

Full Comments Section

In general this report is well written and well organized, and provides a large amount of data that will be very useful to future studies and/or regulatory decisions. Most of the figures are easy to understand and well-integrated into the text. Appendix B presents a very good discussion of the uncertainties associated with the isotope data set for this study.

I do not see any major problems with the report, the majority of my comments are aimed at places in the report where additional clarification is needed and where I think uncertainties associated with some of the conclusions need to be either clarified or stated more strongly.

Answers to the review questions:

- 1) In general, the purpose, scope and objectives of the project are clear. I'd suggest adding a couple of sentences in the relevant sections to indicate that the results of Phase I and Phase II are presented in more detail in other reports.
- 2) Reasons for selection of the various measurements are very clearly presented in the report.
- 3) The experimental design is clear, although I think there should be a bit more mention of the uncertainties associated with defining upgradient and downgradient wells (see specific comments below).
- 4) See general and specific comments about the isotope interpretations below. In general I think this is well presented, but a few edits & clarifications are still needed.
- 5) The conclusions are well supported by the results.
- 6) 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.
- 7) In general the uncertainties are well addressed, I have added specific comments in places where I think some of the uncertainties either need to be more clearly stated, or need to be stated in the body of the report as well as at the end and/or in the appendices.

Isotope Data, General

I think that some edits still need to be made regarding how the isotope data is presented in the body of the report. While Appendix B provides a very good discussion of the uncertainties associated with using isotopes to determine nitrate sources, within the body of the report there are several places where conclusive statements are made about nitrate sources to certain wells without the necessary explanations/caveats regarding the associated uncertainties. Within the discussions of many of the other compounds there

was better emphasis on what statements were the researchers' interpretations of the data, while there were several places where isotope interpretations were presented in ways that indicate definitive conclusions which I think over-reach the strength of the current data set. For example, on page 40 one sentence reads "For WW-04, the possible sources are fertilizer and animal waste, while the dominant source for WW-05 is animal waste". I think that this conclusion needs to be phrased differently to acknowledge the existing uncertainty- possibly use "WW-05 appears to be animal waste based on the elevated $\delta^{15}\text{N-NO}_3$ values". Later on the same page the sentence "The isotopic data provide good evidence that animal waste is a dominant contributor to the nitrate contamination for WW-05" is a more accurate statement.

My primary concern regarding the isotope data is that due to limitations inherent in the study (well location, unknown depths, and unknown mixing/ flow paths, and potential mixed land use), the local end-member isotope values aren't well-defined, and potential effects of partial denitrification (which will increase isotope values while decreasing nitrate concentrations) couldn't be assessed for this study. I think the isotope data provide good indications of different sources of nitrate to different wells, and this is very well explained in Appendix B, but having what appear to be definitive statements about nitrate sources within the main body of the text could be very easily challenged by readers of the report.

Some specific suggestions related to how the isotope data are reported:

Within the body of the isotope data tables, the phrase "Fertilizer & Animal Waste" is used, even though in the table footnotes it is clarified that the interpretation is indeterminate- it could be all fertilizer, all animal, or a mixture. I suggest changing what is written in the table to "fertilizer and/or animal waste" which would be more accurate. The wells in which the higher $\delta^{18}\text{O-NO}_3$ values suggest an atmospheric source are a bit more complicated- I think the most accurate phrasing might be "fertilizer and/or animal waste, with atmospheric contribution", since the $\delta^{15}\text{N-NO}_3$ values are inconclusive, but the $\delta^{18}\text{O-NO}_3$ values indicate that there has to be some sort of atmospheric contribution, either from specific fertilizers containing atmospheric nitrate, or from caliche leaching of long-term atmospheric nitrate deposition.

The overall isotope assessment of WW-02 should be changed to indeterminate- the nitrate concentration is slightly elevated in comparison to the lowest concentration wells, and there's no way to determine from the isotope & concentration data whether the nitrate came from soil cycling, or if there is simply a very small amount of either fertilizer or animal/human waste derived nitrate in the well. This does seem to be the only well where the isotopic composition and the concentration indicate that soil cycling can't be ruled out, but it isn't the only possible explanation.

Other general comments:

I think it would be very useful to include some brief comparisons between the different land uses for the distributions of the various compounds, which would be particularly valuable to future studies that might be interpreting well data in areas with very mixed land use. For example, are there any apparent trends in distributions of pesticides

between the different land uses? Did anything stand out as more frequently detected (or detected at higher concentrations) in the downgradient dairy wells in comparison to the downgradient septic and agricultural wells? It seems like atrazine was found across several different land uses- maybe include a comment about this and an brief evaluation of whether this means it might not be particularly helpful in future studies.

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.

If you anticipate controversy related to the release of this report, I think it might be worth mentioning early in the report that the dairies included in this study are expected to be fairly typical of dairy operations within the Yakima Valley, and that it is unlikely that the findings of elevated downgradient nitrate are unique to these particular dairies. However, I noticed that you said you selected dairies with over-application of fertilizers, so maybe they aren't typical. It would be worth some sort of very brief statement regarding whether you might expect conditions at these particular dairies to be applicable to other dairies in the area- I don't know how many dairies get flagged for over-application of N.

In the aerial photos of the Haak Dairy and the Dairy Cluster, it appears that there are a lot of agricultural fields surrounding the dairies. It also appears from the land use maps that there is some sort of agricultural land use (orchards? I can't quite tell if that's the same shade of pink in the land use map) upgradient of the dairies. I think there needs to be some discussion within the body of the report that the wells downgradient of the dairies may be drawing water from mixed agricultural land uses, or there needs to be a clearer presentation of why it is doubtful that surrounding fields that aren't dairy-related wouldn't be likely to contribute nitrate. Are the fields in the photos all/mostly related to the local dairies and received manure applications, how likely/ unlikely is it that nearby fields are getting synthetic fertilizers for non-dairy uses?

Specific comments (in order that they appear in the report):

Pg xi: UJ should be listed under acronyms and abbreviations, also "JN" is listed, but I didn't see it used anywhere in the table.

Pg 4. Last sentences of the introduction paragraph are somewhat confusing, since nitrate concentrations below 0.5 mg/L can often be found in non-impacted groundwater, and it is unclear if the 1.1 mg/L upper range might be applicable to this study area. Maybe re-phrase to clarify.

Pg 4.Purpose & Scope- mention the possibility of synthetic fertilizers as nitrogen sources on dairies, since this is introduced as a unknown quantity later on in the report (unless there is additional information which makes it clear that fertilizers on the dairies must be

a small source of nitrate in comparison to the manure generated). Also, the report later on mentions that manure might be applied to non-dairy croplands.

Pg 7. Nitrogen Cycle- Somewhere in the last three paragraphs on the nitrogen cycle would be a good place to first mention that nitrate can build up in the soils of arid basins under certain circumstances.

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.

Pg 11. It would be helpful to explicitly state that the details of Phase I and Phase II are/will be included in separate reports. When I first read this section it was difficult to tell if this was supposed to be a comprehensive reporting of all Phases, or just Phase III, with summaries of the other two phases.

Pg11. Since Figure 6 doesn't have a caption, the detailed explanation (which now seems to be the second to last paragraph in the Irrigated Cropland subsection) should be moved close to the first mention of Figure 6. At first I wasn't able to figure out how the estimates were derived or what the figure really represented because the explanation was much further along in the section

Pg 11-12 Section goes from Figure 6 to Figure 8, Figure 7 doesn't appear to be mentioned until pg 14- change the order of the figures?

Pg 13. Where does the water discharge from these WWTPs get released? Does it leave the area in surface water, or is it used along with some of the biosolids in land application. If the WWTPs only go to secondary treatment, this could be a source of high N water somewhere in the study area. Briefly mention why this either might be important or explain why it can be ignored for this study (discharge to surface water, tertiary treatment with low final N levels, etc).

Pg 14. Is the Phase II data being evaluated in a separate report? It seems like this dataset would be useful for an analysis of land use vs. nitrate concentrations, but it is difficult to tell from the way this section is written whether or not additional evaluations of the Phase II dataset were done somewhere else.

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.

Pg 16. How far away were other potentially significant land uses from the wells with potential septic influence? Are they reasonably isolated from fertilizer & irrigated fields?

Pg 16. The final paragraph of the Phase 3 section is a bit confusion, particularly because of the sentence that starts “The five groups include:...” but then only lists three categories. Rephrase for clarity.

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.

Pg 21. Microbiology section- it would be easier to follow if the report indicated which samples were tested using MST, rather than listing which samples were not tested.

Pg 24. The discussion of the veterinary pharmaceuticals is somewhat confusing. One sentence states that “Detections of the compounds in Table 3 in water wells would provide evidence that dairies are a likely source of those compounds”, but then further reading makes it sound as if this is not necessarily true since some of the compounds are also used in humans, and the report cites two references saying that some of these compounds have been detected in wastewater treatment facilities. Is it only some of these compounds that can rule out human-derived waste? When other researchers detected these compounds in the wastewater treatment plants, did they conclude that somehow animal waste was entering the treatment facilities?

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. The phrase “the science is still evolving” is somewhat true, but it implies that additional understanding of the fractionations will eventually allow us to distinguish these sources. This isn’t really true- the area of overlap/ undetermined isotope composition has been found in multiple studies, and it is extensive local sampling (including well-constrained end-members) within a single study area, not additional general scientific understanding, that has the potential to allow different sources to be separated with more confidence. I think it is important to make brief mention of how in-situ denitrification and/or mixing can shift the isotope values away from the original source signal. This is fairly well addressed in Appendix B, but I think it needs to be specifically mentioned within the body of the report. Also, some of the wells did have low field values for dissolved oxygen (I’m not too sure how accurate the field measurements are considered to be for this study), so shifts in individual wells due to partial denitrification is a possibility. However, I looked

at the plots of dissolved oxygen vs $\delta^{15}\text{N-NO}_3$ and did not see any trend, so I think it is reasonable to rule out in-situ denitrification as a significant factor.

Pg 27. Specify that the atmospheric $\delta^{18}\text{O}$ of 23.5 per mil is for O_2 gas (to differentiate it from NO_x in the atmosphere).

Pg 28. Not too sure what is meant by “groundwater elevations fluctuate rapidly”- is this fluctuations in depth to groundwater, or rapid travel along a flow path from high to low elevations?

Pg 28. I think it would be a good idea to include a statement about whether or not, or to what extent, the reported age dates can be considered valid. Does the presence of over value samples suggest that all the samples in the area could be altered by local geology, or is this something that would only impact the wells that are already flagged as having invalid SF_6 ages?

Pg 29. What is the function of the Dairy A ditch? Since it is mentioned, indicate whether it carries waste, or just surface water for transport, irrigation, some other use? Is it lined or unlined- I’m wondering if it could leak in a similar fashion to the lagoons and also serve as a local source of rapidly infiltrating water.

Pg 29. The pivot-irrigated fields are clearly visible in the aerial photos- do the other fields around the pivot also receive liquid or solid manure?

Table 5: There seems to be at least a couple of things wrong with the reported values for the lagoons- it should be L-01, -02, and -03 (the table lists L-03, -04, and -05), but the Ammonia values in the table appear to be from L-04, -05, and -06 according to Table A2 in the Appendix.

Pg 32. Paragraph directly following Table 6- Is there a reference for the barium and zinc levels reported for local surface waters?

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.

Pg 41. It’s unclear what the differences are between the dairy supply wells and the domestic drinking water wells. Is there evidence that well construction/ depth/ pumping rates are different, or is the only known difference the choice of use (drinking vs. other uses)? Could the supply wells be considered upgradient or mid-gradient?

Pg 44. The lagoons are mentioned as a potential source for the major ions, but is there any evidence that the lagoons are more important than the sprayfields? If they are using the spray fields partially for liquid manure disposal (instead of balanced entirely for

limited fertilization), it seems like the large areas covered by the sprayfields could be equally as important as the lagoons.

Pg 44. “However, elevated levels of perchlorate were seen in only two wells”- include which wells were elevated, and what the threshold was for defining elevated.

Pg 47. Since the tetracycline was detected in higher levels in the upgradient wells in comparison to the downgradient wells, it seems like it could be coming from mixing along flowpaths with other sources, and not necessarily from the dairies. I think it is quite reasonable to state that the dairy cluster is a possible source, but it seems like the other possibilities should also be clearly stated here.

Pg 48. Dairy cluster- hormones. The upgradient well (WW-06) isn't mentioned as either having hormone detections or not having hormone detections.

Pg 48. first sentence of Dairy cluster- isotopic analysis, chose a different word instead of “completed”, maybe use “performed” or “attempted”, since in the first sentence it says that isotope analysis was completed on all wells, then the next sentence says it couldn't be completed on certain wells.

Table 15. In the table, change to fertilizer and/or animal waste for consistency and accuracy.

Pg 49. Paragraph following Table 15- change “dominant source is animal waste” to something like dominant source appears to be animal waste, or “ $\delta^{15}\text{N-NO}_3$ values indicate that the dominant nitrate source is most likely animal waste”.

Pg 50. The sentence “Table 16 indicates the source of nitrate in the dairy lagoons is animal waste” seems very unclear. Maybe change this to something like “Table 16 provides an assessment of the level of volatilization of the animal waste as indicated by the isotope values”.

Pg 54. 2nd paragraph- need qualifiers on the isotope assessments, the isotope values indicate or suggest the different sources for the different wells, replace “is” with some phrasing that incorporates the uncertainty, or make it clear that the assigned sources are and interpretation based on the evidence.

Pg 54. 3rd paragraph- this says “upgradient wells” but it appears there is only one upgradient well?

Pg 54. 4th paragraph- the phrase “ dominant nitrate source for the pharmaceuticals” doesn't make sense, I'm not too sure what the paragraph is trying to convey.

Pg 54. It's unclear what the sample SP-04 represents, maybe remove it completely from the Appendix tables if it isn't part of the report?

Pg 55. Major ions- I don't think the use of major ions has to be limited to transformations along a flowpath. As you mention earlier in the report (in regards to ion ratios), major ion distributions can also sometimes be indicative of specific water and/or contaminant sources.

Pg 55. Septic Systems- trace elements. It would be interesting to add a few sentences comparing the distributions of trace elements found in these wells with the distributions found in the downgradient dairy wells, even if the conclusion is that they aren't helpful at this time for distinguishing different contaminant sources.

Pg 61. 2nd paragraph. I suggest using animal/human waste instead of just "animal waste". It is stated earlier in the report that animal waste includes humans, but I think clarifying this again will help avoid confusion for people reading the report.

Pg 62. It would be interesting to include a paragraph explicitly comparing the various N concentrations in the field soils with those found in the dairy soils.

Pg 63. Change "only two were detected in the six water wells" to "only two were detected in ANY of the six water wells" in order to clarify that there weren't detections in all six wells.

Ph 63. Pharmaceutical, 1st sentence- change "Nine compounds were detected" to "nine compounds were detected in this well".

Pg 64. Hormone- right after the bulleted list. This sentence is a bit unclear, it says that the hormones are naturally produced by animals, and can be expected in septic systems- does this mean that they are also produced by humans, or do non-human animal produced hormones often reach septic systems. Even though the term "animals" technically includes humans, I'd suggest specifying throughout the report which things are non-human animals only, and which things are human & other animals.

Pg 65. 1st paragraph. I'd suggest including one sentence clarifying that it is the elevated d18O-NO₃ which indicates an atmospheric contribution.

Pg 66. Were these the only wells where bentazon was detected?

Pg 66. What is the approximate distance of the dairy?

Pg 67. Would it be possible to include a general land use assessment for wells 18 and 30. Are they in predominantly residential areas, irrigated croplands, something else?

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.

Pg 69. Give a very brief summary of why the microbial and age dating data weren't useful in identifying sources.

Pg 69. The sentence "the presence of these compounds in theses sources..." is a bit unclear, maybe change to "the presence of these compounds in the primary sources (lagoons, manure piles, soils) but not in the water wells..."

Appendix Table A1: SP-04 seems to be missing from this table. It appears in some tables but not in others?

Appendix Table A3: what does the qualifier KK mean for sample SO-01 NO₃N/Total solid? KK isn't listed in the Acronyms/ Abbreviations section.