qualified.

- The only detected trace organic (DEHP) cannot be reliably attributed to the dairies. DEHP was detected in three downgradient wells, as well as one upgradient well. Although it was detected in some dairy source samples, it was also detected in all of the WWTP influent samples. Further, per U.S. EPA, the trace organic concentrations should be interpreted as "screen" values. Finally, DEHP is widely detected in the environment due to its use as a plasticizer.
- The only detected wastewater pharmaceutical (DEET) cannot be reliably attributed to the dairies. DEET was detected in one downgradient well. Although it was detected in some dairy source samples, it was also detected in all of the WWTP influent samples. Further, per U.S. EPA, the wastewater pharmaceutical concentrations should be interpreted as "screen" values.
- The five detected veterinary pharmaceuticals can have multiple sources (monensin, chlortetracycline, tetracycline, tylosin, and virginiamycin). Tylosin and virginiamycin were detected infrequently. Monensin was detected both upgradient and downgradient, and U.S. EPA concluded, "The detection of monensin in the upgradient well indicates there is an upgradient source of this compound." In addition, the detection of monensin in the field blank samples indicates that it cannot validly be reported as detected in downgradient samples.

  Tetracycline was detected in both upgradient and downgradient wells, is used as a human pharmaceutical, and was detected in one WWTP influent samples. In addition, tetracycline compounds (oxytetracycline) are used as a fungicide and bactericide on tree fruit in Washington State. Regarding tetracycline, U.S. EPA states "given that the concentrations in the upgradient well are higher than the downgradient wells, another source for the tetracycline is likely." U.S. EPA further states, "Given the results, septic systems are a possible source of tetracycline and sulfamethoxazole, both of which can be used by humans, in the residential drinking water wells."
- The three detected hormones (testosterone, androsterone, and androstadienedione) cannot be reliably attributed to the dairies. All three hormones were detected in all three of the WWTP influent samples. Regarding testosterone, U.S. EPA states, "The dairies are a possible source of the testosterone in the downgradient wells; however, given the concentration in the upgradient well, another source for the testosterone is likely." Androsterone and androstadienedione were detected downgradient only in J qualified samples.
- Barium was the only trace inorganic element that increased between the upgradient well and downgradient well at the Dairy Cluster. However, some downgradient concentrations are lower than the upgradient concentration, and some directly adjacent downgradient wells have very different concentrations. These assessments show that comparison a single upgradient measurement to the downgradient measurements is scientifically invalid and produces no meaningful information. In addition, U.S. EPA does not support its assertion that barium is used at the dairies and therefore that the dairies are a potential source.

Regarding the peer review process for the Phase 3 document, U.S. EPA did not conduct an appropriately rigorous peer review in accordance with the spirit of the peer review process as described in U.S .EPA's own guidance. Specifically,

- U.S. EPA's selection of peer reviewers was not transparent, and all four peer reviewers were drawn from federal agencies, potentially limiting the perspectives of provided comments.
- Aside from one peer reviewer, most of the peer review comments received were extremely brief and not adequately rigorous to provide U.S. EPA with sufficient information on the quality of the science presented in the Phase 3 document.
- Of the more rigorous comments received, concerns presented were similar to those we discuss, including the lack of appropriate characterization of contributions from mixed land use, absence of evidence that wells sampled the same aquifers, and misrepresentation of the overlapping ranges of isotopic ratios contributed by different nitrate sources.

In summary, because of the numerous sampling design and analysis issues in the Phase 3 program as well as the potential impact of highly mixed local land uses, we conclude there is insufficient information to determine with scientific certainty whether and how much any of the sources could have contributed to contamination in downgradient wells. In particular, because of the numerous issues highlighted above, no particular location can be implicated as a source of any of the contaminants measured.

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RICHARD C. PLEUS, PH.D.
BIOGRAPHICAL SKETCH

RICHARD C. PLEUS, PH.D., Intertox managing director and toxicologist, is an expert in neurological and reproductive toxicology with over 25 years' experience assessing the risk to humans exposed to chemical and biological agents via food, consumer products, therapeutic agents, and the environment.

Dr. Pleus' current research has focused on emerging contaminants in water, such as endocrine disruptors (EDCs), pharmaceuticals, and personal care products (PPCPs). He has recently been involved with a number of research projects focusing on PPCPs and EDCs in drinking water with the Water Research Foundation (formerly American Water Works Association Research Foundation (AwwaRF)), and the WateReuse Foundation (WRF).

Dr. Pleus' credentials include a B.S. in Physiology, with honors, from Michigan State University, an M.S. in Environmental Health and a Ph.D. in Environmental Toxicology from the University of Minnesota, and postdoctoral research in neuropharmacology at the University of Nebraska Medical Center.

GRETCHEN BRUCE, DABT
BIOGRAPHICAL SKETCH

Gretchen Bruce, DABT, Intertox Director of Toxicology, and has over 20 years of professional experience as a toxicologist and risk assessor assessing risks to human health posed by a wide range of compounds in different media. Areas of particular expertise include the assessment of pharmaceuticals and endocrine disrupting compounds (EDCs) in source and drinking water; characterizing the state of knowledge regarding the toxicity of metals, organics, and nanomaterials; and establishing risks of leachables, extractables, and excipients in consumer drug products.

As a risk assessor, Ms. Bruce has managed and conducted risk assessments for industrial and residential sites in accordance with federal CERCLA/RCRA, state, and local guidance for more than a dozen states. Project experience includes assessing fate and transport and establish site cleanup levels; negotiating with regulatory agencies; designing and conducting field sampling programs and laboratory QA/QC reviews; conducting detailed evaluations of the validity of default assumptions for site-specific assessments; and designing multipathway probabilistic exposure models to characterize the uncertainty and variability in estimated doses.

Ms. Bruce holds a Bachelor of Science degree in Environmental Toxicology from the University of California, Davis, and is certified as a Diplomate of the American Board of Toxicology.