

Comments to Natural Background Groundwater Arsenic Concentrations in Washington State: Results of a Study. Publication Number 14-09-044. – Kennedy/Jenks Consultants, Inc.

Overall comments: While the report does provide a range of background arsenic concentrations in groundwater in Washington state public water supply wells, some clarifications of the source data are needed including handling of non-detect results, availability of well construction data, geochemistry of the water samples, and retention/omission of data based on location (inside/outside selected water basins) or value (e.g., were outliers removed?).

Several variables are mentioned in the report that could affect arsenic concentrations statewide and/or in individual wells including groundwater geochemistry, geology, redox conditions, soil organic matter content, topography, groundwater gradients, well screen lengths and depths, and pumping rates. However, except for well depths, data are not provided or evaluated for the other factors. Focusing solely on well depth has the potential for lumping together a number of these variables without knowing how they individually affect concentrations. As stated at the conclusion of Section 6.0, “In terms of higher naturally occurring arsenic levels, the key variables [in similar studies] are typically: 1) groundwater geochemistry (reduced conditions), and 2) increased soil organic matter / content.” As these variables were not evaluated in the present study, care should be taken in drawing any conclusions about the variables affecting arsenic in Washington state groundwater.

The report addresses natural background on a basin-wide level; however, due to natural variability in groundwater geochemistry, geology, and other variables mentioned above, the spatial scale of variability in natural background could be smaller than basin-level. A discussion of the ways that this study could be applied to other evaluations of natural background, on other spatial scales, would be helpful. Such items could include a discussion of minimum standards of data quality for establishing background, including: the number and spatial distribution of data points, the relevant well depths and other associated factors, and processes for evaluating data quality and anthropogenic influence.

1. Tables and Figures:

- a. Check (and revise numbering as applicable) the order in which the tables and figures are referenced in the text.
 - b. Is there a reason why several tables (14, 15) and figures [5-11 (in Table 1 but not text), 16-19, 22-29]), are not referred to or discussed in the report text?
 - c. Figure 22 is missing.
- 2. Tables 2, 4, and 6 for total sample counts by basin:** Check the total number of samples for Island County (Table 4) and Okanogan Basin (Table 6) vs. Table 2.
- 3. Figure 12:** There is no discussion of outliers in the text, but Figures 12, 15, and 18 show boxplots with outliers removed. If outliers are removed, this needs to be a major discussion topic as there should be a very specific reason for removal of outliers. Outliers make up an important part of the dataset unless they must be rejected for data quality issues.
- 4. Section 1.0 Summary, Page 1:** define units first time used, e.g., micrograms per liter ($\mu\text{g/L}$), in first sentence of second paragraph. Why is Figure 1 in this section?
- 5. Section 3.0 Background, Page 5:** This section provides a general summary of arsenic occurrence and geochemistry. It is not until Section 5.3.2 and later in the document that variables potentially affecting the concentration of arsenic in groundwater are introduced (e.g. redox conditions, pH, soil organic matter content, geology, etc.). Consider moving the summaries of previous studies conducted in Washington and other states from Sections 5.3, 5.4, and 6.0 to Section 3.0 to provide more background earlier in the document.

6. **Section 3.0 Background, Page 6:** Since this is a Washington-specific document, showing Washington state only in this figure would be more helpful and/or add the Washington state data in a separate, zoomed in figure to show more detail.
7. **Section 4.1 Groundwater Arsenic Well Data, Page 7:** Is the data used for this study available in a tabulated format? Several questions about the data itself:
 - a. Is there a summary of the available public water supply well construction data (well, location, installation date, total well depth, screen interval, range or average water column height)?
 - b. Does the dataset include total and/or dissolved arsenic concentrations?
 - c. What water chemistry data is available for the samples [arsenic and other constituent concentrations (e.g., iron, manganese, other metals, anions), dissolved oxygen (DO), oxidation-reduction potential (ORP), pH, temperature, total dissolved solids, turbidity, etc.]?
 - d. Were non-detect (ND) results in the data sources (e.g., DOH database) reported to the method detection limit (MDL) or method reporting limit (MRL)? Please update text in other sections (e.g., Sections 4.5 and 4.7) to clarify this.
8. **Section 4.3 Watershed Basins, Page 8:** Were cleanup sites only used to identify basins? Earlier text indicates that cleanup site data was not used to evaluate arsenic, so it is unclear why cleanup sites are being mentioned in this and the paragraph after unless it's primarily to determine basins. Clarification of the use of cleanup site data could be helpful.
9. **Section 4.5 Non-Detects, Page 9:**
 - a. Third sentence: Please clarify if 'arsenic non-detect' refers to the laboratory MDL or MRL. A range of data is presented, not an average; suggested edit (if these are laboratory MDLs): *"From 2000 to 2002, reported arsenic method detection limits ranged from 6.7 to 8.8 µg/L. However, from 2002 to 2010, reported arsenic method detection limits ranged from 2.1 to 2.5 µg/L."*
 - b. Second paragraph, bullets: These are analytical instruments used for metals analyses, not the methods. Does Ecology have information about the laboratory analytical methods (e.g. EPA Method 6000 series or others) that were included in this study?
10. **Section 4.6 Point Averaging, Page 9:** How much variability existed in arsenic results by well between 2003 and 2010? The second paragraph refers to the variability in the numbers of samples for a given well but does not provide any further information as to how this was handled other than averaging results for each well – a discussion of these data quality aspects would be helpful.
11. **Section 4.6 Point Averaging, Page 9:** The influence of seasonal variability is a potentially important part of understanding and evaluating arsenic background concentrations at cleanup sites and compliance with cleanup levels. If seasonal variability is naturally present, then it should be considered when evaluating compliance at a cleanup site. A discussion of seasonal variability would be useful for evaluation.
12. **Section 4.7 Point Averaging and Non-Detects, Page 10:**
 - a. First bullet: Were the "reported value[s]" in the datasets reported to the MDL, MRL, or PQL for non-detects? Also, how does this comply with WAC 173-340-709(5), with regards to values below the PQL and above the MDL? Are you assuming that everything is reported to the MDL? According to that citation, results below the MDL are to be assigned a value equal to 1/2 the MDL; results above the MDL but below the PQL are to be assigned a value equal to the MDL.
 - b. Were individual sample ND reporting values used or were individual results replaced with a consistent ND value? In Ecology's natural attenuation (NA) guidance [Publication No. 05-09-091A (Version 1.0)] recommends using one value for ND results to avoid biasing trend analyses.
13. **Section 4.8 Background Calculations, Page 11:** The text notes that if the data is not highly skewed, then EPA recommends use of the KM non-parametric method, however, it does not comment on the skewness of this data. Is the data highly skewed? Can you know if it is or isn't with a highly left-censored dataset? What tests were conducted to evaluate whether this is an appropriate test? More information on how

different tests were determined to be appropriate would be helpful, or perhaps just focus this section on what the method(s) were used for calculating the UTLs/BTVs.

14. **Section 4.8 Background Calculations, Page 11:** Under Step 3, third sentence, change "he" to "the".
15. **Section 4.8 Background Calculations, Step 5, Page 12:** Please add more detail about the goodness of fit tests used. What confidence level was used? If multiple tests for goodness of fit were used, which test took precedence, if the results were different? Were there cases when multiple distributions could fit the data, and if so, which distribution was used?
16. **Section 4.9 Correlating Arsenic Concentrations over Depth, Page 12:** Add "was conducted" to second sentence: *"This assessment was conducted for each watershed basin."*
17. **Section 4.10 Sorting Well Depths into Bins, Page 12:** text states that "only arsenic concentrations > 10 µg/L were used for the concentration v. depth analysis." Why not all detections above the MDL? If BTV calculations use all of the data, the same data set should be used for other correlation evaluations. Particularly since the current arsenic MTCA CUL is 5 µg/L and the average MDL is reported (in this study) as being approximately 2.3 µg/L (average of 2003-2010 in Table 3).
18. **Section 4.10 Sorting Well Depths into Bins, Page 12:** Well depth data was sorted into five depth bins by basin and summarized in Table 4 to 10. Why were standardized breaks not used across the state? Figures 16 to 19 plot statewide data in five different depth bins, but without a summary table?
19. **Section 5.1 Summary of Background Levels, Page 13:** second sentence, is the "(90th percentile)" referring to the 90/90 UTL?
20. **Table 1, Page 14:** Some additional measure of the skewness could be helpful. Check # of samples by basin in Tables 1, 2, 4 and 6 for consistency.
21. **Section 5.3.1 Watershed basins, Page 15:** Under key point, add "of arsenic concentrations with depth" to first sentence: *"A statistically significant increasing trend (95% confidence level) of arsenic concentrations with depth was observed in..."*
22. **Section 5.3.1 Watershed basins, Page 15:** For comparisons when plotting a trend graph between depth and concentration, should the well depth ranges be the same for each basin for equal comparison? For a more complete analysis of concentration versus depth, the individual well concentrations should be plotted against the individual well depths, by basin and as a total.
23. **Section 5.3.2 Island County and Puget Sound Lowlands:**
 - a. Page 15: What is the expected effect of different lithologies on the geochemistry of the groundwater?
 - b. Page 16, last sentence: "For the Puget Sound lowlands, higher arsenic levels over depth are a likely artifact of drilling deeper wells and tapping older connate water." Sentence implies that there is a correlation between higher arsenic levels and depth for Puget Sound lowlands, but Section 5.3.1 stated that there was no trend over depth for this basin. Please explain. Also, no geochemical data (e.g. DO, ORP, Fe, Mn, NO₃, etc.) is presented in the report to verify that the water is under reducing conditions; either remove the statement or change the "likely" to "may be". "
24. **Section 5.4, Impact of Longer Well Screen Intervals, Page 17, last paragraph:** stated that "it is likely many of the wells were constructed with longer screened intervals." Are the well construction data, including screen lengths and depths, not available for the wells used in this study? Please provide backup for saying "likely".
25. **Section 5.5, Representative Study Data and Ecology Cleanup Sites**
 - a. Page 17, last paragraph: Was any consideration given to evaluating non-impacted wells with depths < 100 feet at Ecology Cleanup Sites? As opposed to continuing to focus on only public water supply wells.

- b. Page 18: 3rd paragraph, last sentence, the reference to tables should be Tables 11 and 12 only (not Table 10).
26. **Section 5.5, Representative Study Data and Ecology Cleanup Sites, Page 18-19:** This section, in general, contains conclusions or statements that do not seem fully supported by the data.
27. **Section 5.6, Impact of Tacoma Smelter Plume Soil on Groundwater Arsenic Background, Page 19:**
- a. This section is a discussion of anthropogenic impacts, which would be an area-wide question not a background question. This section should be prefaced as such.
 - b. What is the screened interval of the public water supply wells in the 280 square mile area evaluated? Generally, would not expect wells screened >100 feet bgs to be affected by surface soil impacts; but shallow wells (<25 feet bgs) may be affected if leaching to groundwater is occurring.
 - c. Suggest adding “in the Tacoma Smelter Plume footprint” to end of first sentence of fifth paragraph: *“Based on this analysis, there did not appear to be any meaningful correlation between soil and groundwater arsenic levels in the Tacoma Smelter Plume footprint.”*
28. **Section 6.0 Discussion, Pages 21-22:**
- a. This section contains detail about studies addressing specific geologic formations or aquifers in other states; this report would benefit from additional discussion about Washington-specific geology and hydrogeology.
 - b. Third paragraph, Page 21: No data was provided in this study report regarding the geochemistry (e.g. redox conditions) or organic matter content of the groundwater in the Puget Sound region (or other regions). Either modify the report to provide this data or change “likely” to be “may be”.
 - c. Fifth paragraph, Page 22: Other variables are introduced (topography, groundwater gradients, screen length, pumping rate) that may affect arsenic concentration but were not previously discussed and/or data were not provided to demonstrate relevance. This paragraph is more relevant to Section 8.0 Recommendations.
 - d. Note: The report mentions geochemistry, organic matter content, and other variables as important for evaluating arsenic levels; however, these are not useful in the context of evaluating natural background concentrations at cleanup sites. If reducing conditions and increased soil organic content are present, those conditions are not considered by Ecology when determining compliance with the CUL or setting a site-specific background level. These types of variability exist everywhere, how does this affect the calculation of background in terms of reaching compliance with CULs?
29. **Section 8.0 Recommendations:** Recommend that the assessments in Item 3 (geology and related features) and Item 4 (geochemistry), along with evaluation of groundwater arsenic concentrations state-wide, be completed before Item 2 is completed.