# Natural Background Groundwater Arsenic Concentrations in Washington State

## Study Results

By
Charles San Juan, LHG

**For the**
Toxics Cleanup Program
Washington State Department of Ecology Olympia, Washington

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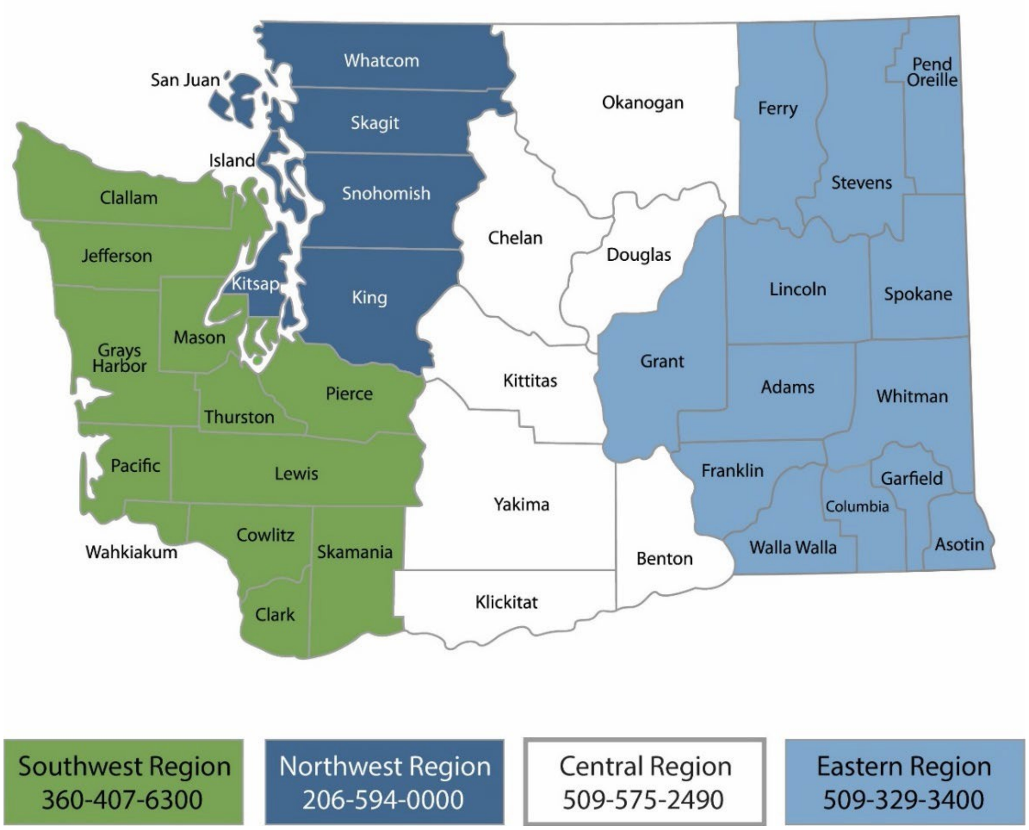


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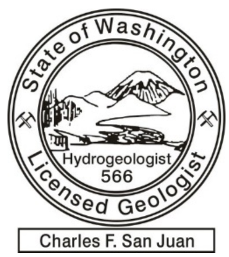


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State of Washington

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# Acronyms & Abbreviations

| Acronym or Abbreviation | Definition |
|---|---|
| **BTV** | background threshold value (EPA ProUCL) |
| **CL** | confidence level |
| **CUL** | cleanup level |
| **D** | Detect result |
| **DDT** | Dichlorodiphenyltrichloroethane |
| **DOH** | Washington State Department of Health |
| **Ecology** | Washington State Department of Ecology |
| **EPA** | United States Environmental Protection Agency |
| **GFAA** | graphite furnace atomic absorption spectrometry |
| **GIS** | Geographic Information System |
| **GOF** | goodness of fit |
| **ICP/MS** | inductively coupled plasma / mass spectrometry |
| **KM** | Kaplan-Meier |
| **MCL** | Maximum Contaminant Level |
| **MTCA** | Model Toxics Control Act (RCW 70A.305 RCW) |
| **MTCA Cleanup Rule** | Model Toxics Control Act regulations (Chapter 173-340 WAC) |
| **NAWQA** | National Water Quality Assessment Program (USGS Studies) |
| **ND** | non-detect |
| **PSW** | public supply well |
| **TCP** | Toxics Cleanup Program |
| **U** | Laboratory code for non-detect |
| **UCL** | upper confidence limit |
| **UG/L** | micrograms per liter (parts per billion) |
| **UTL** | upper tolerance limit |
| **USGS** | United States Geological Survey |
| **WRIA** | Water Resource Inventory Area |

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# 1.0 Summary

This report presents the results of a study begun in 2010 by the Washington State Department of Ecology's (Ecology) Toxics Cleanup Program (TCP). The study evaluated natural background groundwater arsenic levels in Washington State. "Natural background" means not altered by human activity and is defined in the Model Toxics Control Act (MTCA) Cleanup Rule as "…the concentration of hazardous substance consistently present in the environment that has not been influenced by localized human activities." (WAC 173-340-200).

Ecology's current groundwater arsenic cleanup level of 5 micrograms per liter (µg/L) is within the range of natural background. It is also below the federal drinking water arsenic standard of 10 µg/L established by the Environmental Protection Agency (EPA).

Using an arsenic cleanup level that is lower than natural background or federal standards can delay cleanups by requiring additional monitoring.

This report proposes to help resolve the problem by first defining natural background, then providing information that helps cleanup project managers and others determine the appropriate level of natural background for groundwater arsenic at their site. Ecology will develop an implementation memo that describes the process for using the background level as a target for cleanups.

Groundwater arsenic data from 5,457 public supply wells were used for this study. A total of 11,888 records from 2003 to 2010 were assessed. Average arsenic concentrations for individual wells were calculated. EPA's ProUCL statistical program was then used to calculate background levels. Background values were calculated for seven areas or watershed basins: 1) Island County, 2) Okanogan, 3) Puget Sound, 4) Snohomish, 5) Spokane, 6) Southwest Washington, and 7) Yakima. A concentration depth study was also performed.

Using EPA's ProUCL statistical methods, the range of background arsenic levels was found to be 4.9 – 15.4 µg/L. Groundwater arsenic levels statewide ranged from < 1 to 150 µg/L. The highest background arsenic levels were found in Island (i.e., Whidbey Island), Okanogan and Snohomish watershed basins. The lowest levels were observed in Yakima and Spokane basins.

A statistically significant (slope slightly above zero) trend (95% confidence level) of arsenic concentrations with depth was observed in five basins: Island County, Okanogan, Puget Sound Basin, Snohomish and Southwest. A statistically significant (slope slightly below zero) decreasing

trend in arsenic concentrations over depth was observed in the Spokane Basin.
Lastly, a statistically insignificant trend in arsenic concentrations over depth was observed in the Southwest Washington area (Vancouver and Clark County).

Based on these results, it appears that there is not a relationship between well depth and arsenic concentrations. This is thought to be the result of high public supply well-pumping rates (e.g. > 500 or 1,000 gpm). This, in turn, can result in inter-well mixing zones. These mixing zones can affect arsenic concentrations over depth by dilution.

The most important finding of this study is that Ecology’s current groundwater arsenic standard of 5 µg/L is at the low end of the statewide natural background range (4.9 – 15.4 µg/L). Natural background groundwater arsenic concentrations are provided in Table 2.

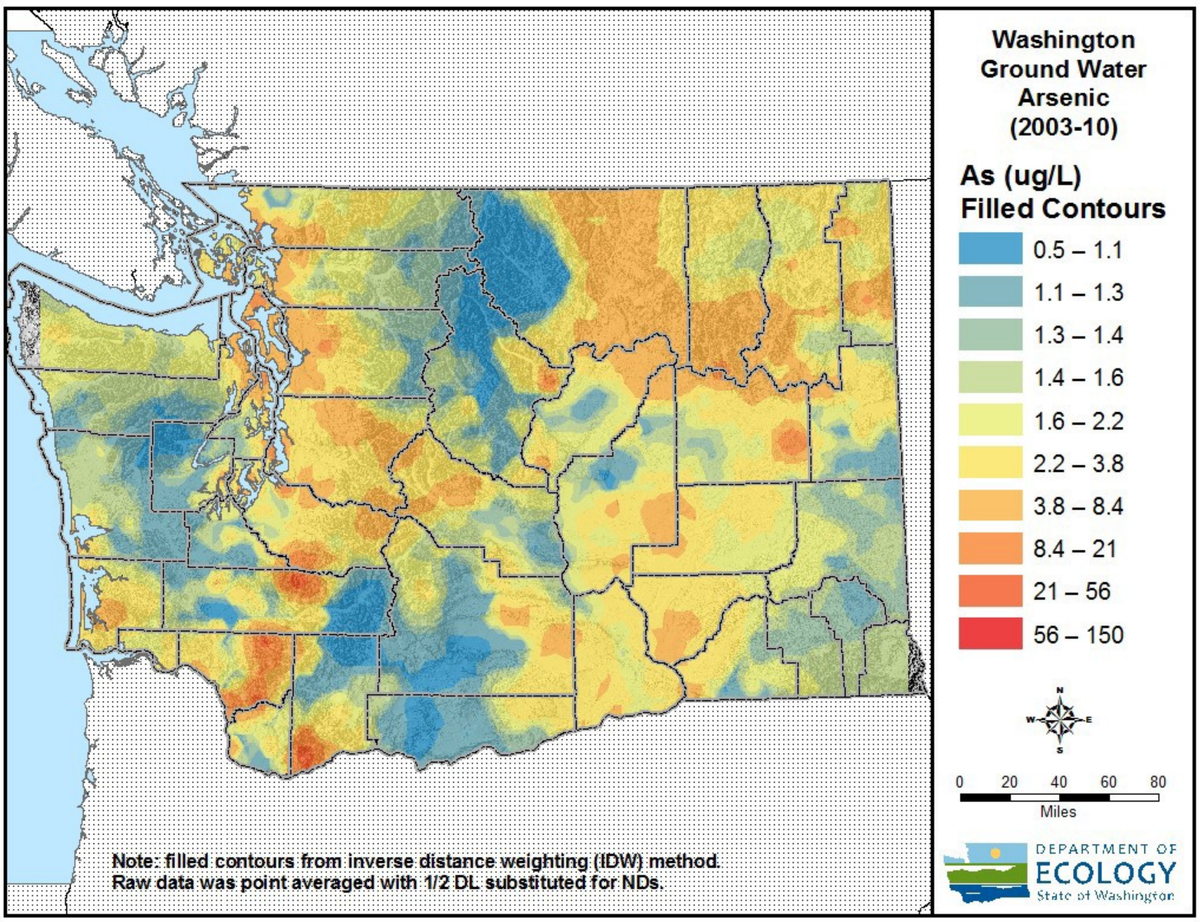



**Figure 1:** Statewide filled contour map of natural background groundwater arsenic concentrations.

# 2.0 Purpose and Applicability

Beginning in 2010, Ecology conducted a study to determine natural background groundwater arsenic concentrations in Washington State.

This report presents the results of that study. It is intended to help Ecology staff, environmental consultants, local governments, and others who conduct cleanups under the Model Toxics Control Act (MTCA, Chapter 173-340 WAC). The rule does not require clean up to levels that are less than natural background. Thus, having a better understanding of the natural background levels will improve the cleanup process.

This study was initiated for three reasons:

- Ecology's current groundwater arsenic cleanup level of 5 µg/L is within the range of natural background of 5 – 15 µg/L (Welch, et al. 1988).
- The 5 µg/L cleanup level is less than EPA's current 10 µg/L arsenic drinking water maximum contaminant level (MCL).
- The current arsenic standard of 5 µg/L is based on an outdated survey of ambient contaminant levels (e.g., for metals) throughout Washington (PTI 1989).

Widespread use of this outdated 5 µg/L arsenic standard has delayed site cleanups in some cases. For example, it is not uncommon for Ecology staff to observe trace detection levels (5 – 15 µg/L) of groundwater arsenic at many cleanup sites. If an arsenic level of > 5 µg/L is detected, then it would typically result in additional investigation. Without the proper context of natural background, additional monitoring and site characterization could yield inconclusive results that could lead to frustration and costly delays. It is hoped that the results of this study will help eliminate those delays and accelerate the pace of cleanups.

# 3.0 Arsenic Occurrence and Geochemistry

Arsenic has several oxidation states (+5, +3 and +1 and -3 valences). Dissolved arsenic in groundwater is typically +3 arsenite. In their research, Welch et al. (1988 & 2000) found that:

- Ambient groundwater arsenic concentrations vary by both climate and geology.
- Higher groundwater arsenic concentrations (> 10 µg/L) are typically found in the Western United States.
- Groundwater arsenic concentrations > 10 µg/L are more typically the result of geochemical changes in iron oxide. Arsenic may be released by reactions of iron oxide with natural or anthropogenic organic carbon (e.g., petroleum products). Arsenic releases may also occur as a result of iron oxide reacting with alkaline groundwater from various geologic environments, such as felsic volcanic rock or alkaline aquifers.

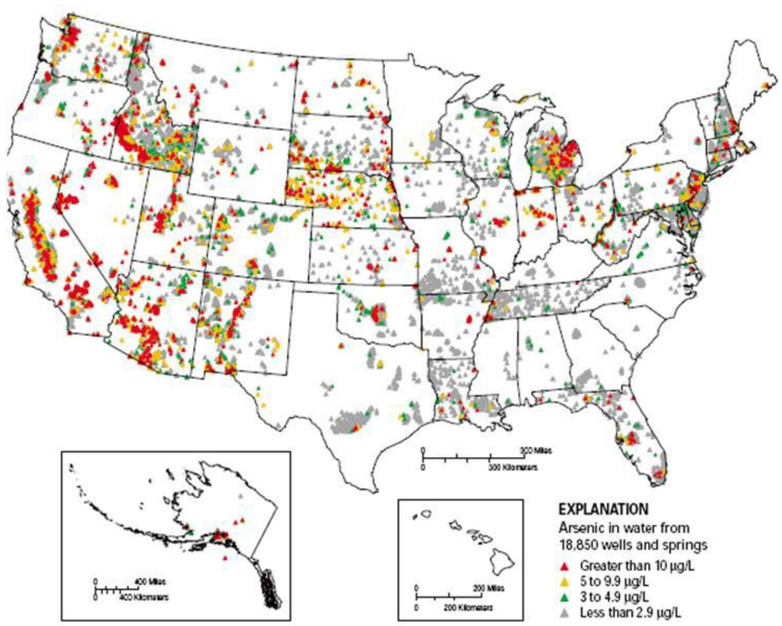



**Figure 2**: Occurrence of groundwater arsenic in the U.S. (USGS 2000)

# 4.0 Study Methods

## 4.1 Groundwater Arsenic Well Data

Total (not dissolved) arsenic data was extracted from the Washington Department of Health (DOH) Drinking Water Division Sentry database. A total of 18,032 groundwater arsenic records, dated between 2000 and 2010, were assembled. The data came from 6,758 drinking water wells that ranged in depth from 10 to 2,134 feet. Well depth was the only well construction parameter that was extracted (from the DOH database). If you need additional details on well construction (for the public supply wells used in this study), then please go to the Ecology well log viewer. Lastly, baseline geochemical (or water quality) data (e.g. pH, redox, etc.) was not extracted (beyond the scope of this study).

## 4.2 Using Public Water Supply Well Data for Background

Use of chemical data from public water supply wells is a common method for measuring water quality. The USGS has historically used public supply well data for various surveys, including the National Water Quality Assessment (NAWQA) studies.

Public supply well data was used for this study. The reason for this is because public supply well groundwater has, for the most part, not been impacted (contaminated) by human activity. “Natural background” is defined in the MTCA Cleanup Rule as “…the concentration of hazardous substance consistently present in the environment that has not been influenced by localized human activities” (WAC 173-340-200). Ecology cleanup site groundwater has been altered (i.e., contaminated) by human activity. Therefore, this data was deemed unsuitable for this study. By comparison, however, groundwater from public supply wells is typically less altered by human activity. Likewise, a small fraction of groundwater from some public water supply wells has been treated before use; however, water purveyors will typically not treat for arsenic because of the high cost.

## 4.3 Watershed Basins

For this study, spatial variability in natural background arsenic levels was addressed by subdividing the state into watershed basins. Subdividing the state into watershed basins allows you to calculate a unique natural background value for each basin. Geographic Information System (GIS) mapping techniques and three layers of data (arsenic, cleanup sites, and public supply wells) were used to subdivide the state into watershed basins. Once the raw data was point averaged (to 5,457 records), it was spatially mapped. As of

2017, Ecology had a record of roughly 12,000 cleanup sites. The cleanup site locations were mapped and the 5,457 wells used in this study were added as a separate layer.

Seven basins were identified based on the density of cleanup sites, public water supply wells, and arsenic levels. The Puget Sound lowlands, for example, were identified as having a high density of cleanup sites and public water supply wells. Parts of the lowlands were also identified as having higher arsenic levels. Similarly, other areas of the state (e.g. Vancouver) have a high density of cleanup site and public supply wells.

**Key point:** cleanup site density and location was used to identify and select watershed basins. However, groundwater arsenic data, from cleanup sites, was not used.

Figure 3 shows the seven watershed basins that resulted from this identification process:

1. Island County
2. Okanogan
3. Puget Sound lowlands
4. Snohomish
5. Spokane (Lower / Middle and Hangman)
6. Southwest WA (Upper Chehalis, Cowlitz, Lewis, Grays / Elochoman, and Salmon-Washougal
7. Yakima (Naches and Upper / Lower Yakima).

Basins were further subdivided by Ecology's Water Resource Inventory Area (WRIA), per WAC 173-500-040. Lastly, for three basins—Southwest, Spokane, and Yakima—several individual WRIA basins were grouped together to comprise one aggregate basin. As above, this "clumping" of basins was based on density of cleanup sites and public supply well density.

## 4.4 Data Filtering

Only data from upland public wells were used. Background threshold values, for the seven watershed basins, are based on data from public supply wells that are located within those basins (n = 4,566 of 84% of the total data of 5,457). Data from public supply wells located outside the seven basins (n = 891 or 16% of the total data of 5,457) was not used to calculate background threshold values. If the water system source was surface water, then those data were removed.

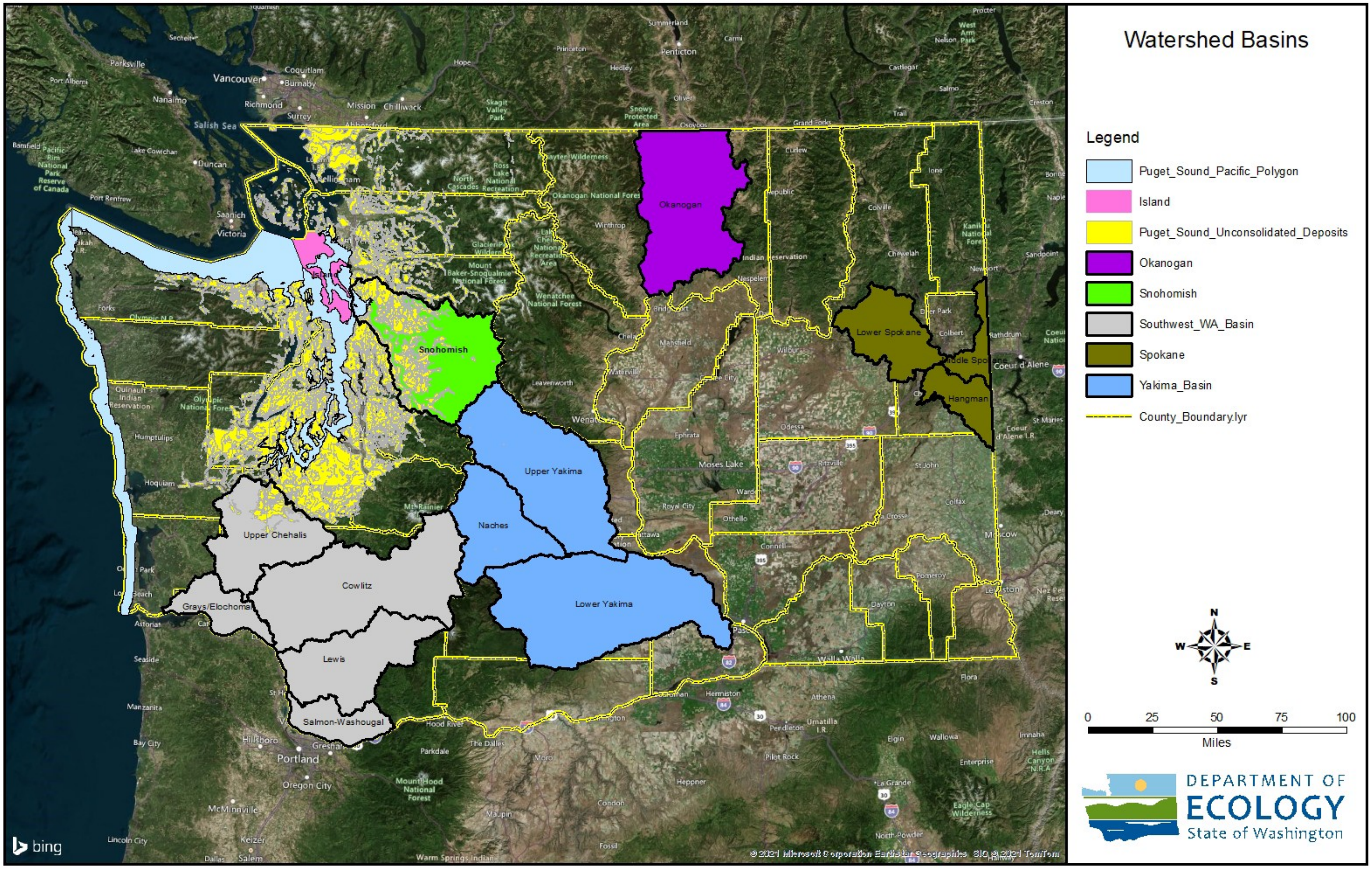



**Figure 3**: Statewide watershed basins

## 4.5 Non-Detects (NDs)

For this study, non-detect (ND) is equivalent to “State Detection Reporting Limit” or “SDRL” (Washington Department of Health Drinking Water, WAC 246-390-010). It is understood and acknowledged that analytical laboratories quantify substances to the more common terms of Method Detection Limit (MDL) or Method Reporting Limit (MRL). However, for drinking water analysis, you are required to meet the “SDRL”. Some labs will report to values that are less than the SDRL – these may be either MRL or MDL.

Of the 18,032 data records used in this study, 7,408 of them (41%) were above laboratory arsenic detection limits, varying from 0.5 to 100 µg/L (10,624 non-detects or 59%). The number of non-detects (ND) per year, including min, average and max values, is provided in Table 1. The average arsenic non-detect result, over the seven-year time frame (2003-10) was between 1 and 1.3 ug/L.

The variability in laboratory detection limits is primarily a result of lowering the federal arsenic drinking water standard from 50 µg/L to 10 µg/L in 2000-2002. Starting in 2000, water purveyors and labs had to adjust arsenic detection limits to the new 10 µg/L standard. Additionally, since labs do not use the same protocols or methods, detection and reporting limits can vary. Moreover, analytical methods have become more refined and precise, with results that can vary when compared over time. For arsenic, analytical methods include:

- EPA Method 7010 - Graphite furnace atomic absorption spectrometry (GFAA), and
- EPA Method 200.7 - Inductively coupled plasma / mass spectrometry (ICP/MS).

Key point: Due to this variability, and to reduce possible impacts of any statistical bias, Ecology used only data from 2003 to 2010 for this study. Because of higher detection limits (e.g. up to 25 or 50 ug/L), data from 2000 to 2002, was not used for background calculations.

**Table 1:** Average arsenic non-detect results over time

| Year | *Count (n) | Min (ug/L) | Average (ug/L) | Max (ug/L) |
|---|---|---|---|---|
| **2003** | 1,063 | 0.5 | 1.0 | 1.0 |
| **2004** | 844 | 0.5 | 1.1 | 5.0 |
| **2005** | 631 | 0.5 | 1.0 | 5.0 |
| **2006** | 460 | 0.5 | 1.1 | 5.0 |
| **2007** | 1,708 | 0.5 | 1.3 | 2.5 |
| **2008** | 530 | 0.3 | 1.2 | 1.5 |
| **2009** | 694 | 0.5 | 1.3 | 50.0 |
| **2010** | 25 | 1.0 | 1.2 | 1.5 |
| **Total** | **5,955** | | | |

*Note – the total number of non-detects (5,955) is based on the raw (non-averaged) data.

## 4.6 Point Averaging

Since there were multiple sampling events per well and the samples size varied, the average arsenic concentration was calculated for each well.

Once the original data (n = 18,032 results) were point averaged and filtered to the 2003-10 timeframe, it resulted in a sample size (n) of 11,888 results. The number of wells dropped from 6,758 to 5,457. This background study is therefore based on average groundwater arsenic levels from 5,457 wells that were sampled in the seven years between 2003 and 2010.

**Key point:** given that the data was averaged and the original data was not collected at regular intervals over time, a seasonality analysis[2] was not performed.

## 4.7 Point Averaging and Non-Detects

- All non-detects (NDs) were assigned a value of one-half (½) the reported "SDRL" value. (WAC 246-390-010; WAC 173-340-709(5)(a))

- If the data was all NDs, all values were assigned a value of ½ (one-half) the "SDRL" and then averaged.

[2] In time series data, seasonality is the presence of variations that occur at specific regular intervals less than a year, such as weekly, monthly, or quarterly. Seasonality may be caused by various factors, such as weather, vacation, and holidays and consists of periodic, repetitive, and generally regular and predictable patterns in the levels of a time series (Wikipedia).

## 4.8 Background Calculations – Statistical Protocol

Using goodness of fit (GOF) tests on left-censored[3] datasets can be problematic, especially when there is a high percentage (e.g. > 40 %) of non-detects (EPA 2013b). For this study, more than half the statewide data, or 53%, was non-detect (2,870 of 5,457 samples). The most significant occurrence of non-detects was observed in the Southwest Washington basin with 71% non-detect.

Due to the large number of non-detects (NDs) in this study, Ecology used EPA's ProUCL 5.0 software (EPA 2013b) to calculate upper tolerance limits (UTLs)[4] / background threshold values (BTVs). Although Ecology's MTCAStat statistical program could be used to calculate background levels (90th percentile, WAC 173-340-709(3)(c)), EPA's ProUCL software has more "robust" features for censored (non-detect) data sets. Additionally, WAC 173-340-709 requires use of the 90th percentile. For this study, EPA ProUCL software was used to calculate 90/90 UTLs. In other words, the UTL was calculated at 90% coverage (as opposed to some other value, such as 95%).

Detailed procedures on how to use the ProUCL 5.0 software to calculate background threshold values (BTVs) are provided in Chapter 10 of the ProUCL Version 5.0.00 User Guide (EPA 2013a). The following steps summarize how arsenic BTVs were calculated:

**Step 1. Group the data.**

- The data was first sorted and grouped by the seven watershed basins (Island County, Okanogan, Puget Sound, Snohomish, Southwest, Spokane, and Yakima).

[3] Left-Censored Data Set: An observation is left-censored when it is below a certain value (also known as a detection limit) but it is unknown by how much. Left-censored observations are also called non-detect (ND) observations. A data set consisting of left-censored observations is called a left-censored data set. In environmental applications, trace concentrations of chemicals may indeed be present in an environmental sample (e.g., groundwater, soil, sediment) but cannot be detected and are reported as less than the detection limit of the analytical instrument or laboratory method used. (EPA 2013b)

[4] Upper Tolerance Limit (UTL): A confidence limit on a percentile of the population rather than a confidence limit. For example, a 95% one-sided UTL for 95% coverage represents the value below which 95% of the population values are expected to fall with 95% confidence. In other words, a 95% UTL with coverage coefficient 95% represents a 95% UCL for the 95th percentile. (EPA 2013b)

**Step 2. Calculate the average arsenic concentration for each individual well.**

- The reason this was done is because some wells were sampled more than others. Therefore, to balance the data, the average arsenic concentration (for each individual well) was calculated.

**Step 3. Assign "0" and "1" codes for non-detect, detect values.**

- In many cases, the point-averaged data was a mixture of detects and non-detects. If the point-averaged data was comprised of all non-detect values, then it was assigned a "0" code for non-detect. If the point-averaged data was a mix of non-detects and detects, it was assigned a "1" code for detect.

**Step 4. Evaluate the data distribution (goodness of fit).**

- All of the data (ND at ½ DL and D) was used to determine a distribution. A 5% significance level was used.

**Step 5. Calculate background threshold values and record results.**

- If the data followed a discernible distribution (e.g. lognormal, etc.), then a 90/90 UTL, based on the recommended distribution was used.

- If the data did not follow a discernible distribution (5% significance level), then a non-parametric 90/90 UTL was used.

**Note**: results that would be considered statistical outliers were not removed. All non-detects (ND) were assigned a value of ½ the detection limit (SDRL).

**Box Plots and Histograms**

- Box plots and histograms of arsenic concentrations, by watershed basin, were also constructed.

## 4.9 Correlating Arsenic Concentrations over Depth

Public water supply well depths varied from 10 to 2,134 feet; therefore, an assessment of arsenic levels, over depth, was performed for each watershed basin. For this analysis, the point-averaged data, for each basin, was used to construct X,Y scatter plots. A linear regression of concentration (dependent variable) v well depth (independent variable) was performed for each basin. If the regression line slope, at a 95% confidence level, was positive, than an increasing concentration trend over depth was assumed. Likewise, if there was a negative slope, then a decreasing concentration over depth was assumed. If there was not a statistically significant slope (95% confidence level), then an insignificant slope was assumed. Lastly, the coefficient of determination (R-Sq), for each regression, was calculated and tabulated.

# 5.0 Results

## 5.1. Background Summary

Natural background (90/90 UTL) groundwater arsenic concentrations are provided in Table 2. For all seven basins, the data distribution was non-parametric (5% significance level). Therefore, a non-parametric upper limit (90% UTL with 90% coverage) was used as the background threshold value (BTV).

### 5.1.1. Puget Sound Basin

The Puget Sound Basin was the second largest basin that was evaluated (over 5,000 square miles). The total sample size (n) was 2,790 (1,386 non-detects or 50%). The data did not follow a discernible distribution (0.05); therefore, the non-parametric upper limit (90% UTL with 90% coverage) background threshold value is 8 ug/L. A graduated symbol map, of Puget Sound groundwater arsenic concentrations, is provided in Figure 4.

### 5.1.2. Island County

In terms of size, Island County was the smallest watershed basin evaluated (517 square miles). However, the background threshold value for Island County (13.3 ug/L), was the third highest of the seven basins assessed. The total sample size (n) was 428 (74 non-detects or 17%). The data did not follow a discernible distribution (0.05); therefore, the non-parametric upper limit (90% UTL with 90% coverage) background threshold value is 13.3 ug/L. A graduated symbol map, of Island County groundwater arsenic concentrations, is provided in Figure 5.

For Island County, the increased groundwater arsenic levels may be the result of over-pumping wells with longer screened intervals. Water shortages have been a historical problem in Island County. The landmass is long and narrow, which affects surface water runoff and groundwater storage. Consequently, water wells have been drilled to deeper depths. It is speculated that within Island County, increasing arsenic levels with depth is the result of withdrawing older connate (fossilized) groundwater. Geochemically, this older connate water is likely more reduced, e.g. with a slightly lower pH and higher iron (Fe) and manganese (Mn) signature, which makes it more mineralized. The impact of reduced groundwater (<50 mV oxidation reduction potential) on arsenic mobilization has been well documented by Hering (et al., 2009) and Whitlock and Kelly (2010). Aside from drilling wells into deeper and older water, there may also be a salinity intrusion issue. For example, if deeper wells are over-pumped, it could result in salinity intrusion, which in turn would create more reduced groundwater and higher arsenic levels.

### 5.1.3. Okanogan

The Okanogan Basin (north-central Washington) encompasses 2,100 square miles. Most of the public supply wells for this area are located in the Okanogan River valley. The total sample size (n) was very small (58) with 12 non-detects (21%). If you use all the data (ND @ ½ DL and D), then the distribution is non-parametric. Thus, the non-parametric upper limit (90% UTL with 90% coverage), for the Okanogan Basin is 15.4 ug/L. A graduated symbol map, of Okanogan Basin groundwater arsenic concentrations, is provided in Figure 6.

### 5.1.4. Snohomish

The Snohomish basin total sample size (n) was small (207) with 78 non-detects (38%). If you use all the data (ND @ ½ DL and D), then the distribution is non-parametric. Thus, the non-parametric upper limit (90% UTL with 90% coverage), for Snohomish, is 13.6 ug/L. A graduated symbol map, of Snohomish groundwater arsenic concentrations, is provided in Figure 7.

### 5.1.5. Spokane

The Spokane Basin total sample size (n) was small (205) with 78 non-detects (38%). The data did follow a discernible distribution (lognormal at 0.05) and the percent non-detect was less than 50%. Therefore, the lognormal upper limit (90% UTL with 90% coverage) background threshold value is 5.3 ug/L. A graduated symbol map, of Spokane groundwater arsenic concentrations, is provided in Figure 8.

### 5.1.6. Southwest

The Southwest watershed basin (Vancouver area and Clark County, as well as Grays Harbor, Lewis, Pacific, Skamania, Thurston and Wahkiakum Counties) was the second-largest basin evaluated (6,099 square miles). The sample size (n) for this area was relatively small (488) and 71% (345) of the data was non-detect. The data did not follow a discernible distribution (0.05). Therefore, the non-parametric upper limit (90% UTL with 90% coverage) background threshold value is 4.9 ug/L. A graduated symbol map, of Southwest basin area groundwater arsenic concentrations, is provided in Figure 9.

### 5.1.7. Yakima

The Yakima Basin was the largest area evaluated (6,154 square miles). The total sample size (n) was relatively small (390) with 216 non-detects (55%). The data did not follow a discernible distribution (0.05). Therefore, the non-parametric upper limit (90% UTL with 90% coverage) background threshold value is 6.0 ug/L. A graduated symbol map, of the Yakima Basin groundwater arsenic concentrations, is provided in Figure 10.

### 5.1.8. Box Plots and Histograms

Box plot and histograms, of arsenic concentrations for each watershed basins, are provided in Figures 11 and 12.

## 5.2. Well Locations and Depths

A map of well locations and depths is provided in Figure 13. A well depth box plot is provided in Figure 14 and a histogram in Figure 15. For this study, the average water supply well depth of the 5,457 wells was 238 feet, with a range between 10 to 2,134 feet.

## 5.3. Concentration vs. Depth

This section provides the results of an assessment of watershed basin arsenic levels over depth (see also Appendix A figures and tables). A description of the methods used for this analysis is provided in Section 4.9.

### 5.3.1. Results

A bar chart, of average statewide arsenic concentrations v depth, is provided in Figure 16. The Jenks optimization method (see Glossary) was used to select the well depth bins for Figure 16. A box plot, of well depth and arsenic concentrations is provided in Figure 17. The number of samples collected over depth is provided in Figure 18.

A statistically significant (slope slightly above zero) trend (95% confidence level) of arsenic concentrations with depth was observed in five basins: Island County, Okanogan, Puget Sound Basin, Snohomish and Southwest. A statistically significant (slope slightly below zero) decreasing trend in arsenic concentrations over depth was observed in the Spokane Basin. Lastly, a statistically insignificant trend in arsenic concentrations over depth was observed in the Southwest Washington area (Vancouver and Clark County; see Appendix A, Figures 19 and 20 scatter plots including coefficient of determination “R-square” values).

Based on these results, it appears that there is not a relationship between well depth and arsenic concentrations. This is thought to be the result of high public supply well pumping rates (e.g. > 500 or 1,000 gpm). This, in turn, can result in inter-well mixing zones. These mixing zones can affect arsenic concentrations over depth by dilution.

### 5.3.2. Discussion

The regression line slope (concentration v depth) was near zero for all seven basins. What this implies is that there was no relationship between arsenic concentrations and well depth. Also, the coefficient of determination (R-Square) value, for six of the seven basins was < 2.1%, implying that only 2.1% of the variability in arsenic concentrations can be explained by well depth.

### 5.3.3. Impact of Well Screens and Inter-Well Mixing Zones

To increase water production and pumping rates, public water supply wells are often constructed with longer well screens. In some cases, the length of these screened intervals may be significant (> 100 feet, e.g. see Figure 21, City of Tacoma Well #8A, perforations from 101-285 ft). If a well is constructed with a longer well screen, then pumping, especially at higher rates (e.g. 500 – 1,000 gpm), can result in inter-well mixing zones (e.g. older water at depth is mixed with shallower (younger) water). This, in turn, can impact groundwater arsenic levels.

For example, Jugens et al. (2014) studied the groundwater age-distribution in a public water well screened across a deep alluvial aquifer in Albuquerque, New Mexico (see Figure 22). The well screen interval was about 800 feet, ranging from roughly 400 to 1,200 feet below land surface.

The study results found that during the winter months, when there was less demand for water and pumping rates were lower, arsenic levels increased to > 20 µg/L. This increase was thought to be a function of older connate (fossil) water entering the well at depth. The older water—about 21,000 years old—was more enriched in arsenic (as a result of silicic volcanism in the nearby Jemez Mountains).

Conversely, during the summer months, when water demand peaked and pumping rates increased, arsenic levels tended to decrease to about 10 µg/L. This decrease was attributed to a higher fraction of younger (shallow recharge) groundwater entering the well. The younger water was not as mineralized and contained less arsenic.

In a similar study, Gotkowitz, et al. (2004) found that redox conditions in a well can change rapidly with pumping and water withdrawals. In their study, a well in a northeastern Wisconsin sandstone aquifer was pumped at zero, low, and high pumping rates. The corresponding arsenic concentration range for these pumping rates was 1.8 – 22 µg/L. Study results indicated that the well borehole environment can facilitate microbiological growth. This growth can lead to geochemical reactions that affect borehole geochemistry. Therefore, well borehole water, with longer residence times, can be impacted by the reduction of arsenic-bearing iron (hydr)oxides.

In conclusion, for this study, it is likely that many of the wells were constructed with longer screened intervals. This means that the individual well arsenic results would be a composite average of the screened interval. This may explain why there was no clear trend in arsenic levels over depth for some of the basins.

## 5.4 Impact of Tacoma Smelter Plume Soil on Groundwater Arsenic Background

Since 2005, Ecology has been working with Pierce County and other local governments on cleanup of what has come to be known as the Tacoma Smelter Plume (TSP) footprint. This area has been impacted by airborne fallout from the former Asarco Tacoma (Ruston) smelter. Specifically, surface soil (0 to 6 inches) is enriched in lead and arsenic.

During initial peer review of this study report, concerns were raised about the possible impacts of increased soil arsenic from the smelter. The concern was that increased soil arsenic levels would result in higher groundwater arsenic levels.

As a check, the mass of soil arsenic over the estimated area of the Tacoma Smelter Plume footprint was calculated. The results found that over the lifetime of the former Asarco Tacoma (Ruston) smelter, approximately 2.2 million pounds of arsenic were added to the soil (Appendix B, Table 4; see also Figure 23). The size of this footprint is estimated at 280 square miles.

Groundwater arsenic levels from public supply wells within this 280 square mile footprint were also checked. The results found that there were 450 public supply wells within this 280 square mile footprint. However, the average concentration for these 450 wells was approximately 3-4 ug/L (Appendix B, Figure 24).

Based on this analysis, there did not appear to be any relationship between soil and groundwater arsenic levels in the Tacoma smelter plume footprint. Although the Tacoma Smelter Plume surface soil (0 – 2 inches) is enriched in soil arsenic, the underlying groundwater has not been impacted.

**Table 2:** Groundwater arsenic background calculation statistical results (EPA ProUCL)

| Basin | ISL | OKG | PSB | SNO | SPK | SW | YB | Units |
|---|---|---|---|---|---|---|---|---|
| **Area** | 517 | 2,098 | 5,148 | 1,910 | 1,626 | 6,099 | 6,154 | Sq Mi |
| **Number of Samples (n)** | 428 | 58 | 2,790 | 207 | 205 | 488 | 390 | |
| **Number of Detects** | 354 | 46 | 1,404 | 129 | 127 | 143 | 174 | |
| **Number of Non-Detects** | 74 | 12 | 1,386 | 78 | 78 | 345 | 216 | |
| **Percent Non-Detect** | 17% | 21% | 50% | 38% | 38% | 71% | 55% | |
| **Min** | 1.3 | 1 | 0.8 | 1.2 | 0.9 | 0.7 | 1 | ug/L |
| **Max** | 51 | 18.9 | 76 | 76 | 21.3 | 152.4 | 30.3 | ug/L |
| **Mean** | 6.7 | 5.7 | 3.8 | 5.7 | 3.1 | 4.2 | 3.1 | ug/L |
| **Median** | 5.0 | 4.1 | 2.3 | 3.0 | 2.7 | 2.0 | 2.0 | ug/L |
| **StdDev** | 6.6 | 4.4 | 4.2 | 6.8 | 2.0 | 11.6 | 2.3 | ug/L |
| **Variance** | 43.7 | 19.1 | 18.0 | 45.7 | 4.0 | 134.7 | 0.8 | ug/L |
| **CoeffOfVar** | 1.0 | 0.8 | 1.1 | 1.2 | 0.6 | 2.8 | 5.5 | ug/L |
| **Background Threshold Value (90% UTL with 90% Coverage)*** | **13.3** | **15.4** | **8.0** | **13.6** | **5.3** | **4.9** | **6.0** | ug/L |

ISL = Island County. OKG = Okanogan Basin. PSB = Puget Sound Basin. SNO = Snohomish County. SPK = Spokane Basin. SW = Southwest WA. YB = Yakima Basin.

*The reported Background Threshold Value (BTV) is a Nonparametric Upper Limit. No distinction was made between Detects (D) and Non-Detects (ND).

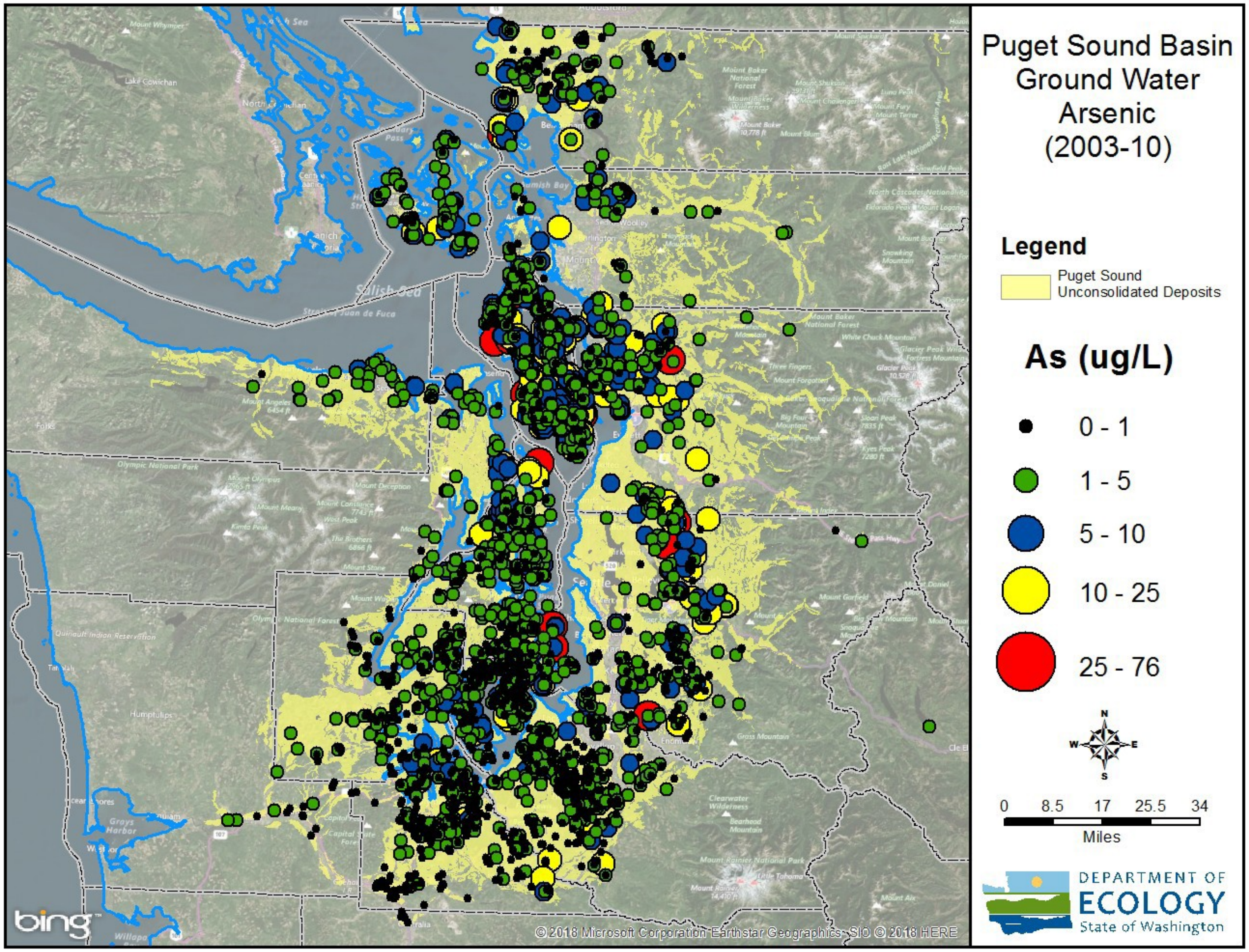



**Figure 4:** Puget Sound Basin groundwater arsenic

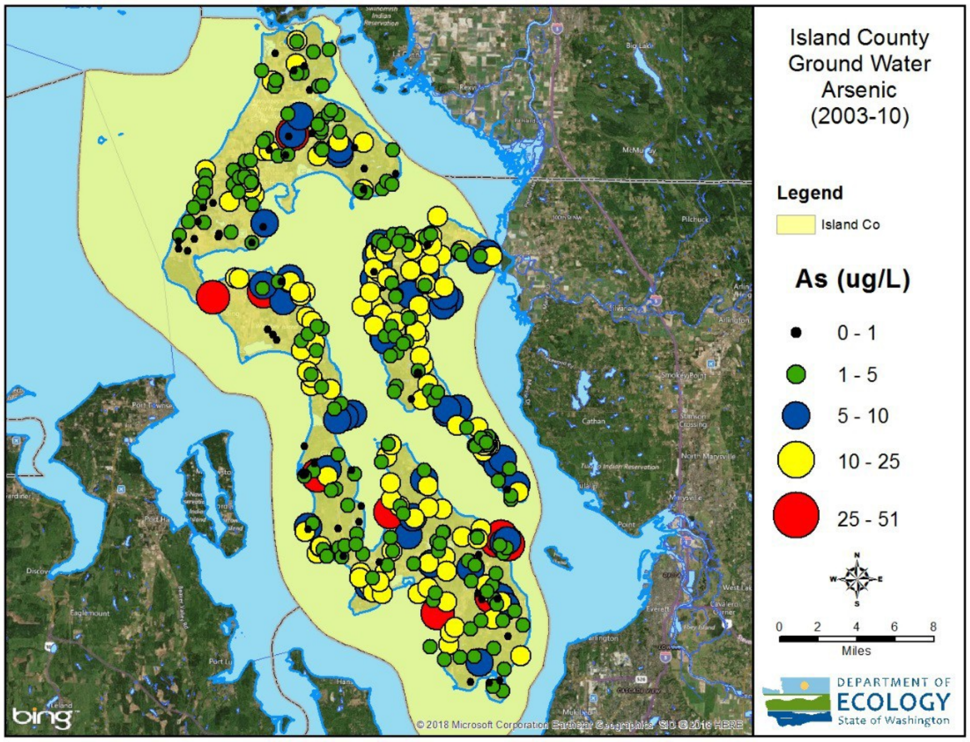



**Figure 5:** Island County groundwater arsenic

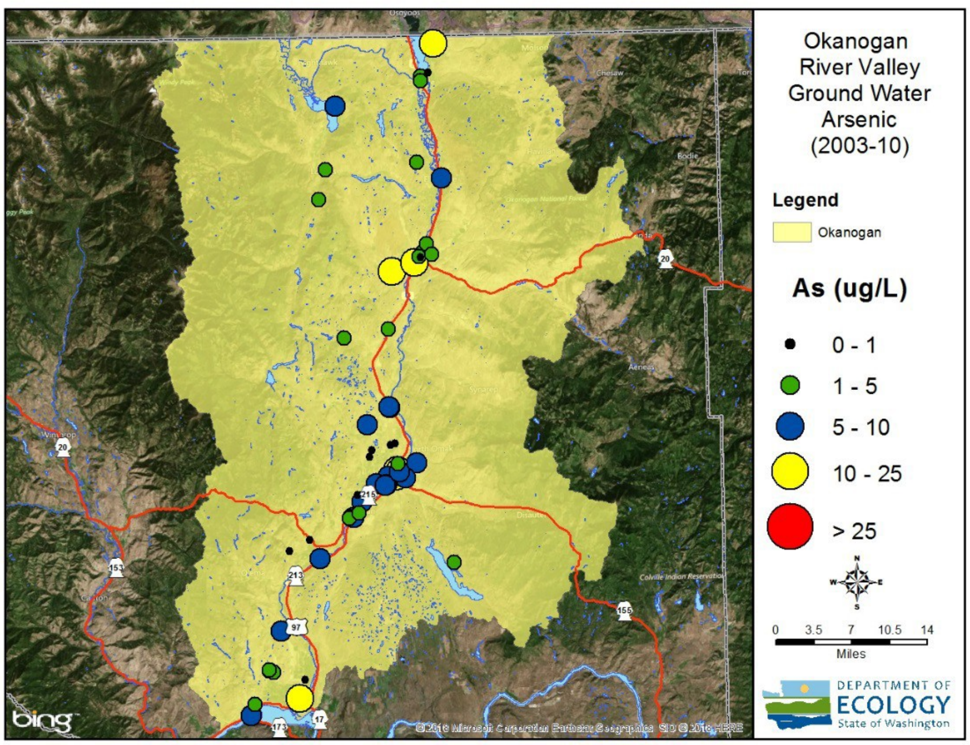



**Figure 6:** Okanogan River Valley groundwater arsenic

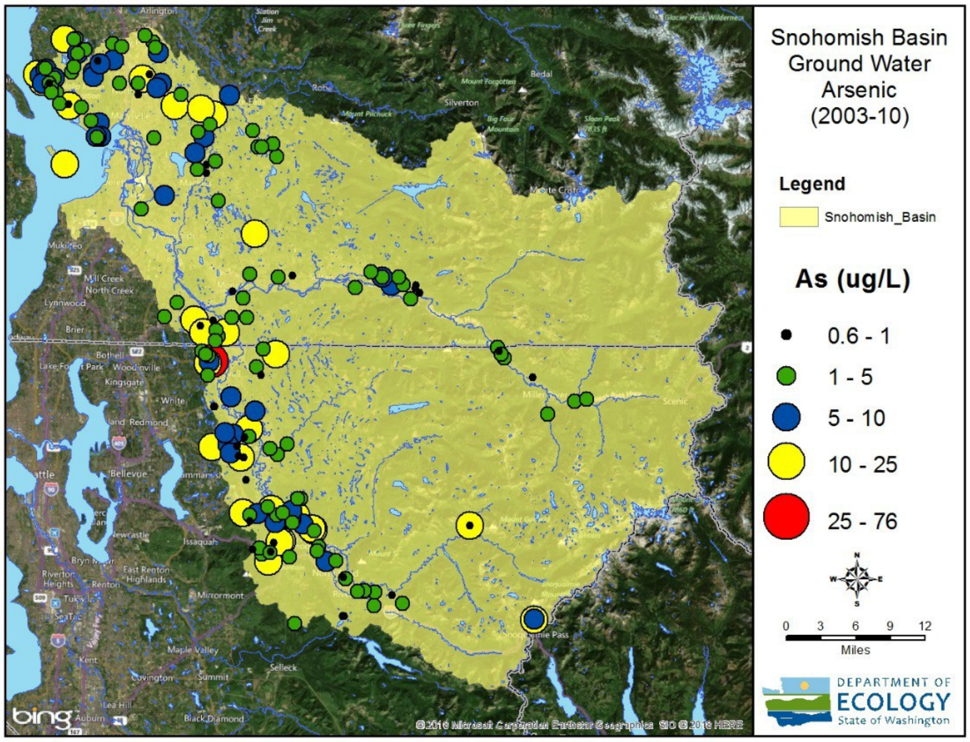



**Figure 7**: Snohomish basin groundwater arsenic

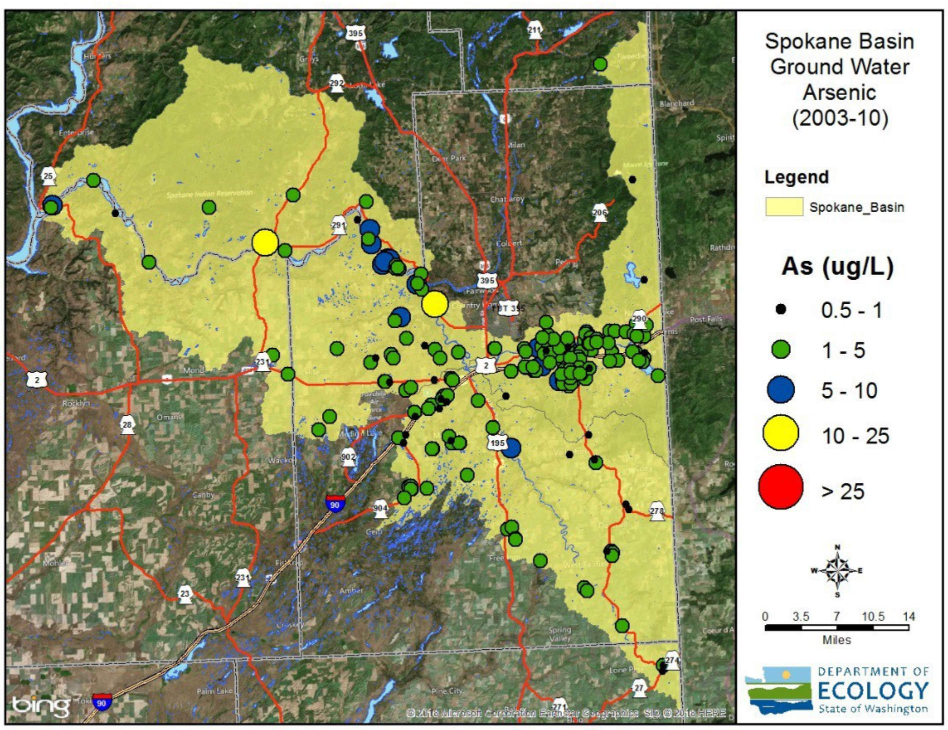



**Figure 8:** Spokane basin groundwater arsenic

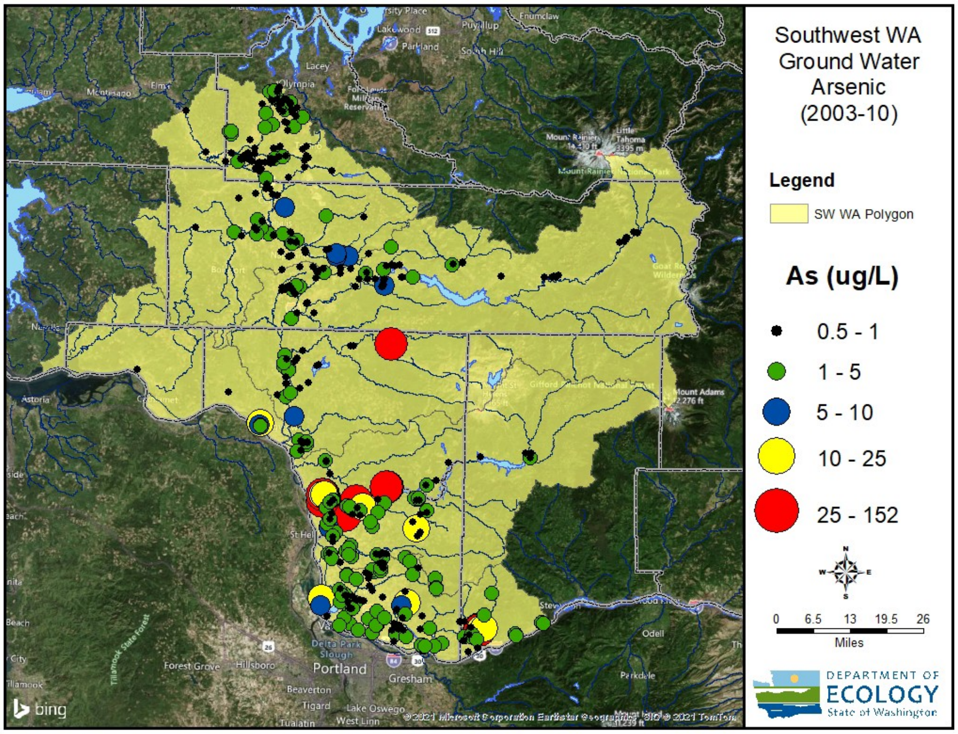



**Figure 9:** Southwest Washington groundwater arsenic

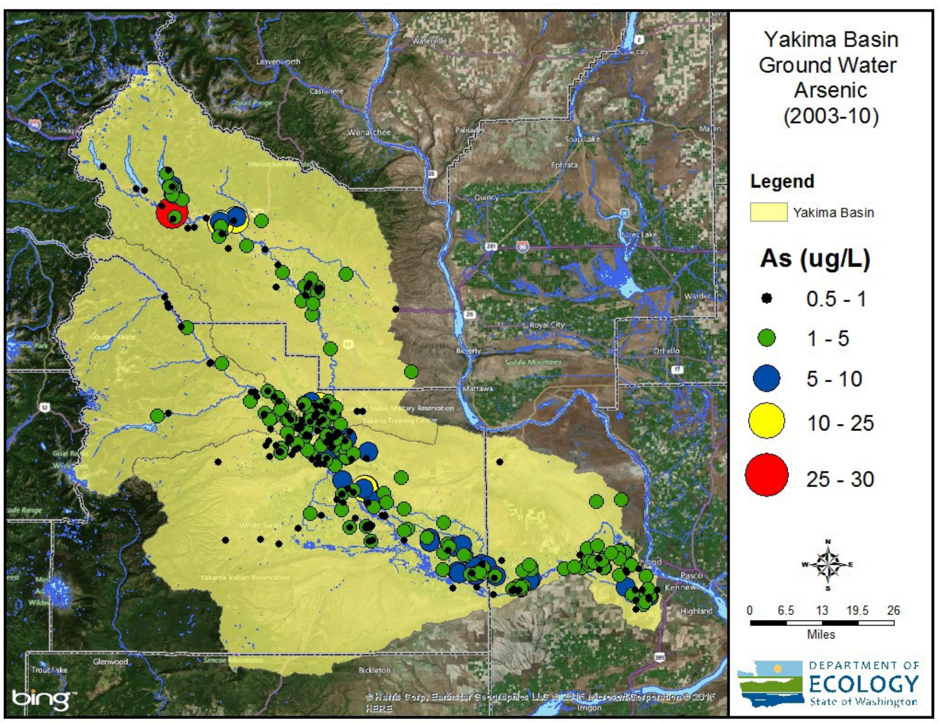
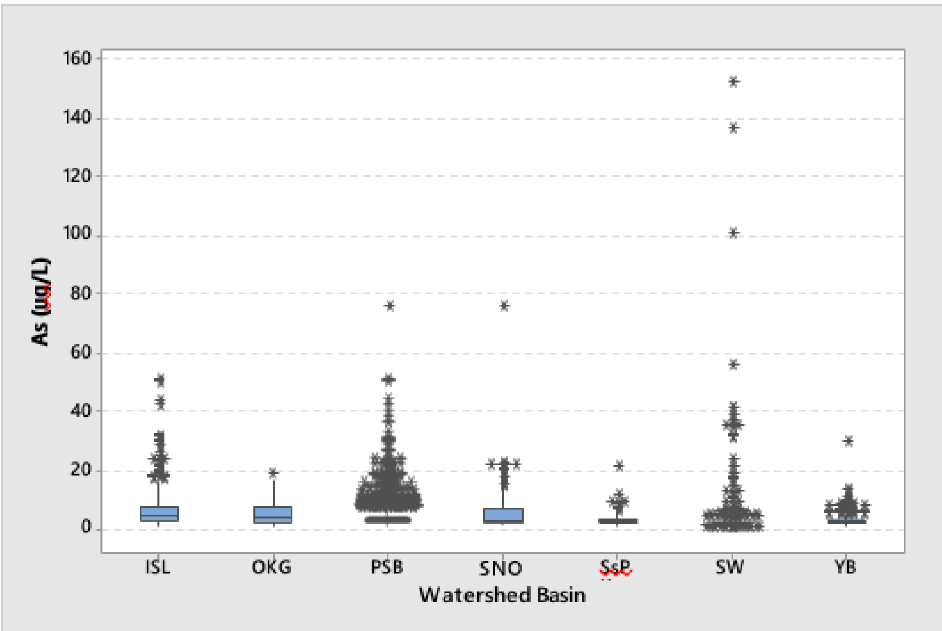



**Figure 10:** Yakima basin groundwater arsenic

**With Outliers (Outlier = 1.5 X interquartile range (Q3-Q1))**




**Without Outliers**

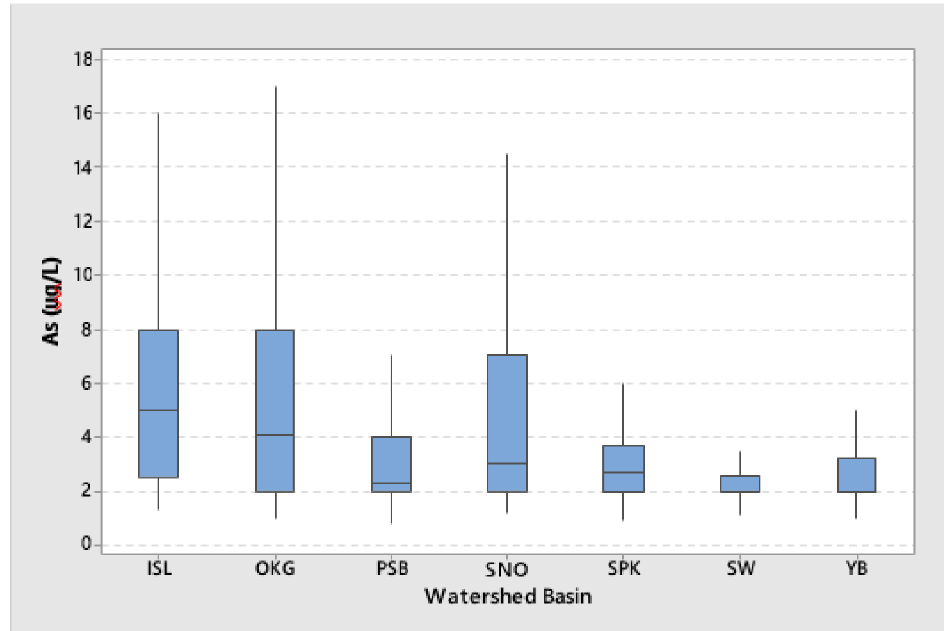
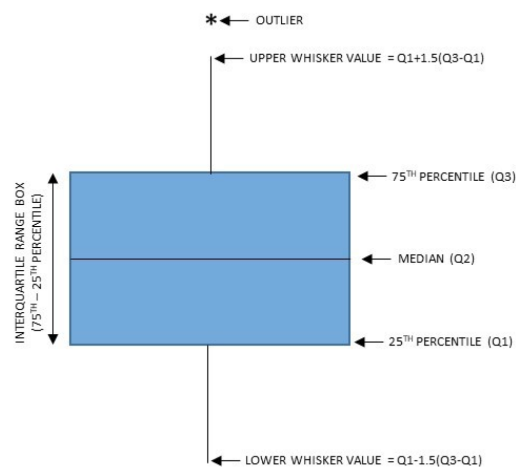



**Figure 11:** (three figures) Measured arsenic concentrations v. basin box plots.

All = Statewide. ISL = Island County. OKG = Okanogan Basin. PSB = Puget Sound Basin. SNO = Snohomish Basin. SPK = Spokane Basin. SW = Southwest WA. YB = Yakima Basin.

**Note:** the right box plot (outliers removed) was provided to make it easier to see the range box for each basin; however, outliers were not removed for background threshold value (BTV) calculations.

**BOX PLOT LEGEND**



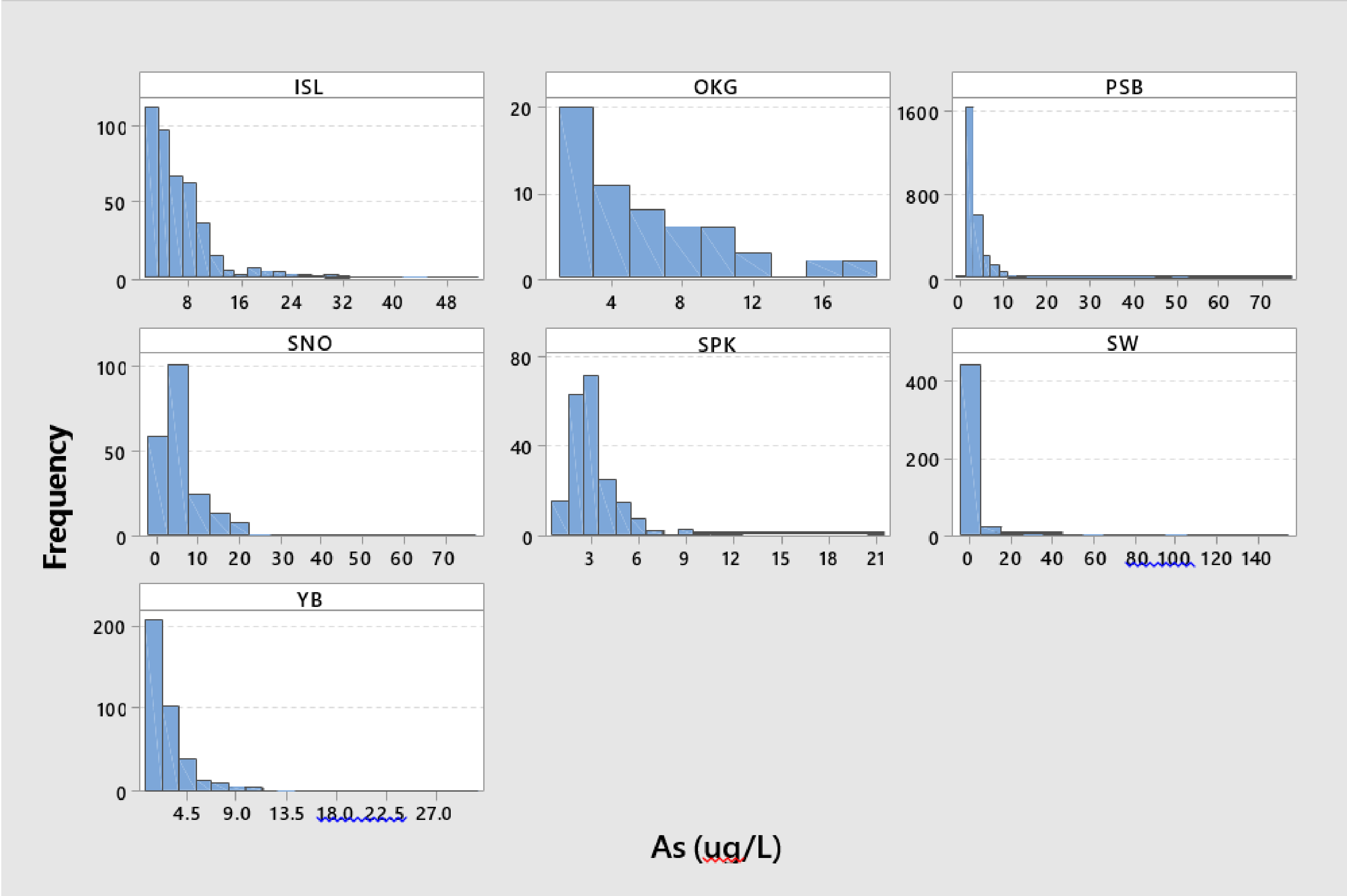
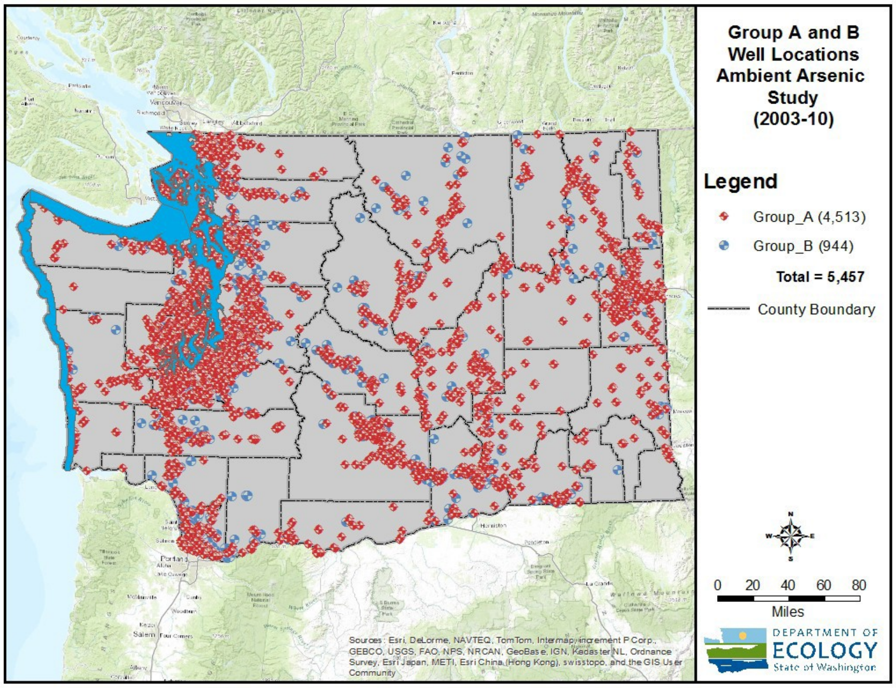



**Figure 12:** Groundwater arsenic concentration histograms (by watershed basin)

All = Statewide. ISL = Island County. OKG = Okanogan Basin. PSB = Puget Sound Basin. SNO = Snohomish Basin. SPK = Spokane Basin. SW = Southwest WA. YB = Yakima Basin.

**Locations**




**Depths**

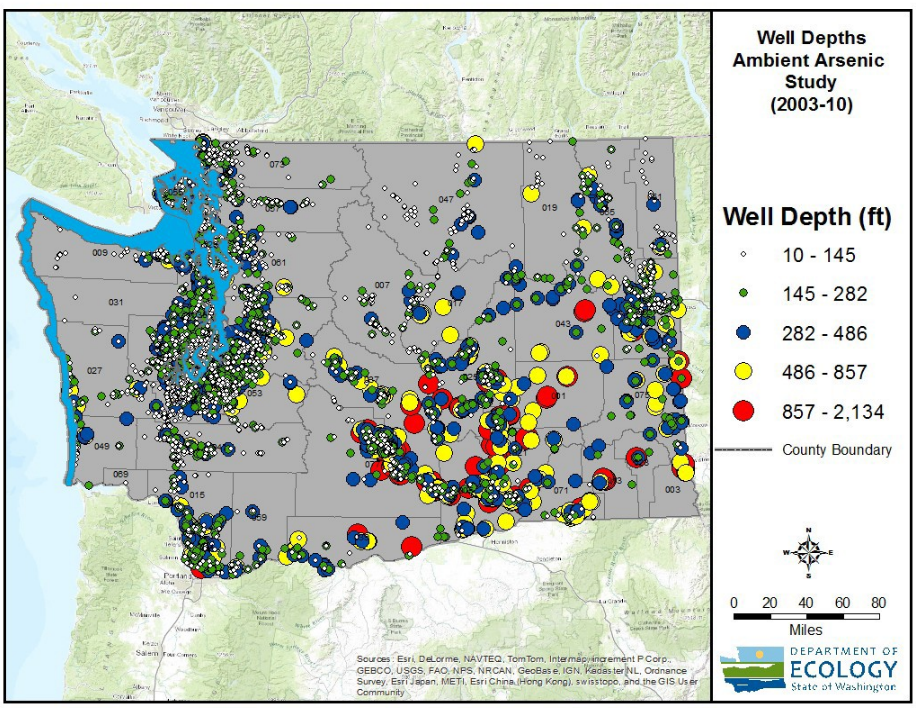



**Figure 13:** (two figures): Group A and B well locations / depths.

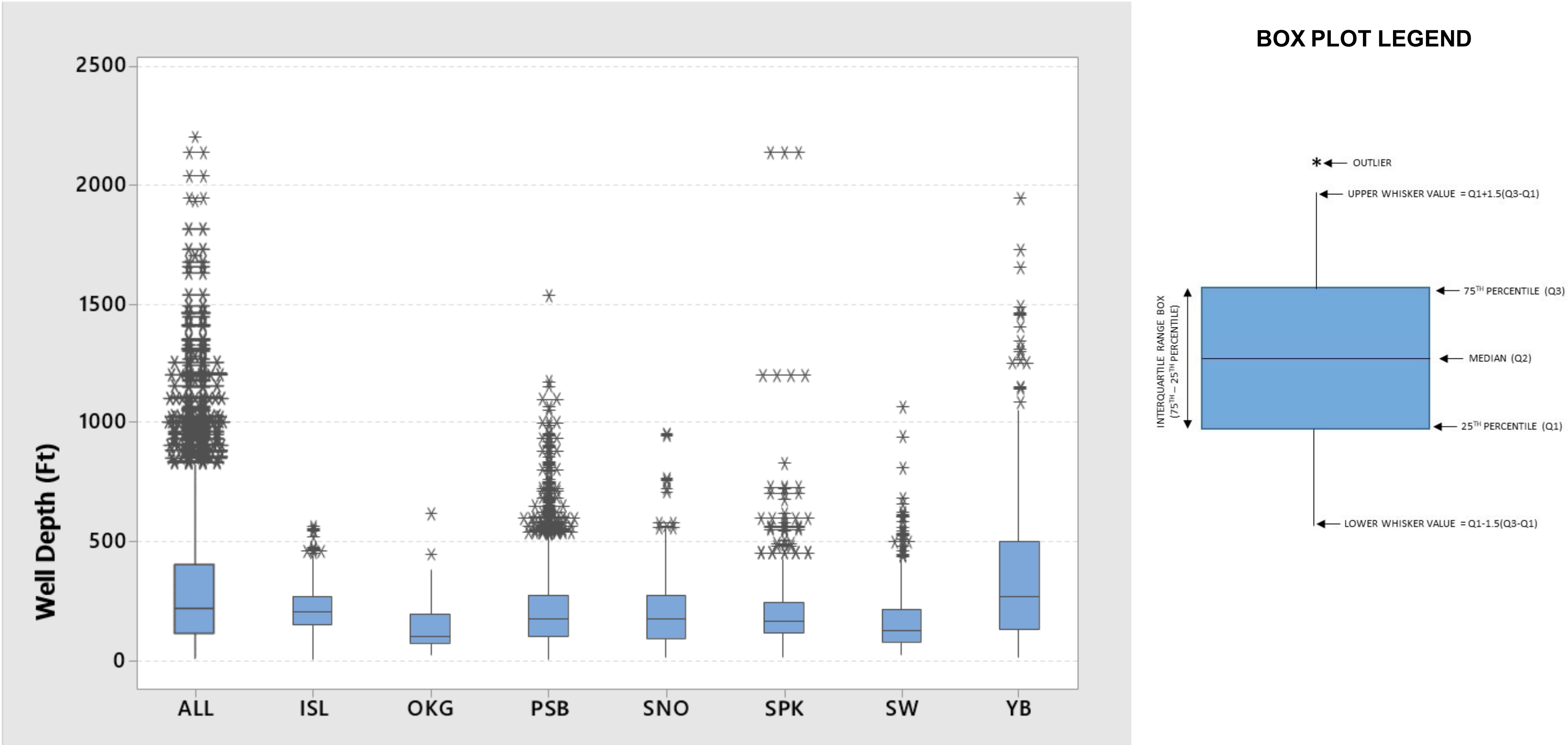



**Figure 14:** Well depth box plot.

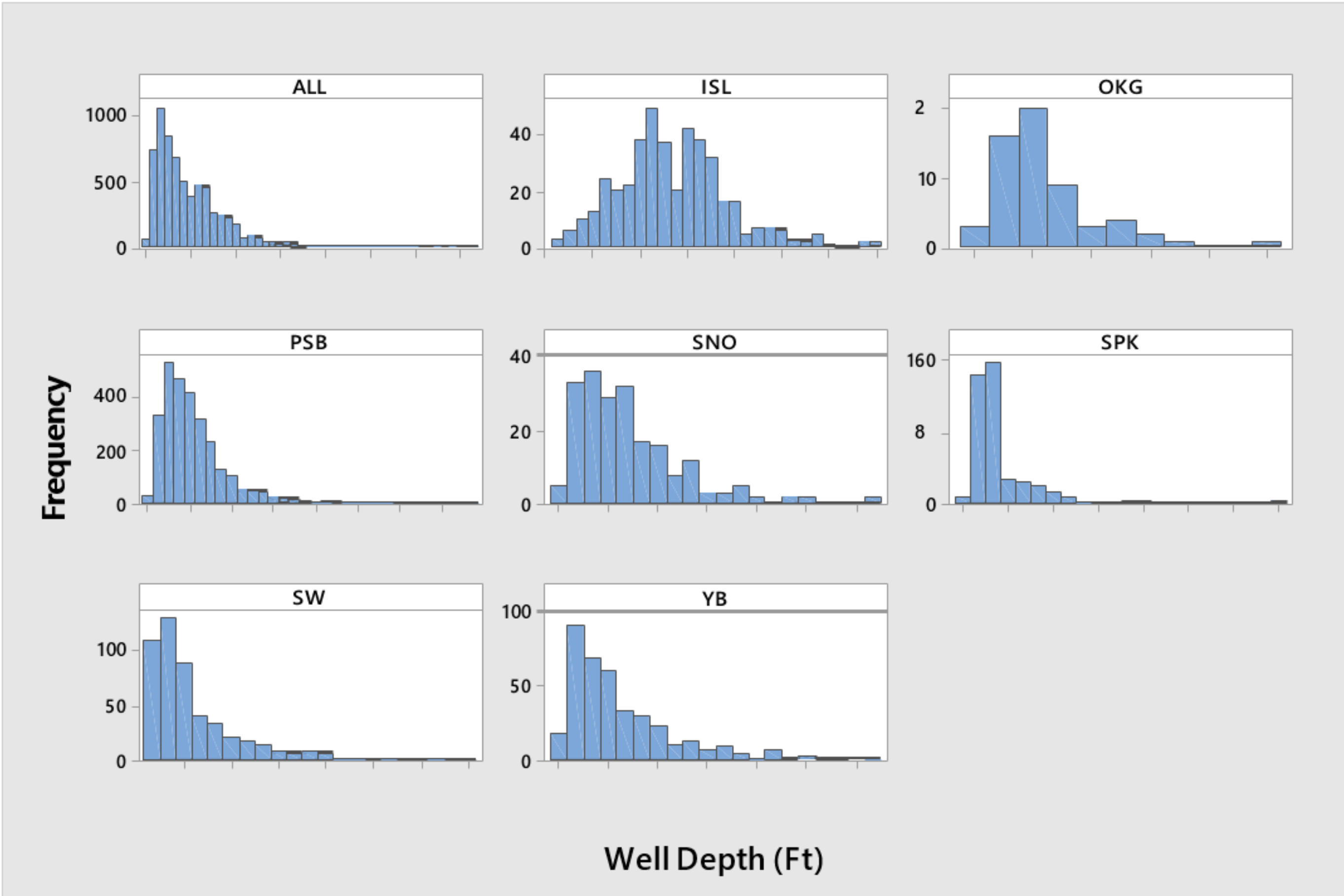



**Figure 15:** Well depth histogram.

# 6.0 Discussion

A brief synopsis of how this study compares to other studies on naturally occurring groundwater arsenic levels is provided here.

The range of background arsenic levels (4.9 – 15.4 µg/L) from this study is consistent with others, including Welch, et al. (1988 and 2000).

One of the key findings of this study was the higher levels of groundwater arsenic within the Puget Sound region. The higher levels are likely an artifact of deeper and older reduced groundwater. These reducing conditions are likely the result of organic matter microbial oxidation, which is supported by the following studies.

Erickson and Barnes (2005) studied public supply wells (PSWs) with elevated arsenic levels. The PSWs are located in the upper Midwest (North and South Dakota, Minnesota, and Iowa).

Much of this area is within the footprint or northwest provenance of Wisconsin-aged drift. The ice-age drift is comprised of a fine matrix enriched in organic carbon. Biological activity in this organic carbon creates the right geochemical conditions for arsenic mobilization (reduction / desorption of metal oxides). Study results found that 12% of the wells within the glacial drift footprint had arsenic levels > 10 µg/l. Conversely, only 2.4% of the wells outside this footprint had arsenic levels > 10 µg/L.

In their study of Lake Geneva glacial deposits in Wisconsin, Root, et al. (2010) identified an organic-rich aquitard called the Foxhollow till. This till unit separates the upper and lower units. Arsenic levels above this aquitard tended to be "low" (5 – 30 µg/L). However, below the aquitard, much higher arsenic levels were detected (> 30 µg/L). Higher arsenic levels within the lower unit are thought to be the result of geochemically reduced groundwater (oxidation of organic matter and metal hydroxides with arsenic-rich sulfides).

Likewise, in their study of northeastern Ohio, Matisoff, et al. (1982) found high levels of arsenic that were thought to be the result of reduced groundwater from either methane gas leakage or an organic-rich till unit. Like northeastern Ohio, the Puget Sound region is mantled with glacial till. Therefore, higher groundwater arsenic levels within the Puget Sound lowlands may in part be an artifact of glacial till enriched in organic matter.

Warner (2001) studied arsenic levels in the Lower Illinois River Basin deep glacial drift aquifer. Study results found that higher arsenic levels were more typically associated with the organic- rich carbonate bedrock. This bedrock layer underlies the drift unit and is thought to be the parent source for arsenic with the glacial drift. It was found that arsenic concentrations > 25 µg/L were primarily in the form of arsenite (As +3).

In their study of central Illinois, Kelly, et al. (2005) identified high arsenic levels in sand and gravel (or glacial outwash) aquifer. Like other studies, it was concluded that reduced geochemical conditions and higher organic carbon levels resulted in higher groundwater arsenic concentrations.

Michigan, like many of the Midwest states, has been through extensive glaciations. Studies conducted by the USGS have identified high levels of arsenic (up to 200 µg/L) in groundwater throughout several counties in southeast Michigan. These higher arsenic levels are found in the Mississippian age Marshall sandstone, which is the principal bedrock aquifer for the region. For southeast Michigan, arsenic-rich pyrite is thought to be the principal source. A similar situation occurred in the Verde Valley, Arizona where livestock were being poisoned by high levels (400 – 500 µg/L). A subsequent investigation by Uhlman (2008) found that the groundwater arsenic was associated with groundwater in contact with arsenic-bearing minerals.

In summary, the results of this natural background groundwater arsenic study are consistent with similar studies. In terms of higher naturally occurring arsenic levels, the key variables are typically: 1) groundwater geochemistry (reduced conditions), and 2) increased soil organic matter / content. If the groundwater is geochemically reduced (less than 50 mV oxidation- reduction potential), then it will oxidize the soil organic matter. This geochemical trigger results in the release of arsenic from iron oxides (reductive desorption and dissolution). Low- lying topography, with flat groundwater gradients, may also result in higher arsenic (i.e., not enough dilution; Smedley and Kinniburgh 2002).

**Key point** - aside from well depth, other variables (e.g. geochemistry, soil organic carbon, etc.) that can affect arsenic mobilization, were not evaluated for this study. Consequently, care should be taken when evaluating the results of this study. Likewise, it is hoped that future research will be initiated to assess factors affecting the variability of arsenic levels here in Washington (see also Section 8.0 recommendations).

# 7.0 Conclusion

Groundwater arsenic data from 5,457 public water supply wells over a seven-year timeframe (2003 to 2010) were used to calculate natural background groundwater arsenic concentrations (background threshold values or "BTVs"). The study results indicate that in Washington, natural background arsenic concentrations vary from 4.9 – 15.4 µg/L across the state. The highest levels of natural background arsenic were observed in the Okanogan River valley (15.4 µg/L), Island County (13.3 µg/L) and the Snohomish basin (13.6 µg/L). The lowest background levels were observed in the Southwest Washington, Yakima, and Spokane basins (4.9 – 6.0 µg/L).

An analysis of arsenic concentrations v well depth found that the regression line slope was near zero for all seven basins. What this implies is that there was no relationship between arsenic concentrations and well depth. Also, the coefficient of determination (R-Square) value, for six of the seven basins was < 2.1%, implying that only 2.1% of the variability in arsenic concentrations can be explained by well depth.

In conclusion, this study provides a snapshot of natural background groundwater arsenic levels over a seven-year timeframe between 2003 and 2010. The study results are from a large population of public water supply wells (5,457) with varying depths that range from 10 to 2,134 feet. It is believed that the quantity and quality of data used for this study meet the study objective: to define the natural background arsenic in groundwater in Washington state.

# 8.0 Recommendations

1. Ecology should consider the results of this study for future MTCA site cleanup rule (Chapter 173-340 WAC) revisions. Specifically, the current Ecology arsenic cleanup level of 5 µg/L is within the range of natural background and is therefore too low in some parts of the state.

2. Ecology should develop an implementation memo to provide guidance on how to use data from this study. This memo would be used to make site-specific decisions and demonstrate the appropriate use of background levels as targets for cleanup.

3. An assessment of the potential impacts of geology and related features on arsenic levels is needed. A detailed assessment of basin geology (etc.) was deemed beyond the scope of this study. It is recognized and understood that subsurface geology impacts groundwater arsenic levels. However, the intent of this study was to take a snapshot assessment of Washington groundwater arsenic data dated circa 2003–10. It is hoped that future researchers may be able to examine this issue more thoroughly.

4. More detailed assessments of groundwater geochemistry and arsenic levels over depth are needed. Higher arsenic levels over depth (such as those found in Island County) are thought to be an artifact of older connate (fossilized) and geochemically-reduced groundwater. Much of the Puget Sound region is mantled with what is thought to be more organic rich till units (such as Vashon, etc.). However, this hypothesis needs further evaluation since groundwater geochemistry was not assessed in this study.

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# Glossary

| Term | Definition |
|---|---|
| **ambient** | Of the surrounding area or environment. Ambient is a common term used interchangeably with "natural background." |
| **connate water** | Water trapped in sediment at the time the sediment was deposited. Often referred to as fossil water, which describes very old groundwater found in deep aquifers or bedrock. |
| **Group A/B wells** | Public or private water supply wells regulated by the Washington Department of Health (DOH). |
| **Jenks natural breaks classification method** | A data classification method designed to determine the best arrangement of values into different classes. |
| **left-censored data set** | An observation is left-censored when it is below a certain value (also known as a detection limit) but it is unknown by how much. Left-censored observations are also called non-detect (ND) observations. A data set consisting of left-censored observations is called a left-censored data set. |
| **natural background** | Defined in the MTCA cleanup regulation as a: "…concentration of hazardous substance consistently present in the environment that has not been influenced by localized human activities" (WAC 173-340-200). All soils and groundwater have some level of naturally occurring minerals and metals, such as arsenic. |
| **non-detect** | A term to describe the level (also known as the concentration) at which a lab can measure or detect a substance by some method. |
| **pH** | A measure of the acidity or alkalinity of a solution on a log scale. |
| **ProUCL** | A statistical software package developed by EPA. It is used to establish background levels, determine outliers in data sets, and compare background and site sample data sets for site evaluation and risk assessment. |
| **R-Sq** | R squared is the coefficient of determination - the proportion of the variation in the dependent variable that is predictable from the independent variable. |
| **upper tolerance limit** | A confidence limit on a percentile of the population rather than a confidence limit on the mean. |
| **Voronoi map or diagram** | Provides a way of dividing space into a number of regions. |
| **watershed basin** | A basin encompasses all of the land dissected by streams and creeks.<br>A watershed basin is a portion of land drained by a river and surrounding tributaries. Washington has 62 water resource inventory areas (WRIA) or basins. These basins are used to adjudicate water rights. |

# Units of Measurement

| Unit | Definition |
| --- | --- |
| **Gpm** | Gallons per minute |
| **mV** | millivolts |
| **µg/L** | micrograms per liter (parts per billion) |

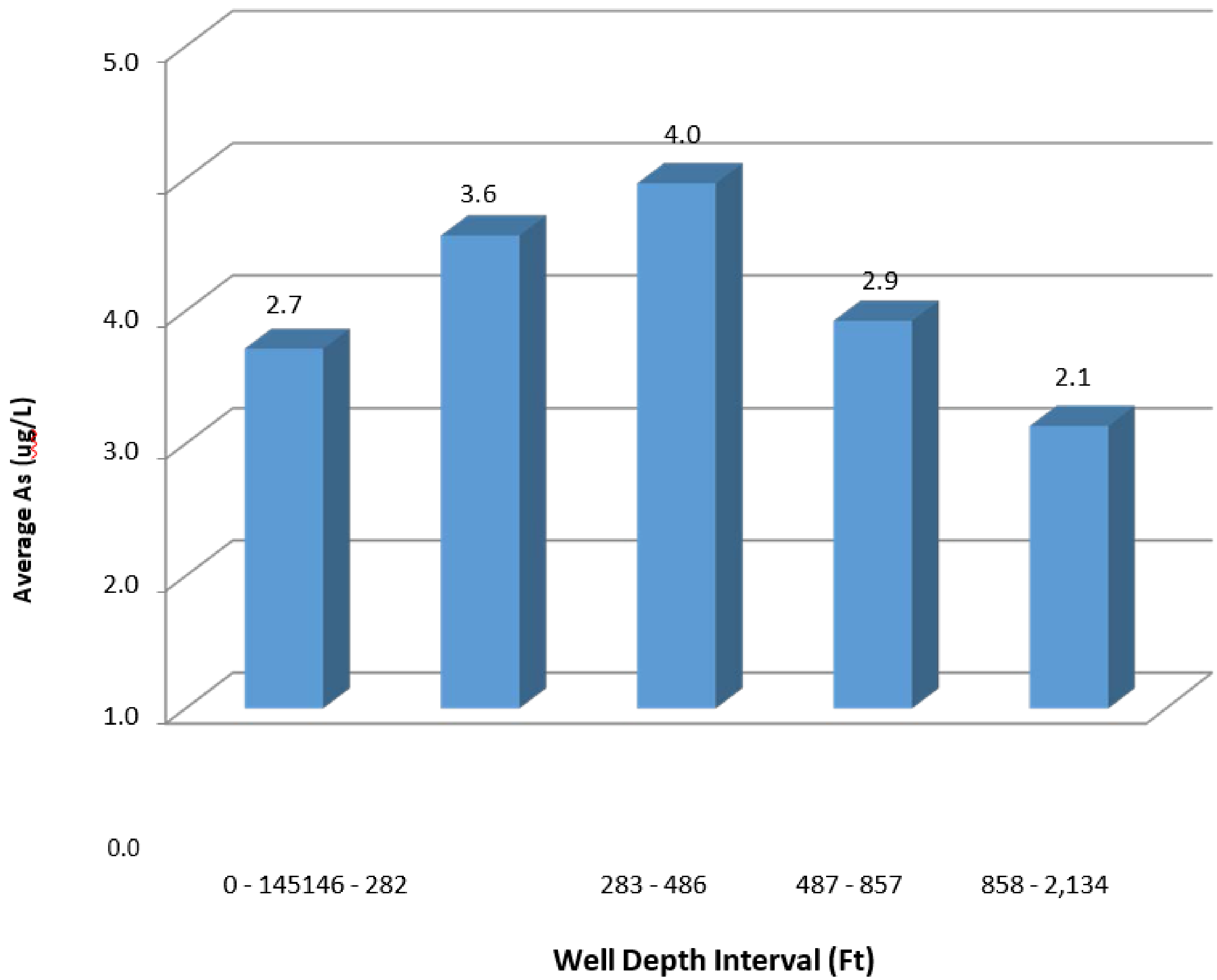
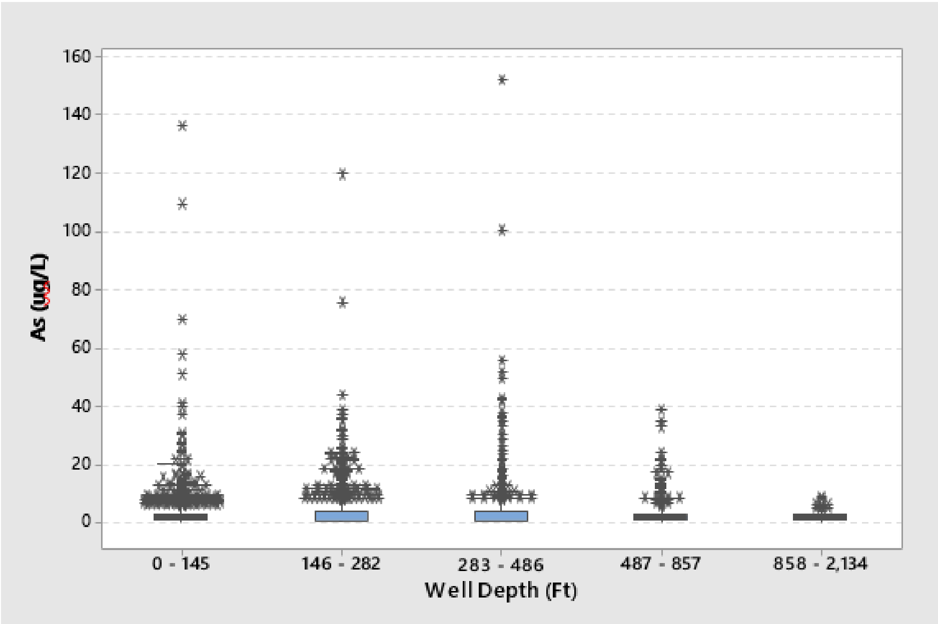
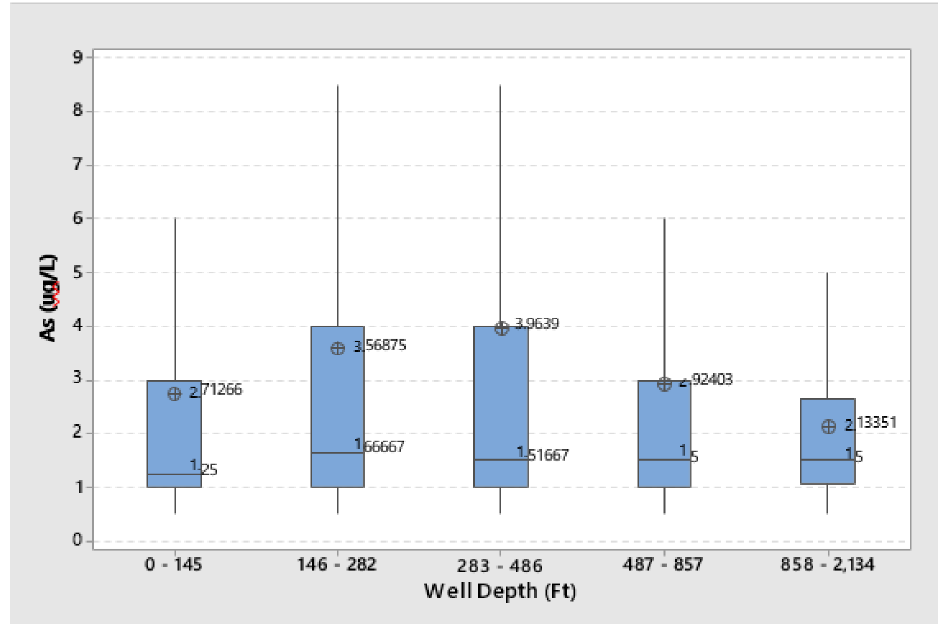



**Figure 16:** Statewide average arsenic concentration v. well depth bar chart.

**With Outliers (Outlier = 1.5 X interquartile range (Q3-Q1))**

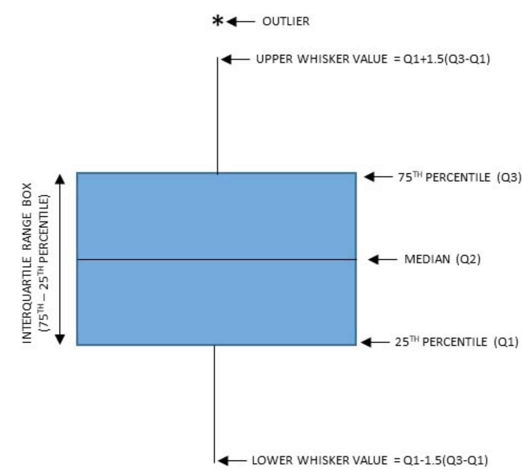



**Without Outliers**




**Note:** the right box plot (outliers removed) was provided to make it easier to see the range box for each basin; however, outliers were not removed for background threshold value (BTV) calculations.

**BOX PLOT LEGEND**



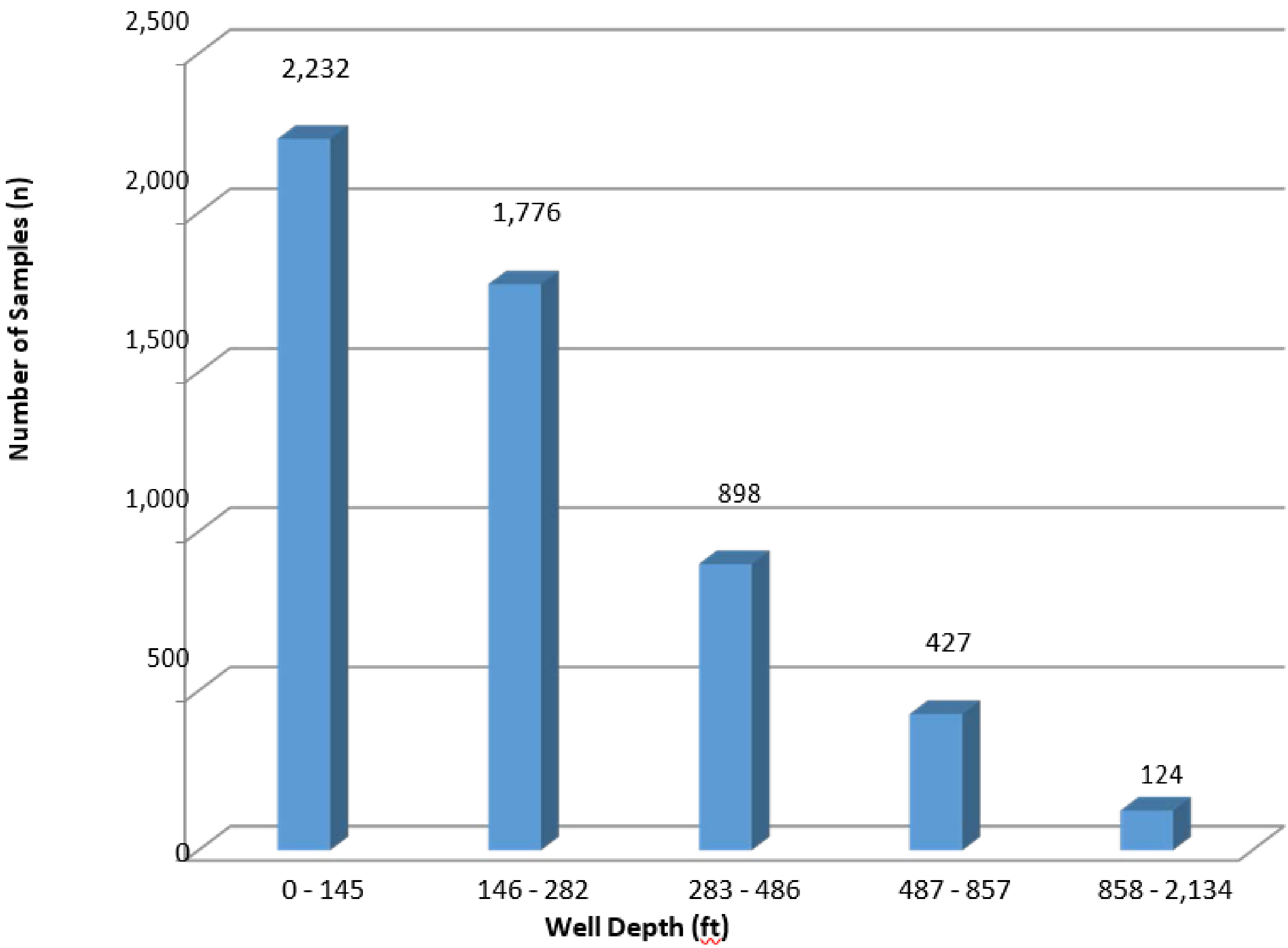



**Figure 18:** Number of samples (statewide) over depth bar chart.

# Appendix A: Arsenic Concentration v Depth Plots

## Overview

Arsenic concentration v. well depth plots, for each of the seven basins, are provided in Appendix A. This information supplements the Section 5.3 discussion. Summary results of a trend analysis (regression line slope) of arsenic concentration v. well depth are also provided (Table 3).

**Table 3:** Watershed basin arsenic concentration v. well depth statistical (regression) summary.

| Basin | Sample Size (n) | R-Sq (%) (a) | Lower 95% CL (b) | ession Line Slope (c) | Upper 95% CL (c) | P-value | Statistically Significant Slope? |
|---|---|---|---|---|---|---|---|
| **ISL** | 428 | 1.8% | 0.0028 | 0.00939 | 0.0159 | 0.005004 | **Yes** |
| **OKG** | 58 | 16.0% | 0.0059 | 0.01538 | 0.0248 | 0.001877 | **Yes** |
| **PSB** | 2,790 | 0.8% | 0.0014 | 0.00235 | 0.0033 | 0.000004 | **Yes** |
| **SNO** | 207 | 2.1% | 0.0003 | 0.00581 | 0.0113 | 0.037549 | **Yes** |
| **SPK** | 205 | 2.1% | -0.0027 | -0.00138 | -0.0001 | 0.035962 | **Yes** |
| **SW** | 488 | 1.7% | 0.0035 | 0.01072 | 0.0180 | 0.003805 | **Yes** |
| **YB** | 390 | 0.3% | -0.0011 | -0.00038 | 0.0003 | 0.291233 | **No** |

ISL = Island County. OKG = Okanogan Basin. PSB = Puget Sound Basin. SNO = Snohomish Basin. SPK = Spokane Basin. SW = Southwest WA. YB = Yakima Basin.

(a) R-Sq = coefficient of determination.
(b) From the Excel data analysis regression package.
(c) Linear regression of average well depth (X) v. arsenic concentration (Y).

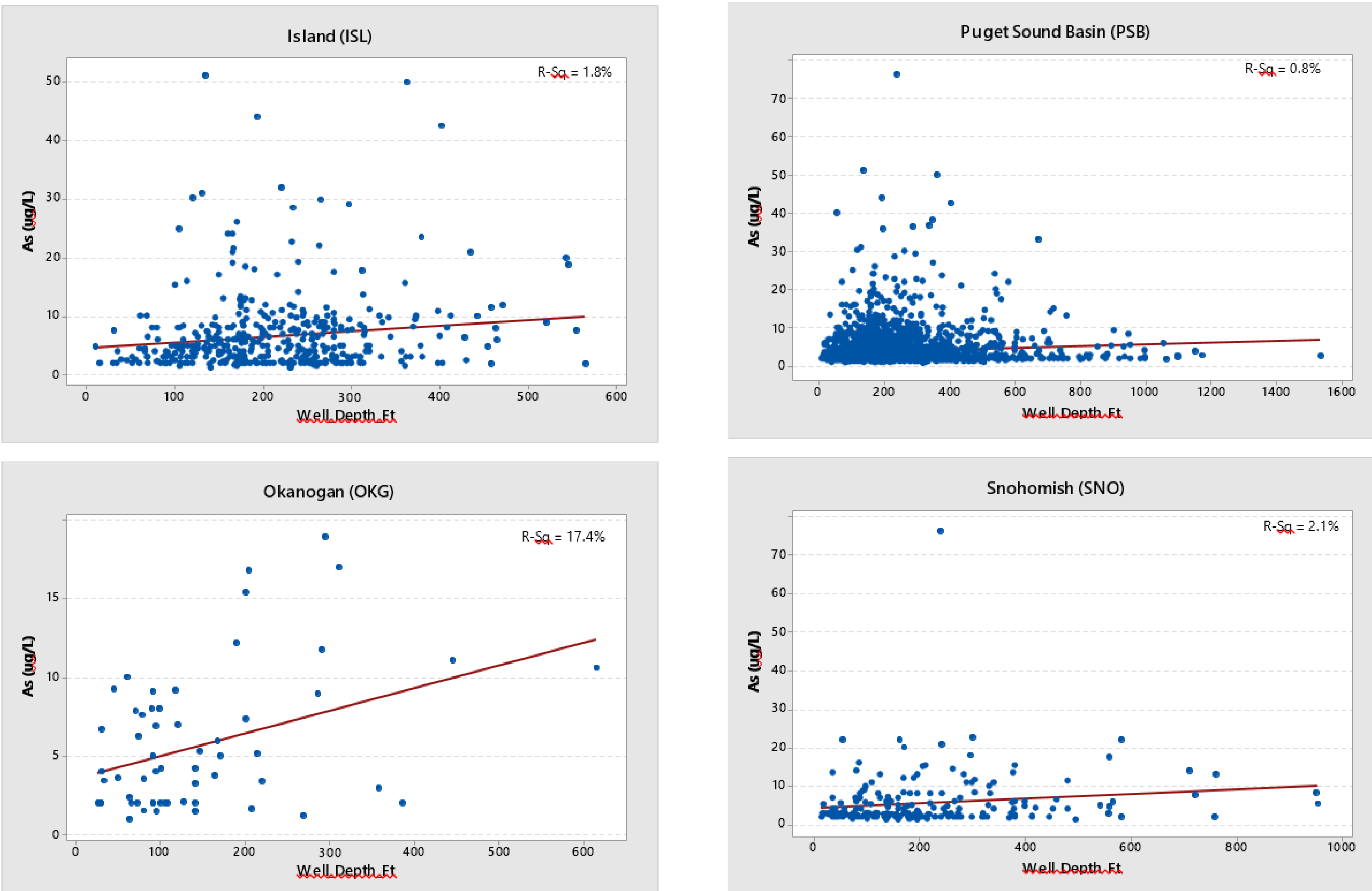



**Figure 19: (**four figures) Watershed basin arsenic concentration v. well depth (Island, Okanogan, Puget Sound and Snohomish).

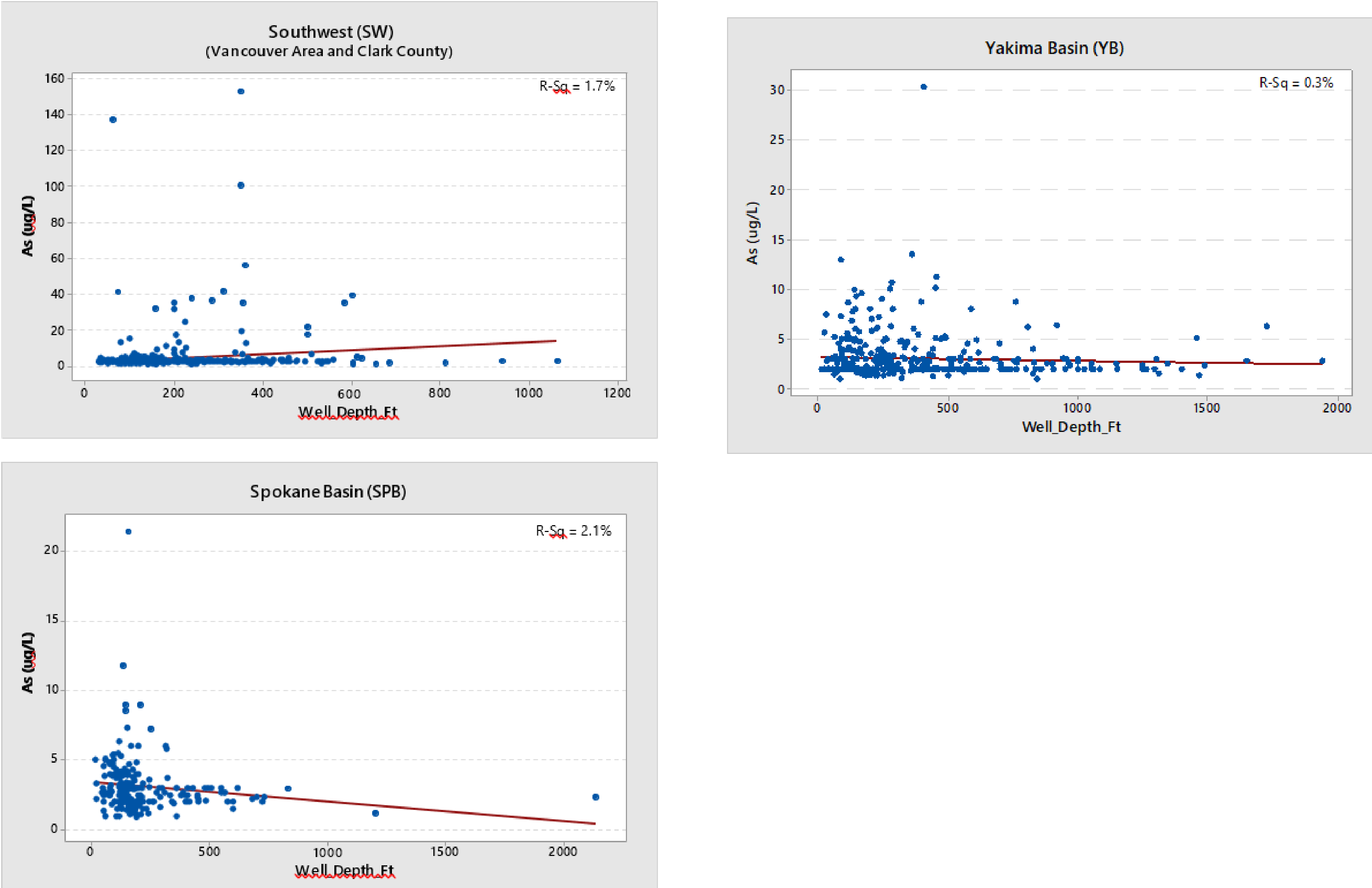
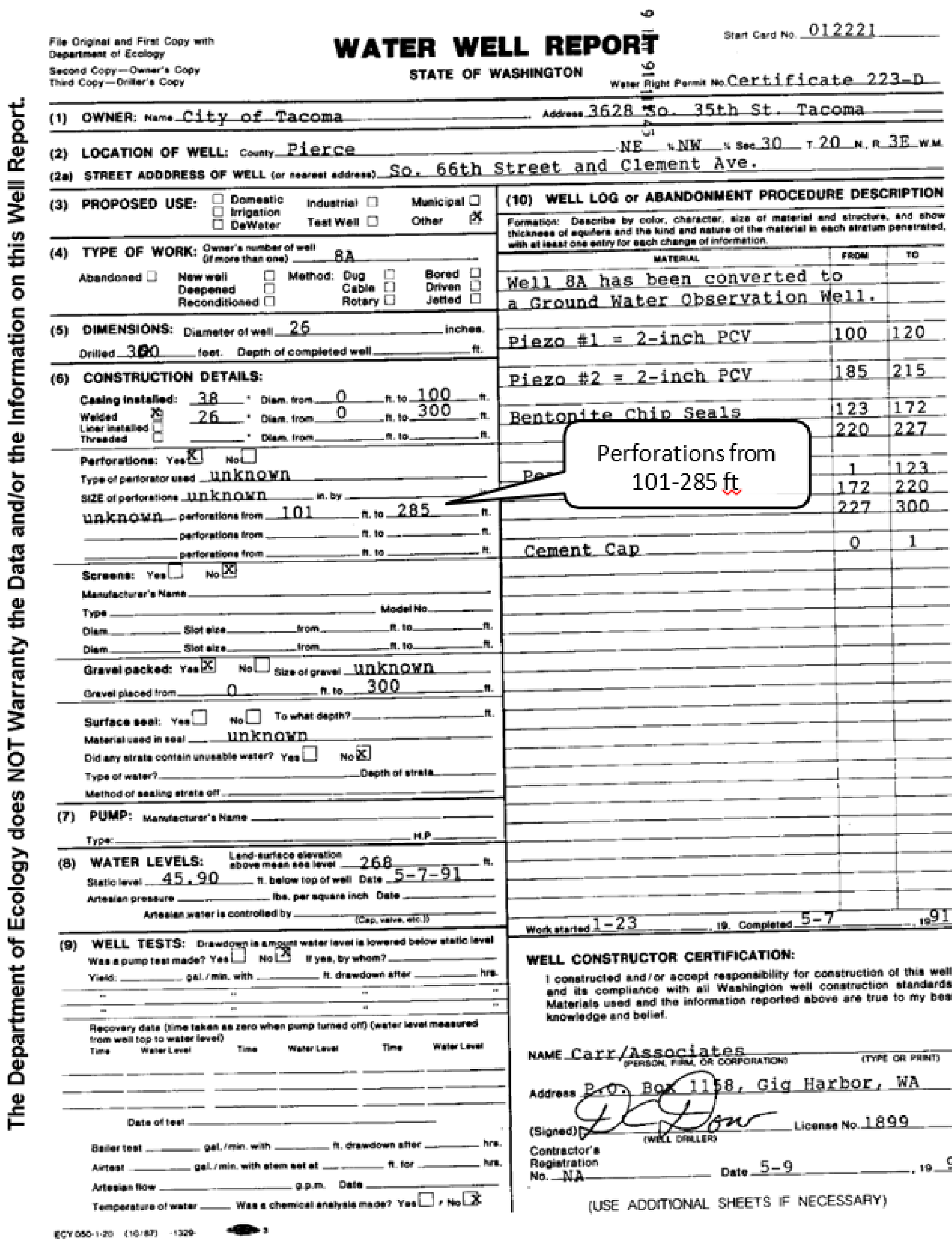



**Figure 20:** (three figures) Watershed basin arsenic concentration v. well depth (Southwest, Spokane and Yakima).



The Department of Ecology does NOT Warranty the Data and/or the Information on this Well Report.

File Original and First Copy with Department of Ecology
Second Copy—Owner's Copy
Third Copy—Driller's Copy

**WATER WELL REPORT**
STATE OF WASHINGTON

Start Card No. 012221
Water Right Permit No. Certificate 223-D

(1) OWNER: Name City of Tacoma  Address 3628 So. 35th St. Tacoma

(2) LOCATION OF WELL: County Pierce  NE ¼ NW ¼ Sec. 30 T. 20 N., R. 3E W.M.

(2a) STREET ADDRESS OF WELL (or nearest address) So. 66th Street and Clement Ave.

(3) PROPOSED USE: ☐ Domestic ☐ Irrigation ☐ DeWater  Industrial ☐ Test Well ☐  Municipal ☐ Other ☒

(4) TYPE OF WORK: Owner's number of well (if more than one) 8A
Abandoned ☐ New well ☐ Deepened ☐ Reconditioned ☐  Method: Dug ☐ Cable ☐ Rotary ☐ Bored ☐ Driven ☐ Jetted ☐

(5) DIMENSIONS: Diameter of well 26 inches.
Drilled 300 feet. Depth of completed well ___ ft.

(6) CONSTRUCTION DETAILS:
Casing installed: 38" Diam. from 0 ft. to 100 ft.
Welded ☒ 26" Diam. from 0 ft. to 300 ft.
Liner installed ☐
Threaded ☐ ___" Diam. from ___ ft. to ___ ft.

Perforations: Yes ☒ No ☐
Type of perforator used unknown
SIZE of perforations unknown in. by
unknown perforations from 101 ft. to 285 ft.
perforations from ___ ft. to ___ ft.
perforations from ___ ft. to ___ ft.

Screens: Yes ☐ No ☒
Manufacturer's Name
Type ___ Model No. ___
Diam. ___ Slot size ___ from ___ ft. to ___ ft.
Diam. ___ Slot size ___ from ___ ft. to ___ ft.

Gravel packed: Yes ☒ No ☐ Size of gravel unknown
Gravel placed from 0 ft. to 300 ft.

Surface seal: Yes ☐ No ☐ To what depth? ___ ft.
Material used in seal unknown
Did any strata contain unusable water? Yes ☐ No ☒
Type of water? ___ Depth of strata ___
Method of sealing strata off ___

(7) PUMP: Manufacturer's Name ___
Type: ___ H.P. ___

(8) WATER LEVELS: Land-surface elevation above mean sea level 268 ft.
Static level 45.90 ft. below top of well Date 5-7-91
Artesian pressure ___ lbs. per square inch Date ___
Artesian water is controlled by ___ (Cap, valve, etc.)

(9) WELL TESTS: Drawdown is amount water level is lowered below static level
Was a pump test made? Yes ☐ No ☒ If yes, by whom?
Yield: ___ gal./min. with ___ ft. drawdown after ___ hrs.
Recovery data (time taken as zero when pump turned off) (water level measured from well top to water level)
Time / Water Level / Time / Water Level / Time / Water Level
Date of test ___
Bailer test ___ gal./min. with ___ ft. drawdown after ___ hrs.
Airtest ___ gal./min. with stem set at ___ ft. for ___ hrs.
Artesian flow ___ g.p.m. Date ___
Temperature of water ___ Was a chemical analysis made? Yes ☐ No ☒

(10) WELL LOG or ABANDONMENT PROCEDURE DESCRIPTION
Formation: Describe by color, character, size of material and structure, and show thickness of aquifers and the kind and nature of the material in each stratum penetrated, with at least one entry for each change of information.

| MATERIAL | FROM | TO |
|---|---|---|
| Well 8A has been converted to a Ground Water Observation Well. | | |
| Piezo #1 = 2-inch PCV | 100 | 120 |
| Piezo #2 = 2-inch PCV | 185 | 215 |
| Bentonite Chip Seals | 123 | 172 |
| | 220 | 227 |
| Pe[illegible] | 1 | 123 |
| | 172 | 220 |
| | 227 | 300 |
| Cement Cap | 0 | 1 |

Perforations from 101-285 ft

Work started 1-23, 19__. Completed 5-7, 1991

WELL CONSTRUCTOR CERTIFICATION:
I constructed and/or accept responsibility for construction of this well, and its compliance with all Washington well construction standards. Materials used and the information reported above are true to my best knowledge and belief.

NAME Carr/Associates (PERSON, FIRM, OR CORPORATION) (TYPE OR PRINT)
Address P.O. Box 1158, Gig Harbor, WA
(Signed) [signature] (WELL DRILLER) License No. 1899
Contractor's Registration No. NA Date 5-9, 1991

(USE ADDITIONAL SHEETS IF NECESSARY)

ECY 050-1-20 (10/87) -1329-

**Figure 21**: Example public supply well with open screened interval (City of Tacoma Well #8A).

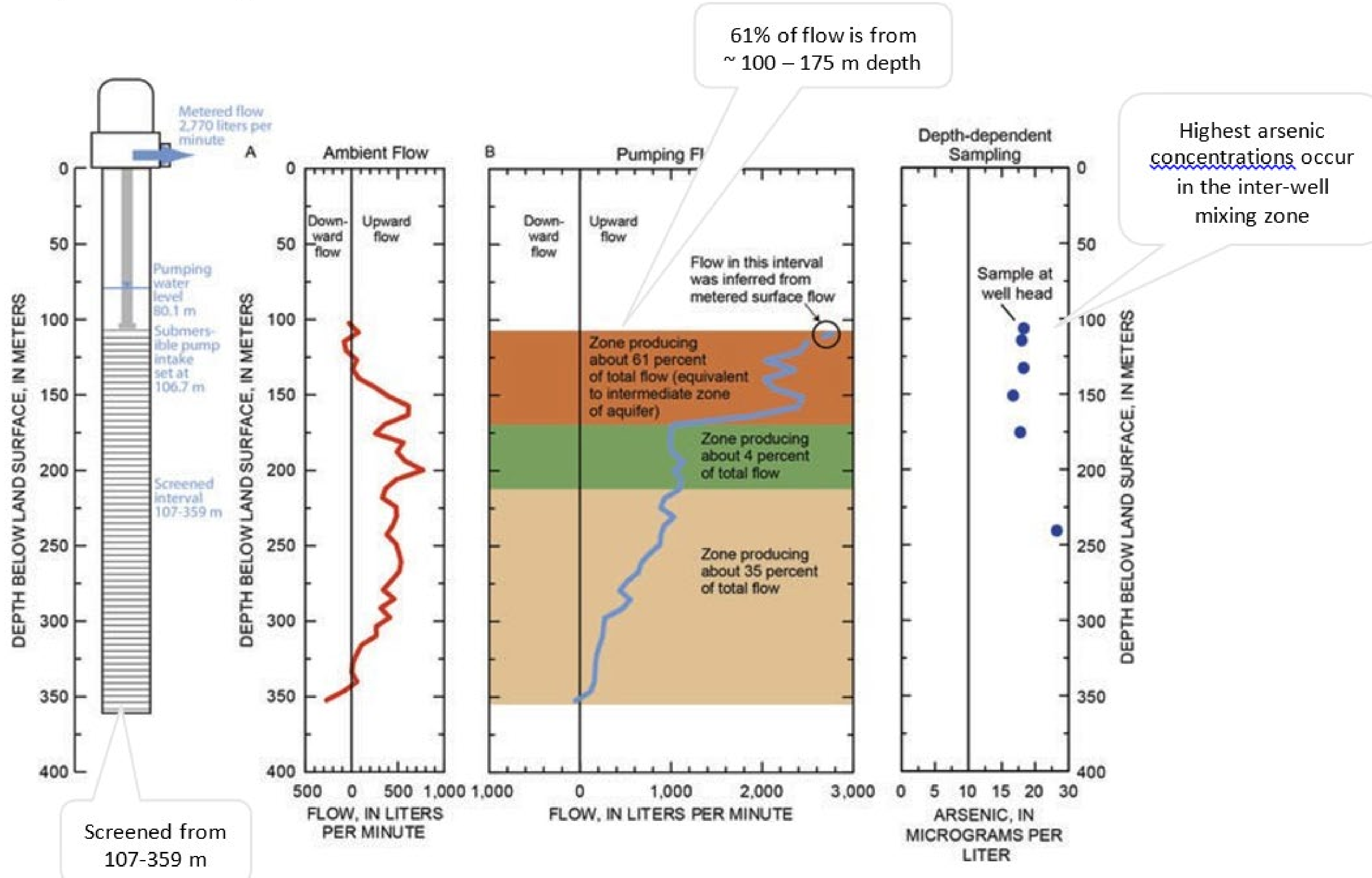



**Figure 22:** Well screen interval, flow rates and arsenic concentrations v. depth (Jugens et al., 2014).

**Key point** – inter-well mixing zone affects arsenic concentrations; therefore, no meaningful correlation between well depth and arsenic levels.

# Appendix B: Tacoma Smelter Plume (TSP) Soil Arsenic

## Overview

Appendix B contains information on the Tacoma Smelter Plume (TSP) soil arsenic. A brief analysis of the possible correlation between this surface soil arsenic and underlying groundwater is also provided. This information supplements the Section 6.0 discussion.

## Impact of Arsenic from Human Activity

Ecology has defined “natural background” as not altered by human activity (WAC 173-340-200). Although arsenic occurs naturally, there are several areas in Washington that have been impacted by arsenic from human activity. Among them are smelting operations and areas impacted by the historical use of arsenical based pesticides.

The Asarco mining company operated a copper smelter in Ruston near Tacoma. Airborne fallout from this smelting operation has enriched surface soil lead-arsenic levels. This fallout zone has come to be known as the Tacoma Smelter Plume (TSP) lead-arsenic footprint. Asarco also operated a smelter in Everett and the same problem (airborne fallout of lead-arsenic) has occurred there as well.

Widespread use of arsenical-based pesticides has also impacted orchard lands throughout Eastern Washington, such as Yakima County and others. Lead-arsenate was the most widely used pesticide, which was used to control gypsy moths (Peryea 1998). However, with the advent of DDT (Dichlorodiphenyltrichloroethane), most lead-arsenate pesticide use in Washington was discontinued after the Second World War (WWII).

Consequently, it is acknowledged that arsenic from human activity may be an issue. Specifically, if arsenic from human activity (e.g. smelters, pesticides, etc.) has contaminated surface soils, there is the possibility that it may also have impacted groundwater.

To address this issue, this study briefly examines possible impacts of remnant soil arsenic (from human) activity on groundwater.

## Methods

Possible impacts of soil arsenic on groundwater (due to human activity) were evaluated. For this task, soil arsenic data taken from the core of the Tacoma Smelter Plume was compiled.

Area-weighted soil arsenic concentrations, as well as mass, were then calculated. The end calculation resulted in an estimate of the mass of soil arsenic from human activity.

For this assessment, arsenic mass from human activity was defined as that amount above natural background. Ecology (1994) has measured background soil metals levels. The statewide natural background ($90^{th}$ percentile) soil arsenic level is 7 mg/kg.

## Soil Arsenic Data

Soil arsenic data from the TSP footprint was extracted from Ecology's Environmental Information Management (EIM) database (1,871 records; 0–2 inch depth). Soil arsenic data was extracted from the core of the TSP footprint, which included the areas of Tacoma and vicinity; Vashon Maury Island; Gig Harbor / Longbranch; and the smaller islands, Fox, McNeil, and Anderson.

## Area Weighted Soil Arsenic Levels

Area-weighted soil arsenic concentrations (as well as total mass) were then calculated for this core footprint area. The ArcMap (v 10.8.1) Geostat Analyst tool used to create a Voronoi map. A Voronoi map (or diagram) is a way of dividing space into a number of regions (polygons). You can use the Voronoi method to calculate the average (area-weighted) soil arsenic concentration for each region or polygon. Equation 1 was used to calculate the arsenic soil mass for each Voronoi polygon:

**Equation 1:** $M = C * UCF * \rho * D * V$

M = soil arsenic mass (kg) from human activity
C = average Voronoi diagram soil arsenic
(mg/kg) CF = unit conversion (1 kg / 1E6 mg)
ρ = dry soil bulk density (1.5 kg/L = 42.5 kg/ft3)
D = soil sample depth (2 inches = 0.17 ft)
V = soil volume (ft3) from Voronoi polygon size (acres)

To accurately calculate the soil arsenic mass from human activity, you must subtract the natural background mass. Therefore, Equation 1 was used to calculate the natural background mass (from the statewide 90th percentile natural background arsenic of 7 mg/kg):

Total arsenic (from human activity) = arsenic mass (from human activity) – arsenic mass (natural background)

## Comparing Soil and Ground Water Arsenic

If you know the arsenic mass from human activity, then you can compare to measured natural background ground water arsenic levels. For this assessment, ArcGIS was used to locate public water supply wells that intersect the TSP core footprint area. This search resulted in 450 wells. ArcGIS was then used to construct a Voronoi map of average natural background groundwater arsenic levels (across the core TSP footprint). Equation 2 was then used to calculate the natural background groundwater arsenic mass:

**Equation 2:** M = (A*b*C*n*UCF1) / UCF2

M = groundwater arsenic mass (kg)
A = Voronoi polygon area (ft2) b = aquifer thickness (average well depth = 244 ft)
C = average natural background groundwater arsenic (µg/L)
n = soil porosity (0.43 dimensionless)
UCF1 = unit conversion factor (28.3 L/ft3)
UCF2 = unit conversion factor (1E9 µg/kg)

## Impact of Arsenic from Human Activity on Groundwater

An estimate of the core Tacoma Smelter Plume (TSP) soil arsenic total mass, from human activity, is provided in Table 4. If you use a Voronoi map (Figure 23) to calculate area- weighted soil arsenic levels, then the total estimated arsenic mass, from human activity, is roughly one million kg (2.5 million pounds = 1,130 tons). Therefore, over the lifetime of the Asarco smelter (100 years or circa 1900 to 2000), roughly 2.5 million pounds of arsenic was released to area soils, which equals about 300 square miles.

Over this same 300 square mile area, there are 450 public water supply wells with an average depth of 244 ft. If you use the Voronoi method to calculate average groundwater arsenic levels, then the estimated mass is about 90,000 kg (200,000 lbs; Table 5).

Thus, the surface soil arsenic mass from human activity (1 million kg), is about ten times the natural background groundwater arsenic mass (0.1 million kg).

Key point: If soil arsenic from human activity was leaching or migrating to groundwater, then there would likely be a corresponding increase in groundwater arsenic concentrations. However, for the 450 Tacoma Smelter Plume wells, average arsenic levels were about 3-4 µg/L over depth (Figure 24 box / interval plots). This suggests that although surface soil has been significantly impacted by arsenic from human activity, the underlying groundwater has not.

**Table 4:** Tacoma Smelter Plume soil arsenic mass

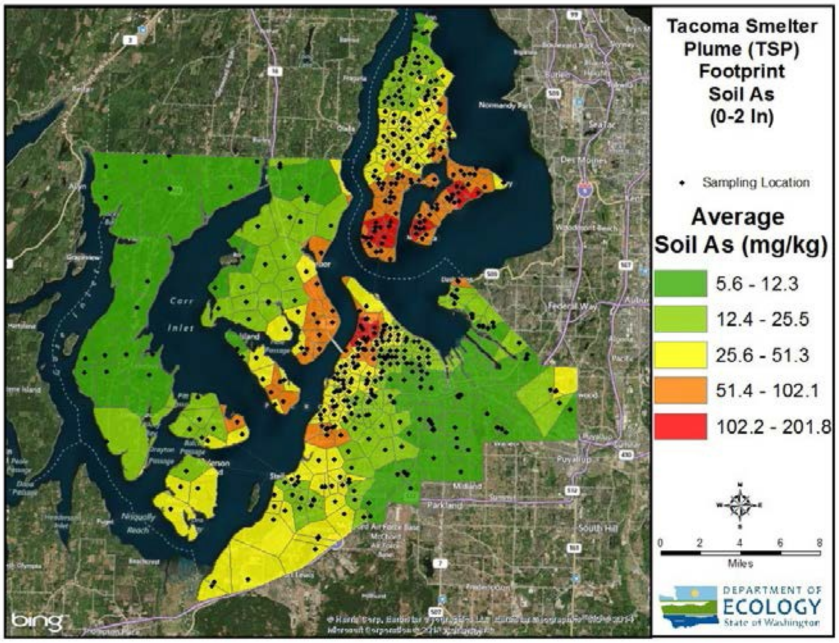
| Area | Area (square miles) | Area (acres) | TSP As (kg) | Natural Background As (b) (kg) | Human As (c) (kg) | Lbs | Tons | Metric Tons |
|---|---|---|---|---|---|---|---|---|
| TSP (a) | 280 | 179,311 | 1,409,787 | 387,059 | 1,022,728 | 2,254,726 | 1,127 | 1.13 |

**Table 5:** Tacoma Smelter Plume groundwater arsenic mass

| Area | Number of Wells (n) | Average Well Depth (feet) | Land Area (square miles) | Land Area (acres) | Natural Background As (kg) | Lbs | Tons | Metric Tons |
|---|---|---|---|---|---|---|---|---|
| TSP (a) | 450 | 244 | 280 | 179,314 | 87,878 | 193,737 | 97 | 0.10 |

(a) TSP = Tacoma Smelter Plume.
(b) Natural background soil arsenic mass = from Equation 1 and natural background soil arsenic = 7 mg/kg (over 280 squares miles, 0–2 inches).
(c) Human activity soil arsenic mass = TSP soil arsenic – natural background arsenic. From Equation 1 and average (area-weighted) soil arsenic (Figure 23 Voronoi diagram).

**Soil**




**Groundwater**

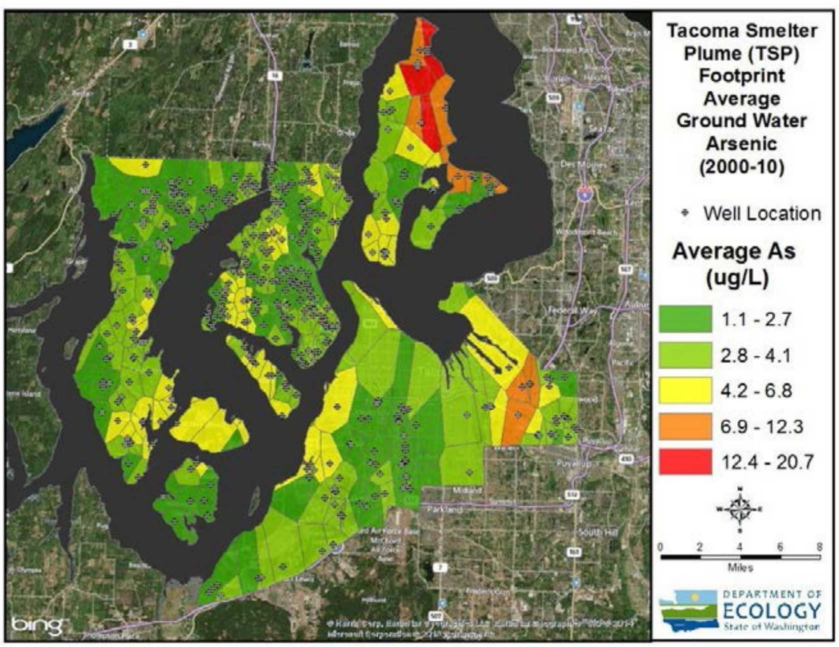
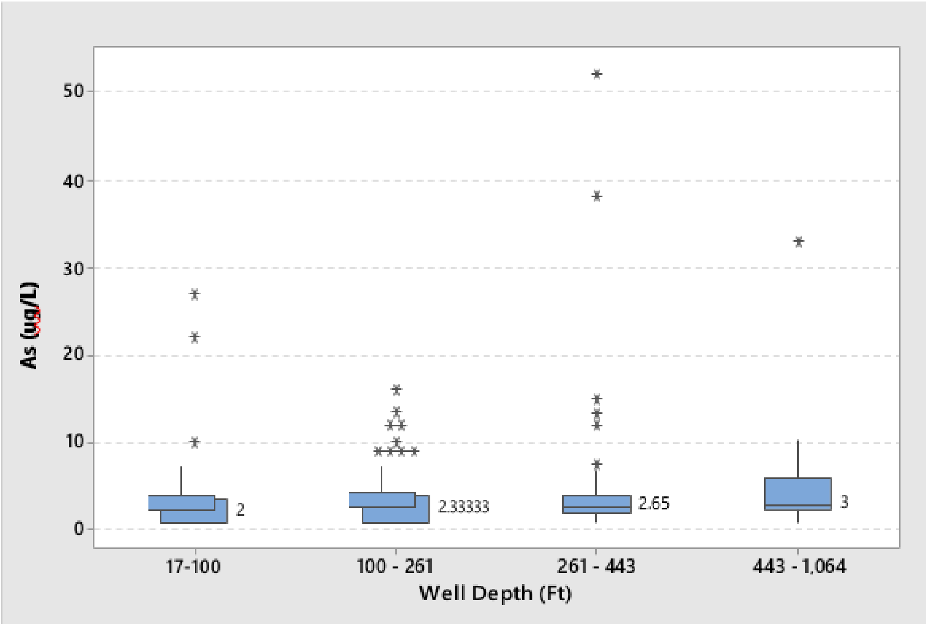
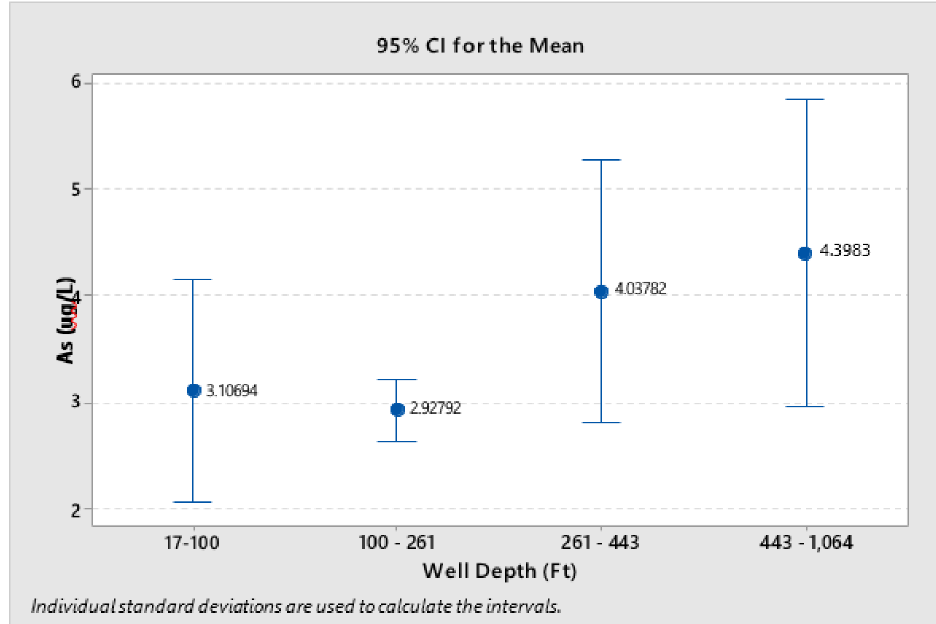



**Figure 23:** (two figures) Tacoma Smelter Plume soil and groundwater arsenic Voronoi maps.

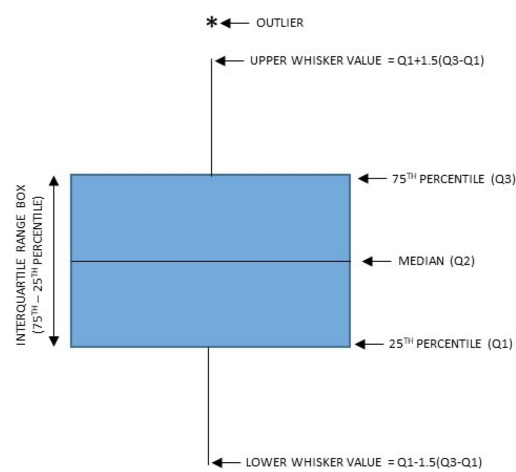
**Box Plot with Median Arsenic Concentrations and Outliers = 1.5 X interquartile range (Q3-Q1)**




**Interval Plot with Average Arsenic Concentrations**




**BOX PLOT LEGEND**



# Appendix C: Responses to Peer Review and Public Comment

## Overview

Ecology originally published this study as a review draft in July of 2021. In November 2021, we finalized it based on comments received during the draft study's public comment period July 15 through August 16, 2021. Appendix C contains comments, Ecology responses, and a description of revisions to the draft natural background arsenic study resulting from the comments.

## Key Changes (Revisions) Summary

The following issues were revised (e.g. by adding clarifying text, changing results, or, removed altogether):

- BTVs, for both Island and Snohomish basins (use all the data, as opposed to just detect data)
- Mean, median, standard deviation, variance and coefficient of variance values (for all basins)
- Concentration v depth analysis (use all the data, as opposed to averaging)
- Comparison of arsenic results from wells < 100 ft deep to all wells (removed)
- Arsenic results (total arsenic and not dissolved; non-detect (ND) is = "less than" or "LT" = "SDRL" or "State Detection Reporting Limit"; arsenic concentrations quantified by EPA Method 200.7)
- SDRL is not the same as the more common terms of "RL" or "MDRL" (i.e. labs may report to values that are less than SDRL)
- ½ DL used for all NDs
- Numbering for all figures and tables, as well as text references
- Inter-well mixing zones and how they affect arsenic concentrations

1. **Comment on Page 8, list of basins.** It is unclear how all areas of the state will be covered by these basins. For example, I live on the Olympic Peninsula, which might partially be covered by Puget Sound lowlands, but not entirely. Because readers might be using this not only for cleanup, but also to evaluate their own groundwater quality (lots of private wells in this area) it would be helpful to explain how other areas were or will be addressed, or how people in those areas should use the results.

   **Response.** If you live in an area outside of the seven watershed basins, we recommend that you check with DOH on the usefulness of the background value from the basin closest to your area. For example, if you live on the Olympic Peninsula, then you would, as mentioned, use the background value for the Puget Sound Basin. For cleanup, you may also use the study data itself to define a background concentration according to WAC 173-340-709. Additional details on how to use and apply the background study values will be provided in a forthcoming implementation memo. Please contact the Ecology Cleanup Project Manager for your site if you would like to consider calculating a site-specific area background value.

2. **Comment on Section 4.11.** Is Microsoft Excel an appropriate tool for doing egressions? Historically its statistical tools have been prone to errors. Why not use R or a more robust statistical software package?

   **Response.** Robust statistical software packages (e.g. R, etc.) have more sophisticated tools for performing regressions. However, the regressions performed for this study (concentration v. depth) are simple and straightforward (i.e. linear with one independent variable) so Ecology deemed Microsoft Excel an appropriate tool for the analysis to support this study.

3. **Comment on Section 5.6.** Good news about groundwater in the Tacoma Smelter plume area! This should alleviate some worries and simplify cleanups in that area.

   **Response.** Thank you. Ecology concurs. As discussed in the study, there was no meaningful correlation between surface soil arsenic (former Ruston Asarco smelter) and public supply well water.

4. **Comment on Section 6.** Could the geologic discussion presented here help evaluate what levels should be applied in areas not included in the basins listed?

   **Response.** Yes, it is hoped that the report discussion will be useful for determining background for areas outside of the study basins in certain circumstances. Please contact the Ecology

Cleanup Project Manager for your site to discuss the applicability of geologic discussion for an area not included in the basins listed.

5. **Comment on Figure 3.** The Puget Sound Basin is not clearly delineated from others in some areas - it appears to overlap into the Snohomish and Southwest Basins. Can this be more clearly outlined like the others? Otherwise there could be double-counting issues?

   **Response**. Figure 3 was revised so that the boundaries between the Puget Sound Basin, Snohomish, and Southwest are more clear (or easier to see). Ecology can provide you the basin shape files upon request for additional analysis with ESRI ArcMap (GIS).

6. **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?)

   **Response.**

   (a) Well construction details - the following text was added to Section 4.1 (well data) –

   *"Well depth was the only well construction parameter that was extracted from the DOH database. If you need additional details on well construction (for the public supply wells used in this study), then please go to the Ecology well log viewer. Lastly, baseline geochemical data (e.g. pH, redox) was not extracted (beyond the scope of this study)."*

   (b) Data from wells located within or outside of the basins – the following text was added to Section 4.4 (data filtering) -

   *"Background threshold values, for the seven watershed basins, are based on data from public supply wells that are located within those basins (n = 4,566 of 84% of the total data of 5,457). Data from public supply wells located outside the seven basins (n = 891 or 16% of the total data of 5,457) was not used to calculate background threshold values."*

   (c) Non-detects - Of the 18,032 data records used in this study, 7,408 of them (41%) were above laboratory arsenic detection limits, varying from 0.5 to 100 µg/L (10,624 non-detects or 59%). The number of non-detects (ND) per year, including min, average and max values is provided in Table 1. Details on non-detects (NDs) and other statistical methods are provided in report Section's 4.5 – 4.8 – the following text was added to Section 4.5 (non-detects):

*"For this study, non-detect (ND) is equivalent to "State Detection Reporting Limit" or "SDRL" (Washington Department of Health Drinking Water). It is understood and acknowledged that analytical laboratories quantify substances to the more common terms of Method Detection Limit (MDL) or Method Reporting Limit (MRL). However, for drinking water analysis, you are required to meet the "SDRL". Some labs will report to values that are less than the SDRL – these may be either MRL or MDL."*

(d) Outliers – the following text was added as the last sentence in Section 4.8 (statistical methods) -

*"Note: results that would be considered statistical outliers were not removed. All non-detects (ND) were assigned a value of ½ the detection limit (SDRL)."*

7. **Comment: 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.

   **Response**. The following text was added (last paragraph, Section 6.0 study conclusion):

   *"**Key point** - aside from well depth, other variables (e.g. geochemistry, soil organic carbon, etc.) that can affect arsenic mobilization, were not evaluated for this study. Consequently, care should be taken when evaluating the results of this study. Likewise, it is hoped that future research will be initiated to assess factors affecting the variability of arsenic levels here in Washington (see also Section 8.0 recommendations)."*

8. **Comment: 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.

   **Response.** Ecology concurs and the forthcoming implementation memo will address how to use the background threshold values. It will also address or provide recommendations on how to perform or conduct a background arsenic determination. Please contact your Ecology Cleanup Project Manager to discuss the applicability of using the study data at your site.

9. **Comment on Tables and Figures.** Check (and revise numbering as applicable) the order in which the tables and figures are referenced in the text. 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? Figure 22 is missing.

   **Response**. The numbering for all of the figures and tables were revised. As you read the document, all figures and tables are referred to in sequential order.

10. **Comment on 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.

    **Response**. Tables 4 and 6 have been replaced by Table 3 (concentration v depth summary). The Table 3 sample size (n) values for both Island County and Okanogan are now consistent with Table 2.

11. **Comment on 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, then 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 and they can only be rejected for legitimate reasons, e.g. data quality, etc.

    **Response**. The outlier box plots compress or “squish” the boxes (and corresponding data ranges), therefore, with and without outlier boxes were provided. See response #6(e); in addition, the following text was added to the Figures 11 and 17 (box plots with and without

outliers) -
*"The right box plot (outliers removed) was provided to make it easier to see the data range (25th to $75^{th}$ percentile) for each basin; however, outliers were not removed for background threshold value calculations."*

12. **Comment on Section 1.0 Summary, Page 1**. Define units first time used, e.g., micrograms per liter (µg/L), in first sentence of second paragraph. Why is Figure 1 in this section?

    **Response**. A definition of the term "ug/L" (micrograms per liter or parts per billion) was added to both the acronyms and abbreviations table and Section 1. Figure 1 (statewide filled contour map) was provided as part of the summary

13. **Comment on 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.

    **Response**. Ecology considered this suggestion and decided to maintain the existing organization. Section 5.3 provides the results of the concentration v depth analysis. The methods for this analysis are provided in Section 4.9. In other words, the study narrative follows the "traditional" issues, methods, results, etc. organizational style. If you move the study results (e.g. concentration v depth) to the overview, then you would need some type of new organization style. Consequently, Ecology prefers, at this point, to keep the organization as is.

14. **Comment on 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.

    **Response. See Figure 1.** Ecology could not provide a version of Figure 2 focused on Washington state because the image quality and resolution of the zoomed version was poor.

15. **Comment on Section 4.1 Groundwater Arsenic Well Data, Page 7**. Is the data used for this study available in a tabulated format?

**Response.** Yes, you may request an Excel data file for additional analysis. The forthcoming implementation memo will provide more details on this.

16. **Comment: Several questions about the data itself.** 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)?

**Response.** Yes, you can access well construction data from Ecology's Washington state well report viewer.[5] The raw data file does have some baseline information (e.g. well depth, location, water system, source, etc.).

17. **Comment: Does the dataset include total and/or dissolved arsenic concentrations?**

**Response.** The arsenic results are total (not dissolved), as quantified by EPA drinking water methods (Method 200.7 inductively coupled argon plasma atomic emission spectrometer (ICAP- AES)). The following text was added to Section 4.0 (first sentence of paragraph one) -

*"Total (not dissolved) arsenic data…."*

18. **Comment: 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.]?

**Response**. When the data query was initiated, water chemistry data was not extracted. Ecology does concur that this would be useful information. However, during the course of this study, Ecology's research into natural background arsenic levels (USGS, 2007) found that redox (ORP) had by far the most impact on data variability. Consequently, it was felt that extracting water chemistry data would make the study more complicated and may not yield significant value (i.e. we already know the impact of redox on arsenic levels).

USGS (2007) Mary Ann Thomas - The Association of Arsenic with Redox Conditions, Depth, and Ground-Water Age in the Glacial Aquifer System of the Northern United States, Scientific Investigations Report 2007-5036.

[5] https://appswr.ecology.wa.gov/wellconstruction/map/WCLSWebMap/default.aspx

19. **Comment: 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.

    **Response**. The non-detect (ND) data that was used for this study are less than or equal to the "State Detection Reporting Limit" or "SDRL" for arsenic. Please note that the SDRL, for arsenic, has varied over time. The more common terms of "MDL" or "MRL" are used by private labs and these values are sometimes less than the SDRL. Each arsenic result had a "LT" (less than) or "EQ" (equal to) code. Clarifying language, for non-detects, was added to Sections 4.5 and 4.7 were updated (see also response #6(c)).

20. **Comment on 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.

    **Response**. The following clarifying text was added to Section 4.3:

    *"Key point: cleanup site density and location was used to identify and select watershed basins. However, groundwater arsenic, from Ecology cleanup sites, was not used to calculate background threshold values."*

21. **Comment on Section 4.5 Non-Detects, Page 9.** 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."

    **Response.** The following clarifying text was added to Section 4.5 (non-detects) -

    *"For this study, non-detect (ND) is equivalent to "State Detection Reporting Limit" or "SDRL" (Washington Department of Health Drinking Water, WAC 246-390-010). It is understood and acknowledged that analytical laboratories quantify substances to the more common terms of Method Detection Limit (MDL) or Method Reporting Limit (MRL). However, for drinking water analysis, you are required to meet the "SDRL".*

22. **Comment on 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?

**Response.** The following clarifying text was added to the last paragraph of Section 4.5 -

- *"Method 7010 - Graphite furnace atomic absorption spectrometry (GFAA), and*
- *EPA Method 200.7 - Inductively coupled plasma / mass spectrometry (ICP/MS)."*

23. **Comment on 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.

    **Response**. Standard deviation results, for each individual basin, for the seven-year study data timeframe (2003-10), are provided in Table 2. The standard deviation range, for the seven basins was 2 to 12. What this suggests is that there really wasn't that much variability in the data. However, for the Southwest basin, the standard deviation was 11.6. This is thought to be the result of a large number of non-detects (71%) and outlier results (e.g. 150 ug/L).

    In summary, given the large sample size (> 5,000) for this study, it's not really practicable to discuss per well variability. The arsenic data file will be public domain and users are encouraged to examine issues like per well variability.

24. **Comment on 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.

    **Response**. The following clarifying text was added to Section 4.6 –

    ***"Key point:*** *given that the data was averaged and the original data was not collected at regular intervals over time, a seasonality analysis was not performed."*

25. **Comment on Section 4.7 Point Averaging and Non-Detects, Page 10.** 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?

**Response**. Values were reported as “state detection reporting limit” or “SDRL.” For additional detail, please see response to comment nos. 6 and 20.

26. **Comment: Non-detect values**. 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. 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.

    **Response**. All non-detect (ND) values were assigned a value of ½ the detection limit (see also Section 4.7 discussion).

27. **Comment on 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.

    **Response**. A skewness “test” or analysis was not performed. However, you can assess skewness from the box plots (Figures 11 and 17). Also, as discussed in Section 4.8, Step 4, prior to calculating BTVs, the data distribution, for each basin, was assessed (goodness of fit testing). The goodness of fit test was based on all the data (ND and D), as opposed to detect (D) only. BTV values were then calculated, based on the Step 4 results and the Section 4.8, Step 5 criteria.

28. **Comment on Section 4.8 Background Calculations, Page 11**. Under Step 3, third sentence, change "he" to "the".

    **Response.** This change was made.

29. **Comment on 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?

**Response**. A 95% confidence level was used and the goodness of fit test was based on all the data (NDs and D), as opposed to detect (D) only. The EPA ProUCL software gives you the option of using full censored data or data without NDs. If you use all the data, then for all seven basins, the data distribution was non-parametric.

30. **Comment on Section 4.9 Correlating Arsenic Concentrations over Depth, Page 12.** Add "was conducted" to second sentence: *"This assessment was conducted for each watershed basin."*

**Response**. Thank you, the Section 4.9 text was revised:

*"Public water supply well depths varied significantly from 10 to 2,134 feet; therefore, an assessment of arsenic levels, over depth, was conducted for each watershed basin."*

31. **Comment on 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).

**Response**. The concentration v depth analysis was revised (please see final study Figures 19 and 20). All of the data was used (as opposed to averaging the data by well depth bins). Scatter (X,Y) plots, of arsenic concentration (y-axis) v well depth (x-axis) were constructed for each basin. A trend analysis of the regression line slope was then performed to determine if the change was statistically significant ($p = 0.05$). Upper and lower confidence levels ($p = 0.05$) were also calculated.

32. **Comment on 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?

**Response**. The sorting well depth data by bins (natural breaks method) was removed. The concentration v depth analysis (Section 4.9) is now based on all the point-averaged data.

33. **Comment on Section 5.1 Summary of Background Levels, Page 13,** second sentence, is the "(90th percentile)" referring to the 90/90 UTL?

    **Response.** The text was revised from “$90^{th}$ percentile” to “90/90 UTL.”

34. **Comment on 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.

    **Response**. In regard to skewness, please see response to comment #27. The total number of samples, per basin, was checked and revised if necessary.

35. **Comment on 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…."*

    **Response**. The concentration v depth analysis, and corresponding text, was revised: 1) well depth bins were removed, and 2) point averaged (individual well) arsenic concentrations were plotted against individual well depths.

36. **Comment on 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.

    **Response.** The concentration v depth analysis was revised: 1) well depth bins were removed, and 2) point averaged (individual well) arsenic concentrations were plotted against individual well depths.

37. **Comment on Section 5.3.2 Island County and Puget Sound Lowlands.** Page 15: What is the expected effect of different lithologies on the geochemistry of the groundwater?

    **Response.** The study did not include discussion of the expected effect of different lithologies on the geochemistry of the groundwater because it is beyond the study scope.

38. **Comment on 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”.

**Response**. Given that the concentration v depth analysis methods were revised, a new results section was added (Section 5.3.1):

*“A statistically significant (slope slightly above zero) trend (95% confidence level) of arsenic concentrations with depth was observed in five basins: Island County, Okanogan, Puget Sound Basin, Snohomish and Southwest. A statistically significant (slope slightly below zero) decreasing trend in arsenic concentrations over depth was observed in the Spokane Basin. Lastly, a statistically insignificant trend in arsenic concentrations over depth was observed in the Southwest Washington area (Vancouver and Clark County;. see Appendix A, Figures 19 and 20 scatter plots including coefficient of determination “R- square” values).”*

39. **Comment on 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".

    **Response.** An example of a public supply well (City of Tacoma Well #8A) with a long (perforated) interval was added (Figure 21). In addition, a diagram, from the Jugens et al. (2014) study of the impact of inter-well mixing zones and pumping well flow rates on arsenic concentrations was added (Figure 22).

40. **Comment on Section 5.5, Representative Study Data and Ecology Cleanup Sites; 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.

    **Response.** Yes, however, Ecology decided to extract a large sample size of data from a well-established database (DOH Sentry) because of the labor intensity of obtaining a representative sample size of non-impacted wells with depths <100 feet at Ecology cleanup sites.

41. **Comment on Section 5.5, Page 18: 3rd paragraph, last sentence.** The reference to tables should be Tables 11 and 12 only (not Table 10).

**Response**. All of the study tables and figures were re-numbered. When you read the study, the text and figures are now referred to in sequential order.

42. **Comment on 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.

    **Response**. Thank you. Ecology removed this section (and Appendix B).

43. **Comment on Section 5.6, Impact of Tacoma Smelter Plume Soil on Groundwater Arsenic Background, Page 19.** 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.

    **Response**. Ecology does concur that the Tacoma Smelter Plume footprint was caused by human activity. However, the question or issue being examined here was whether surficial soil arsenic (former Ruston, Tacoma Asarco smelter) has affected groundwater. The broader question of area wide soil is being addressed by Ecology's Tacoma Smelter Plume "Dirt Alert" program.

44. **Comment: 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.

    **Response**. With some clarification on the area of interest, Ecology can provide you with well depths for a particular area studied upon request.

45. **Comment: 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.*"

    **Response**. Text revised as follows:

    *"Based on this analysis, there did not appear to be any correlation between soil and groundwater arsenic levels in the Tacoma smelter plume footprint."*

46. **Comment on Section 6.0 Discussion, Pages 21-22.** 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.

**Response**. Details of geology etc. can be found in the studies conducted by Welch et al. (1988 and 2000). The Washington Department of Natural Resources also publishes information on Washington geology.

47. **Comment on Section 6.0, 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".

    **Response**. Please see response to comment #7.

48. **Comment on Section 6.0, 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.

    **Response**. Please see response to comment #7.

49. **Comment: Variability.** 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?

    **Response.** Please work with your Cleanup Project Manager about conditions specific to your site. Geochemistry (redox) does significantly impact natural background arsenic levels (it's the single most important variable). However, geochemical conditions are variable. Thus, for this study, this is why a large sample size (n = 5,457), over broad state regions (seven watershed basins) was used to calculate background. Key point – the natural background arsenic levels are based on public supply well data from seven watershed basins. Each watershed basin has its own unique geology and geochemical conditions. Consequently, the proposed natural background values, for each watershed basin, are reflective of basin groundwater geochemistry and soil organic carbon levels. The forthcoming groundwater arsenic implementation memo will provide more details on how to use the background values as well as how to conduct site-specific studies (i.e. geochemistry, soil organic carbon, etc.). The implementation memo will be distributed for public comment and you will have an opportunity to review and comment.

50. **Comment on 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.

    **Response**. Ecology decided to release the study now to make it easier to use the study data to define background concentrations in accordance with WAC 173-340-709. The forthcoming groundwater arsenic implementation memo will provide more details on how to use the background values as well as how to conduct site-specific studies (i.e. geochemistry, soil organic carbon, etc.). Ecology will distribute the implementation memo for public comment and you will have an opportunity to review and comment.

51. **Comment: Potential Skewing.** The reporting level was lowered by 2003 to 2 ppb (in response to the lowering of the federal maximum contaminant level (MCL) from 50 ppb to 10 ppb, which became effective in January of 2006). So there is more precise reporting of arsenic levels in public drinking water wells starting in 2003. And after 2010, many of the approximately 165 active sources with levels of arsenic above the MCL began consistently treating to remove the arsenic. And because DOH requires Group A water systems that treat to remove arsenic to monitor the treated water for arsenic on a monthly basis, most of those sources have an increasing number of samples after 2010 that would be less than 10 ppb, and would skew their average lower.

    **Response**. Ecology feels that the large sample size (5,457) for this study and averaging to one result per well has significantly reduced possible bias (e.g. treatment, etc.)

52. **Comment: From 30 years of reviewing arsenic results from drinking water wells, I have observed the following:**

    Arsenic levels have more to do with the aquifer from which the well draws than well depth per se. Many areas of the Puget Sound basin and Island County have aquifers that span large areas but have varying levels of overburden. Wells drawing from the same aquifer containing arsenic have deeper depths if the well is drilled where there are thicker layers of deposits overlying that aquifer. I believe many of the wells in Island County that have arsenic levels greater than the MCL are drawing from the 'sea level aquifer'. However, many of the county's wells would need to be 200 to 300 feet in depth to reach that aquifer. That may account for why there appears to be in increasing arsenic concentration with well depth in Island County.

b) Wells drawing from the top versus the bottom of the same aquifer same aquifer
can have slightly different arsenic levels likely depending on the oxidation/reduction conditions in different portions of the aquifer, as mentioned in the report. Because of arsenic's affinity for oxidized iron, some portions of aquifers that have mobile microparticulate oxidized iron may yield higher concentrations of arsenic as well.

Many of the public water system wells in Washington state serve water systems with less than 500 connections, and many of those wells west of the Cascades have screened intervals of 25 feet or less in length and are not pumping huge volumes of water on an annual basis.

All of the above conditions can contribute to differing levels of arsenic in wells geographically close to one another.

So while the calculated average 'background' concentration of arsenic for Island County is around 13 ppb, there are localized areas where wells in that area commonly have more or less than the calculated average. For instance, around Oak Harbor and Whidbey Island Naval Air Base Ault Field, there are some drinking water wells (public and private) that consistently have 20 to 25 ppb naturally occurring arsenic whereas other wells have 7-9 ppb. Many of these wells are drawing from the "sea level aquifer" and have the top of their open intervals ranging from 30 to - 10 ft MSL.

For these reasons, when updating the MTCA rule, please consider allowing for an assessment of a very localized background level relative to the average background level for the geographic area identified in this report.

**Response**. MTCA Section 709 does allow for site or area-specific natural background demonstrations. Ecology will provide study data file upon request. That way, users can conduct smaller or larger-scale background assessments.

53. **Comment on Section 4.8. Step 3. Assign "0" and "1" codes for non-detect, detect values.** The text discusses the data preparation steps for the ProUCL calculations. The text states when doing point averaging for a well, where all results are non-detect, that "If the result was all non-detect, then half the detection limit was used." The text also states that where the point-averaged data was comprised of all non-detect values, then it was then assigned a "0" code in ProUCL. Please clarify if the point averaged non-detect data were calculated using one-half the detection limit, or if the average was based on the full results. ProUCL guidance states that for a

variable with non-detect observations, the (full) numerical values of the associated detection limits (for less than values) should be entered in the appropriate column associated with that variable. Therefore, calculating the average at one-half the detection limit and entering a "0" code would bias results low.

**Response**. Ecology does acknowledge and understand that substituting ½ for all NDs will bias the data (see also the work of Dennis Helsel, USGS EPA CLU-IN [Methods for Handling Non-Detect or Censored Data](https://clu-in.org/conf/tio/ltmo/Nondetects_handout.pdf)).[6] However, the MTCA regulations require ½ ND for background, 95 UCLs, etc. In this case, given the large number of NDs for some of the basins (e.g. Southwest Washington), the decision was made to use EPA ProUCL and the non-parametric Kaplan Meier method to calculate background threshold values (90/90 UTL).

**Key point** – yes, for this study, ½ was used for all NDs. Again, for each individual well, if the results were a "mix" of non-detects, then ND values were assigned the ½ value and then averaged with the detect results.

54. **Comment on Table 2.** Based on review of the summary statistics for the seven regions, it appears the data for the SW Washington region are much more variable (high standard deviation/variance) and much more non-detect (71 percent), when compared to other regions. This is also the only region where the mean result (9.3 ppb) was higher than the calculated natural background value (4.9 ppb), and where the difference between the calculated parametric (7.5 ppb) and non-parametric (4.9 ppb) UTLs was greater than 2 ppb. Did Ecology conduct sensitivity analysis on a subset of these data (e.g., evaluate more recent data only, if these show fewer non-detects due to improved detection limits) or other evaluations to determine what factors influence the difference between the parametric and non-parametric results? The fact that the lowest natural background concentration statewide was determined for this region is surprising, since Figure 1 shows there are large areas of high arsenic background concentrations in this region when compared to other parts of the state. Additional discussion for the SW Washington dataset would be helpful to support 4.9 ppb as representative of natural background for the region.

    **Response**. The average arsenic concentration (9.3 ug/L) that was reported for the Southwest basin was calculated from detected data only. If you use all the data (ND and D), then the average arsenic concentration is 4.2 ug/L. Consequently, to be consistent, the mean, median, standard deviation, coefficient of variance and variance values, for all basins, were revised and calculated from all the data (see Table 2). As a footnote, the EPA ProUCL software gives you the

[6] https://clu-in.org/conf/tio/ltmo/Nondetects_handout.pdf

option of evaluating the data distribution (Goodness of Fit) on all the data (ND and D) or detects (D) only. The corresponding mean, median, etc. values are reported based on whether you use all the data or only detects. Ecology understands and acknowledges that this is confusing, however, we are hopeful that this clarification will add value.

**Key point** – if you use all the data (non-detects @ ½ detection limit and detects), then the distribution, for all the basins, is non-parametric. If you use the non-parametric 90/90 UTL (no distinction between detect and non-detects), for all the basins, then it changes (increases) the BTV for Island County (from 14.6 to 15.4 ug/L) and Snohomish (11.8 to 13.6 ug/L). In other words, upon further review, Ecology felt that from a statistical standpoint, using all the data for BTVs is a better approach. However, again, to be clear, ½ DL was used for all NDs.

55. **Comment on Section 8. The text states** "Ecology should develop an implementation memo to provide guidance on how to use data from this study to make site-specific decisions and demonstrate the appropriate use of background levels as targets for cleanup." Has Ecology determined if and when an implementation memo will be issued? Such a memo could help clarify 1) do regional natural background values (where higher) supersede the MTCA A criterion, 2) can site-specific natural background determinations supersede regional background values, and 3) include a simple state-wide map that shows which regional values apply where (including at sites not within a region evaluated [e.g., in Chelan County], and sites located in areas where two regions appear to overlap [e.g., in Snohomish County, see Figure 1).

**Response**. Ecology has not determined a timeline for the public review of an implementation memo. We recommend you sign up for the MTCA-SMS Rule Update email list[7] to receive updates on development of additional policies and guidance.

[7] https://public.govdelivery.com/accounts/WAECY/subscriber/new?topic_id=WAECY_102

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