January 14, 2022

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SUBJECT: **Technical Memo: Assessing Dioxins/Furans in Groundwater in the Lower Yakima Valley**

Background

The Washington State Department of Ecology (Ecology) conducted a study to assess the presence of dioxins/furans, nitrate, total lead, and total arsenic in groundwater by sampling 15 private domestic drinking water wells in the Lower Yakima Valley in November 2019 and April 2021. In addition, ancillary measurements for turbidity, alkalinity, dissolved organic carbon, total organic carbon, conductivity, temperature, and dissolved oxygen were conducted.

The wells in this study were chosen in areas where dioxins/furans were detected previously in a privately conducted study. The location of the 15 wells sampled in 2019 and 2021 are illustrated in Figure 1, along with the wells that had detectable levels of dioxins/furans in the private study.

Further details about the study design and methods are described in the Quality Assurance Project Plan (QAPP) (Redding et al., 2020). To ensure data collected for the study was deemed credible, all data collection methods followed water quality data requirements established in Washington State's Water Quality Data Act (RCW 90.48.585). Extensive quality assurance samples were collected and analyzed to help understand variability in the environment.

Dioxins/Furans

Dioxins/furans is a term used for a family of chlorinated chemicals called polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Dioxins/furans are byproducts of (1) combustion processes such as waste incineration, combustion of fossil fuels, and forest fires, and (2) chemical processes such as chlorine bleaching in paper production and manufacturing of some chlorinated pesticides. Dioxins/furans are highly persistent and widely

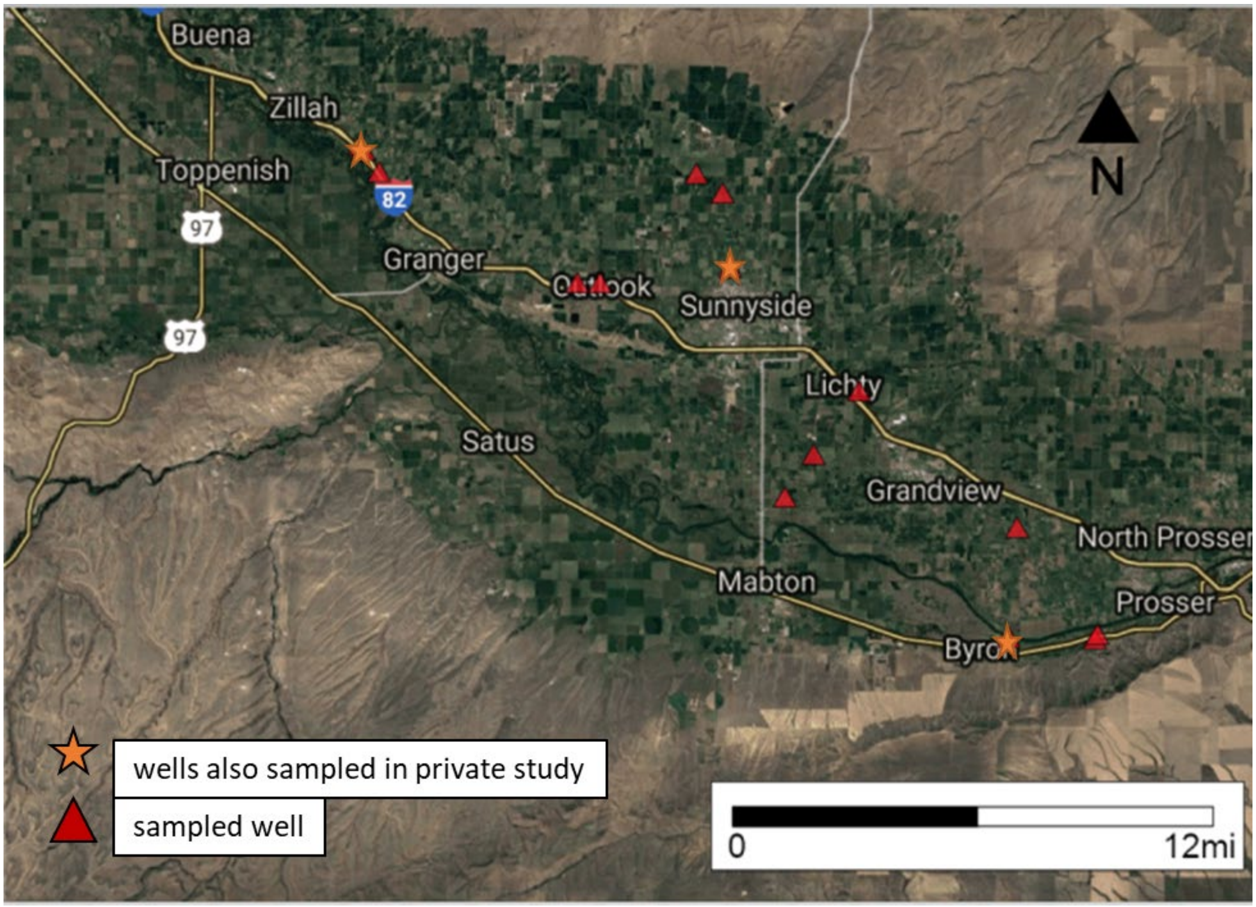

Figure 1. Study area for wells sampled in November 2019 and April 2021.

distributed in the environment. The USEPA determined that some dioxins/furans are probable human carcinogens. Exposure to dioxins/furans can also lead to adverse health effects not related to cancer. Human exposure to dioxins/furans is mostly through food such as meat, dairy products, and fish (ATSDR, 1998).

Seventeen of the 75 individual PCDD molecules (called congeners) and 130 PCDF congeners are considered toxic. These congeners have different levels of toxicity compared to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), which is the most toxic congener.

The 17 toxic congeners generally occur in mixtures so a method for identifying the toxicity of any mixture was developed using Toxic Equivalents (TEQ). To derive a TEQ for a mixture, Toxicity Equivalence Factors (TEFs) are used. A TEF has been developed for each congener and this factor expresses the degree of toxicity as a fraction of the toxicity of the most toxic congener, TCDD, which has the reference value of 1. By multiplying the concentration of each congener found in the mixture with its respective TEF and then adding the values together, a TEQ for that mixture is obtained. This TEQ is often expressed as "TCDD-TEQ". The 2005 World Health Organization mammalian TEFs, described by Van den Berg et al. (2006), are commonly used in summarizing PCDD and PCDF results and have broad international support.

Inorganic Compounds

The private study also analyzed and detected levels of nitrate, total lead, and total arsenic higher than drinking water standards. These chemicals were also monitored as part of this 2019 - 2021 Ecology study.

Ecology measured additional compounds to help characterize groundwater and to help interpret results for dioxins/furans and metals. These ancillary parameters were total organic carbon (TOC), dissolved organic carbon (DOC), alkalinity, and turbidity. Organic carbon may be a factor affecting the transport of PCDD/Fs and metals in water. Alkalinity, as one indicator of the amount of dissolved material in the water, may also be helpful when interpreting results. Turbidity was measured because high turbidity may affect the transport of PCDD/Fs and metals. Turbid groundwater may be present from poorly constructed wells.

Methods

Ecology sampled 15 private domestic wells in November 2019 and April 2021 following protocols described in the study QAPP (Redding et al., 2020). Because constituents in groundwater often vary seasonally, one of the objectives was to sample two different times of the year in an attempt to capture potential variances. The Covid-19 pandemic delayed the spring 2020 sampling until the spring of 2021. Samples were collected for analysis of dioxins/furans (collectively called 'dioxins' in the remainder of this memo), nitrate, total lead, total arsenic, and the ancillary compounds described above. Conductivity, temperature, pH, oxidation-reduction potential and dissolved oxygen were measured in-situ in order to determine adequate well purge time, which assures fresh groundwater is being sampled from the borehole.

Well Construction

Typically, proper well construction is the cornerstone to assuring that water sampled from the well is indicative of groundwater quality, rather than surface contamination, which may be entering the well through a poor surface seal. Ecology selected wells that met this criteria, however, this study also included three wells from the private study that detected dioxins. One of the wells from the private study (ZIL-04) does not have proper well contruction.

Quality Assurance

Quality assurance measures are important to assure credible data. For this study, Ecology used rigorous quality assurance and quality control practices for dioxins to characterize the levels of background contamination, limits of detection, and the variability of sample results. Such rigor is needed because the laboratory method to analyze dioxins is very sensitive, and cross-contamination can easily occur.

The analysis, review, validation, and reduction of results for dioxins, followed accepted procedures. Samples were sent to a laboratory accredited for analyzing dioxins in drinking water using EPA Method 1613B. Laboratory results then underwent EPA Level 4 Data Verification and Validation process (EPA, 2017) by an independent 3rd-party vendor specializing in such work. Ecology then reviewed the validated results and calculated the TCDD-TEQ values for each sample using TEFs as described above. The TCDD-TEQ values were calculated using the convention where results qualified by the laboratory as non-detect are assigned a value of one-half the laboratory detection limit.

While many approaches for addressing non-detect values in data sets have been used (Helsel, 2005; USEPA 2006; USEPA 2000), there are no general procedures that are appropriate in all cases. The selected approach depends on various factors such as the goals of the study, the size and characteristics of the data set, and the potential consequences of introducing bias. Ecology reviewed several common practices and decided to use a conservative approach by setting non-detections at a value of ½ the detection limit for calculating TCDD-TEQs.

Numerous blank samples were analyzed in order to determine the threshold at which dioxins in well samples could be distinguished from dioxins present in the analytical and sampling process. Blank samples consist of ultra-pure water that is free of dioxins and supplied by the laboratory. These blank samples help determine where contamination may be occurring during the sampling and analytical process. Target analytes present in the analytical and sampling system are often referred to as "noise" or "background" contamination.

The types of blanks analyzed for this study included laboratory and field blanks. Laboratory blanks are the analytical method blanks (required by the method) and extra laboratory method blanks. Three types of field blanks were used: travel blanks, transfer blanks, and an equipment blank. Replicates of some types of blanks were used during each 3-day sampling event (i.e., 3 travel blanks were analyzed during each sample event, one blank for each day of the 3 days of sampling).

Field blanks were used to characterize the threshold of background contamination, the level which effectively defines the lower limit of detection for results. Rather than "censor" the results from the drinking water wells, the reported values were retained to help understand the nature of the contamination. Censoring in this case would be the practice of changing the reported sample value to that of a revised detection limit value, this value being the threshold of background contamination.

Ecology considered various approaches to evaluating blanks for their use in delineating this threshold and chose to use the 90th percentile of the field blanks. This value is more conservative (with bias towards greater protection of human health) than the maximum value or the mean plus two standard deviations. Udesky et al. (2019) recommends using the 90th percentile of multiple blanks, and Mueller, et al. (2015) describe how the distribution-free 90th percentile Upper Confidence Limit approach can be appropriate in situations similar to this study. The techniques for evaluating background contamination are described further in Seiders, 2020.

Because the variability of dioxins in water from domestic wells was unknown, many field replicate samples were used to characterize the variability of dioxins and the associated uncertainty around the sampling results. In 2019, duplicate samples were collected at 3 wells. In 2021, triplicate samples were collected at 3 wells, with one well having 2 sets of triplicates collected on different days. Replicate samples were collected from one well (ZIL-04) in both years. This well had high concentrations of dioxins in 2019; as a result, more duplicates were included in the 2021 sampling. Quality assurance results are presented in Appendix A, Tables A1-A4.

The inorganic data, including field replicates, field blanks, and analytical protocols, were reviewed and determined to meet quality assurance standards. Quality assurance results for inorganic parameters are presented in Appendix B, Table B2. Reporting limits for nitrate, lead and arsenic varied between sampling events.

Applicable Water Quality Standards

Results from this study are compared to the drinking water quality standards listed in Table 1 (Chapter 246-290 WAC and 40 CFR Part 141).

Table 1. Drinking water quality standards

Contaminant	Concentration
2,3,7,8-TCDD-TEQ	30 pg/L
Nitrate	10 mg/L
Total Arsenic	10 ug/L
Total Lead	15 ug/L

Results

Results from 2019 and 2021 are in Appendices A and B. Tables A1-A2 contain results for TCDD-TEQ. Table B1 contains the results for all inorganic parameters. All results will be loaded into Ecology's Environmental Information Management (EIM) system.

Dioxins

Results for dioxins are summarized in Figures 2-4. Sample IDs are shown on the x-axis, and concentrations for dioxins, expressed as TCDD-TEQ are shown on the y-axis (which are log scales). The shaded area in each figure shows the extent of the noise in the sampling and analytical system, which was characterized by the detections in the laboratory and field blanks. Results within the shaded area are considered as not detectable according to the techniques described in the methods section.

Numerous blank samples were collected during this study to characterize sample contamination that could be present in the sampling and analytical processes:

- **Laboratory method blanks:** required as part of the analytical method.
- **Travel blanks**: ultra-pure water that is bottled and sealed by the laboratory and travels unopened with the samples in the field, and back to the laboratory.
- **Transfer blanks**: ultra-pure water that is bottled and sealed by the laboratory, and is transferred in the field to an empty bottle provided by the laboratory.
- **Equipment blanks**: ultra-pure water, which is run through sampling equipment.

Figure 2 illustrates detections of dioxins and furans in these blanks.

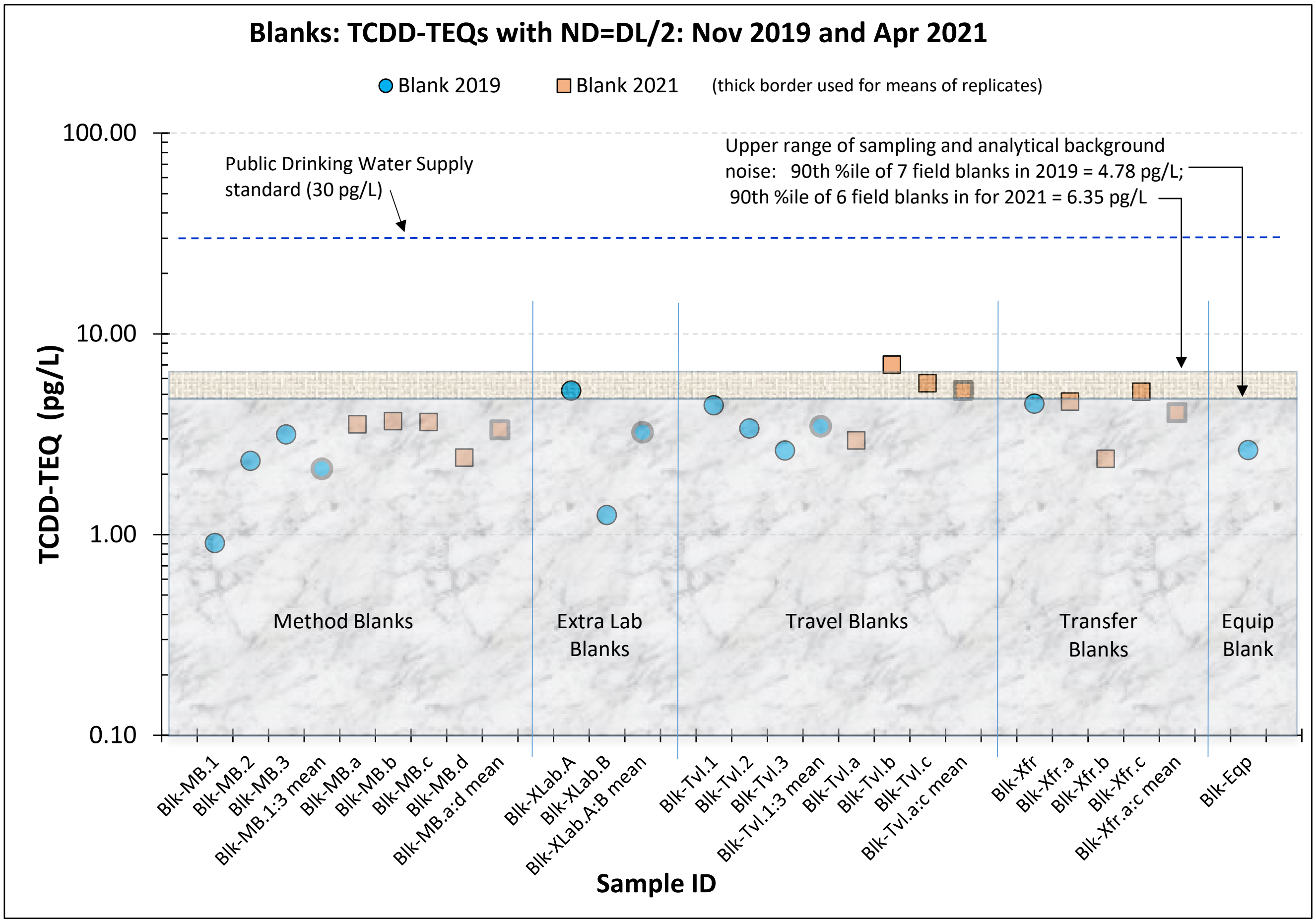

Figure 2 Sample results for quality assurance blanks analyzed in 2019 and 2021.

These detections in blank water illustrate the challenges in measuring contaminants at very low concentrations using sensitive analytical methods. Results from the field blanks were used to define the thresholds where actual concentrations in groundwater would most likely be differentiated from background "noise". The shaded zones in Figures 2-4 represent the upper range of sampling and analytical background noise by using the 90th percentile of all the blanks for each year. Note that these zones are slightly different for the 2019 sampling and the 2021 sampling, and are indicated by different colors. Sample results within these "zones of uncertainty" are considered to be background noise.

All results from all well samples and blank samples collected in November 2019 and April 2021 are shown in Appendix A, Figures A1 and A2. These figures offer another way to look at well results in the context of the various blank samples

Figure 3 illustrates concentrations for dioxins for both sampling events for the 5 wells where replicates were taken. The mean values for each set of field replicates are indicated by thick borders for each symbol. Typically, groundwater sampling projects require a minimum of 10% of the samples to be replicates. This study used 20% replicates in 2019, and 29% replicates in 2021. Also, in 2021, the number of replicates at three of the sites was increased from 2 to 3, and at well ZIL-04 three replicates were collected on separate days (two days apart, for a total of 6 replicates).

Significant variability in concentrations was found at well ZIL-04 during both sampling events, with results ranging from 6.7 pg/L to 93.2 pg/L (Figure 3).

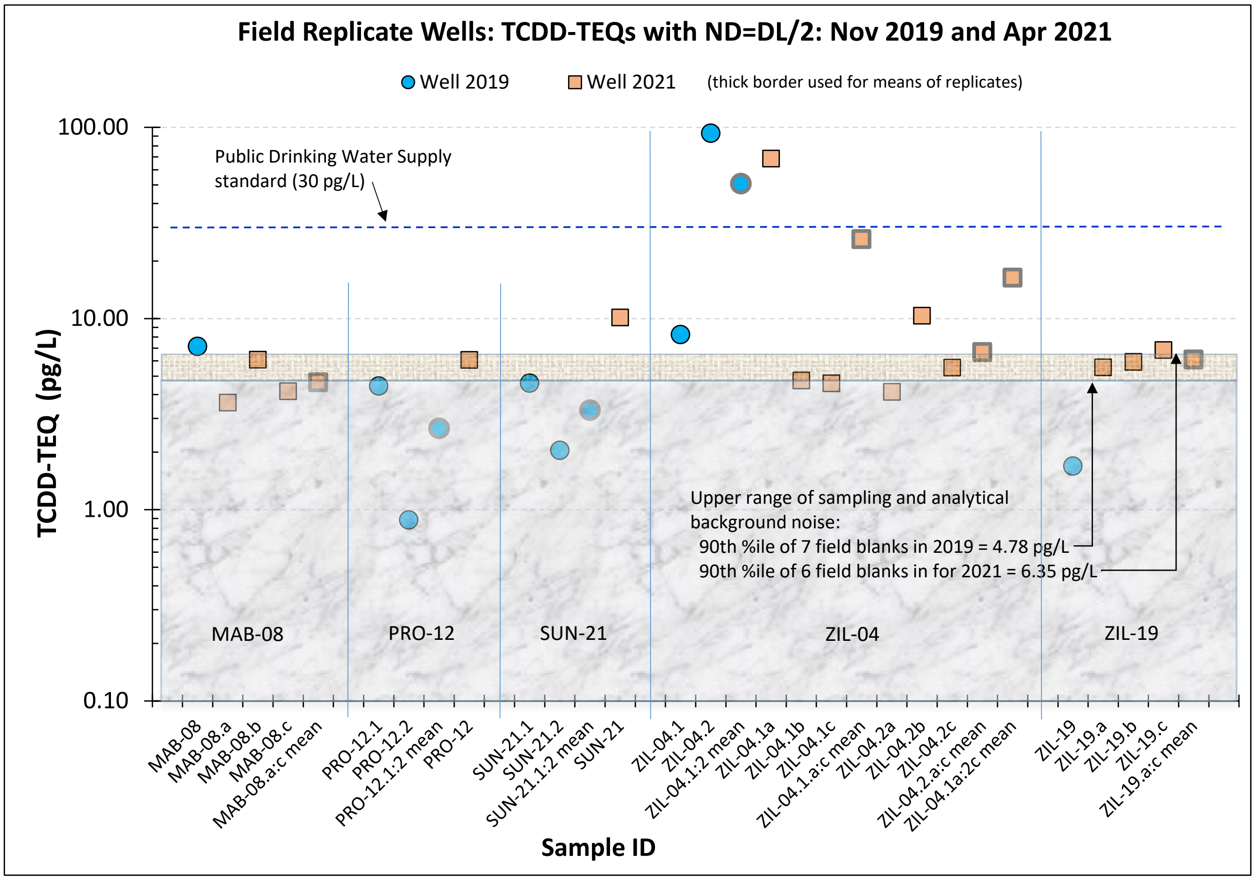

Figure 3. Sample results for field replicate samples taken in 2019 and 2021.

Figure 4 illustrates sample results for 2019 and 2021 for dioxins in relation to the zone of uncertainty from sampling and analytical noise. The means of the field replicates are plotted for wells that had replicate samples taken: ZIL-04, PRO-12, SUN-21, MAB-08, AND ZIL-19. The symbols for these means use a thick border around the symbol.

While dioxins were not detected in most wells, there were detections in some wells. Samples from well ZIL-04 had dioxins (TCDD-TEQ) positively detected each year. Dioxins were detected, but not reliably present, at low levels in two other wells (SUN-21 and MAB-08). However, results from blanks and replicates suggest that detections in these two wells are likely part of the “noise” of the sampling and analytical system.

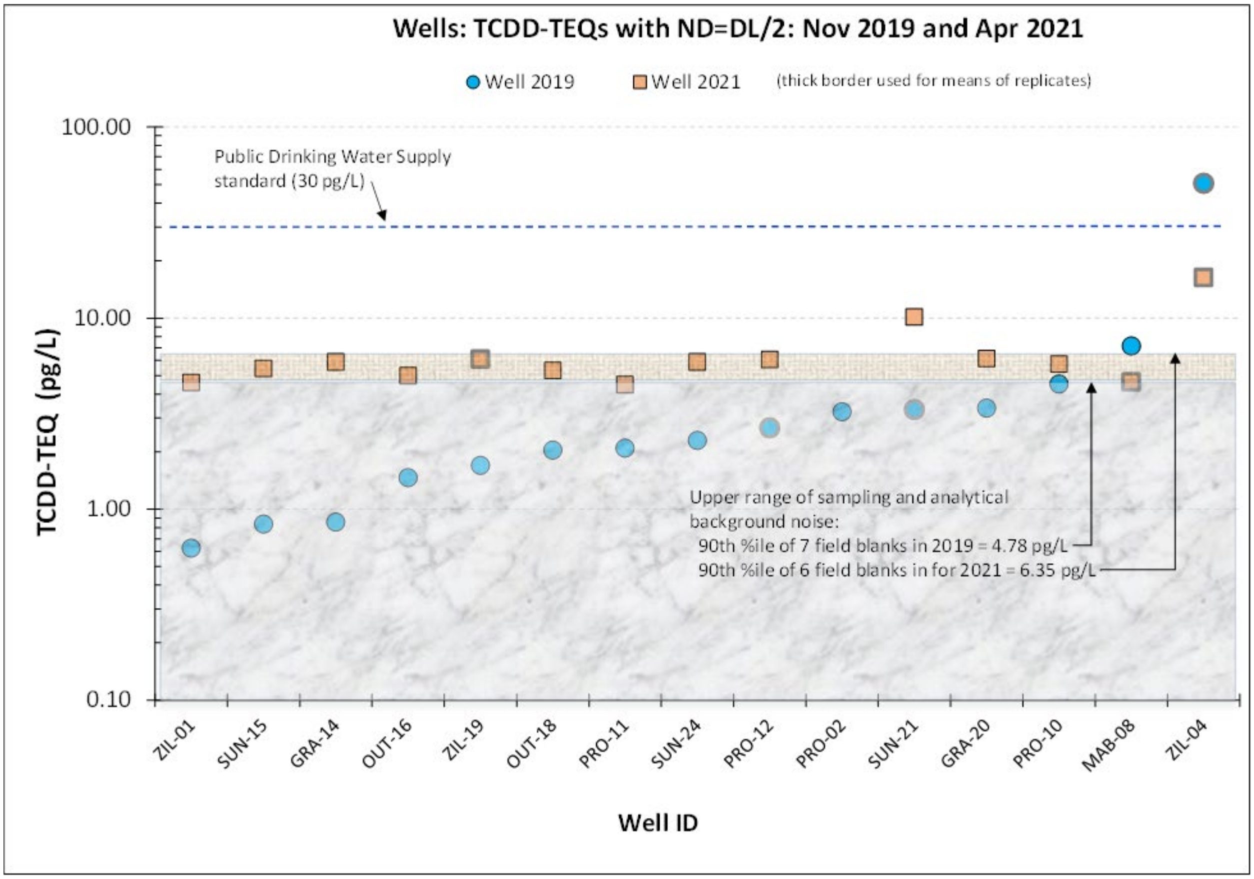

Figure 4. Sample results for wells in 2019 and 2021.
Mean values are used where field replicate samples were taken.

Inorganic Compounds

Inorganic parameters measured during this study were nitrate, total lead, and total arsenic. Ancillary parameters measured were total organic carbon (TOC), dissolved organic carbon (DOC), alkalinity, and turbidity. Inorganic results are presented in Table B1.

Lead

There were no detections of lead in groundwater above the drinking water standard of 15 ug/L. Concentrations ranged from less than detection to 0.54 ug/L. (Note that the detection limit was different in 2019 and 2021.) Lead concentrations are illustrated in Figure 5 for both sampling events.

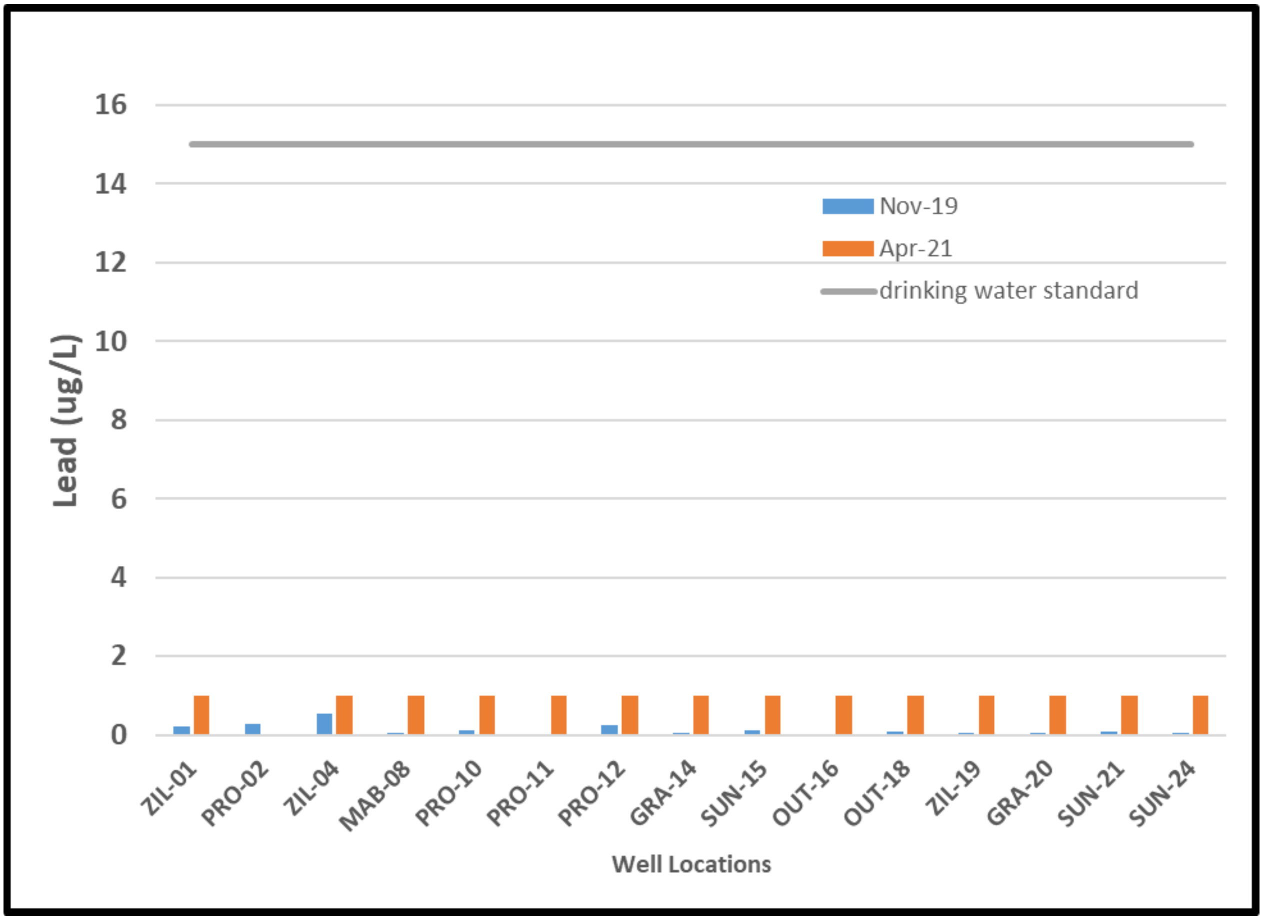

Figure 5. Lead concentrations.

Arsenic

There were no detections of arsenic in groundwater above the drinking water standard of 10 ug/L. Concentrations ranged from 1.2 to 9.18 ug/L. The laboratory reporting limit for arsenic is 1 ug/L. Arsenic concentrations are illustrated in Figure 6 for both sampling events.

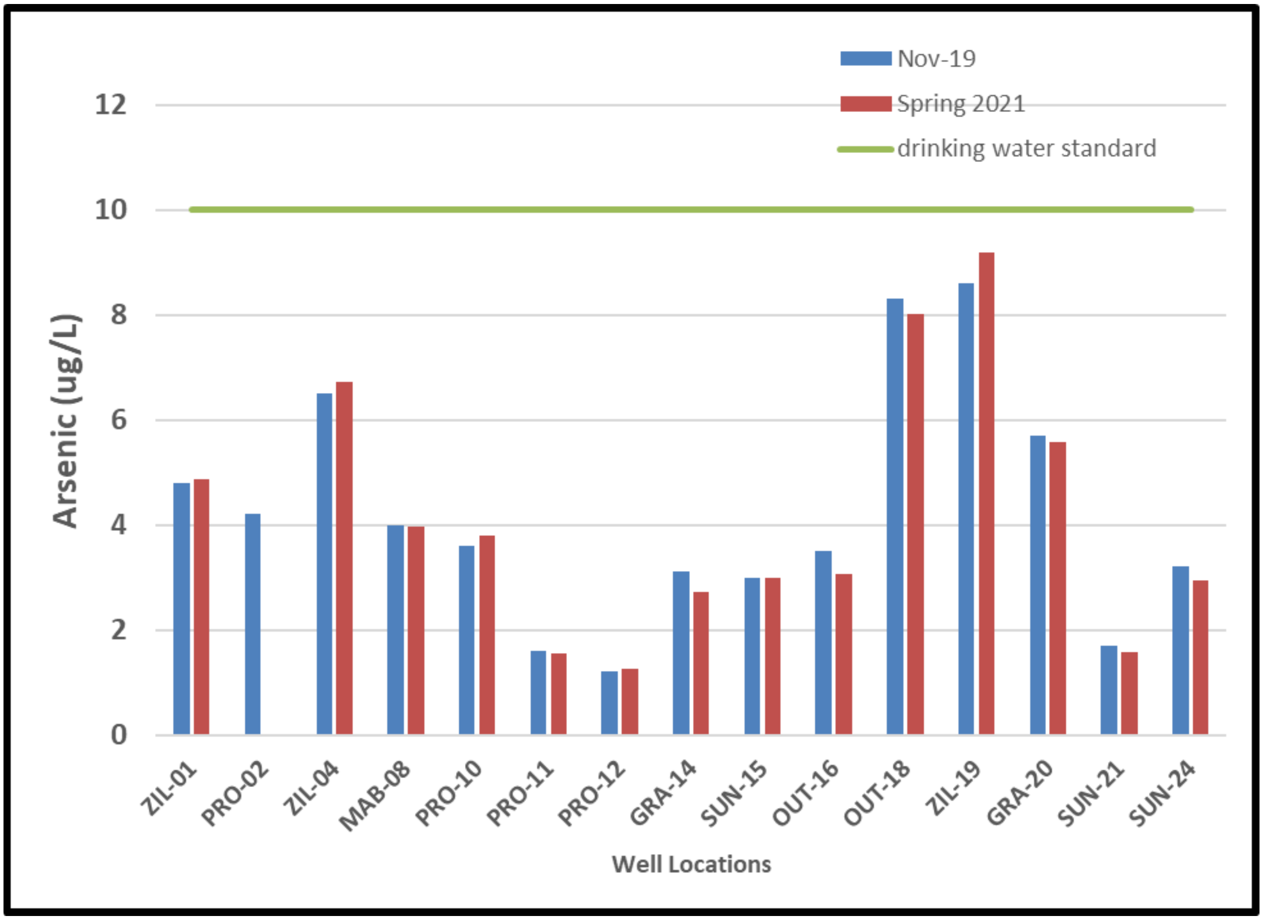

Figure 6. Arsenic concentrations.

Nitrate

In 2019, one well had a nitrate concentration higher than the drinking water standard of 10 mg/L. Concentrations ranged from non-detect at 0.01 to 25.9 mg/L. In 2021, three wells had nitrate concentrations higher than the drinking water standard of 10 mg/L. Concentrations ranged from non-detect at 0.01 to 22.4 mg/L. Nitrate concentrations are illustrated in Figure 7 for both sampling events.

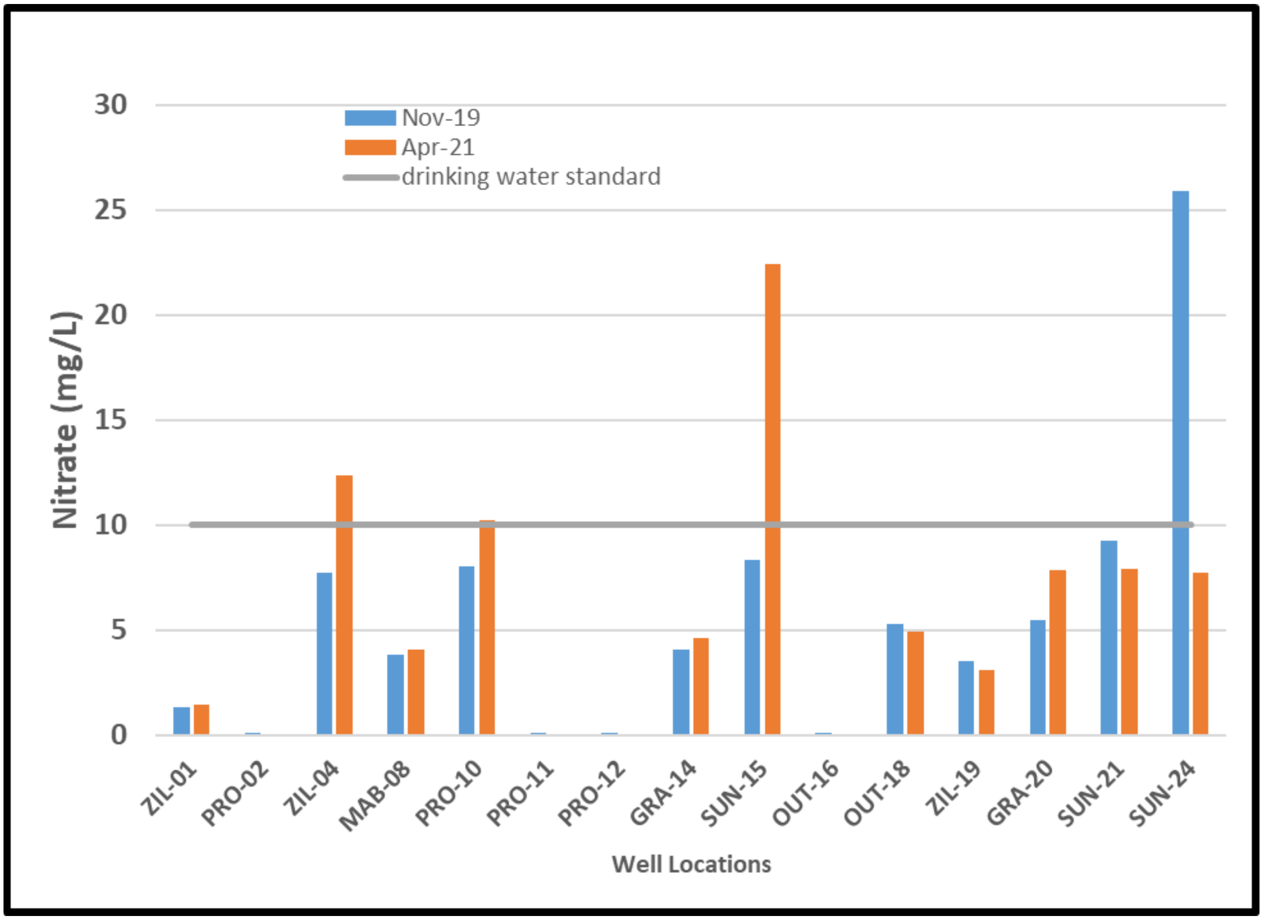

Figure 7. Nitrate concentrations.

Total Organic Carbon, Dissolved Organic Carbon, Alkalinity, and Turbidity

These ancillary parameters were measured to help assess possible conditions that might indicate (1) issues with well construction or (2) influences from sources that might be associated with the presence of dioxins/furans. No correlations were found with dioxins/furans, lead, arsenic, or nitrate.

Discussion

The goal of this study is to assess the presence of dioxins/furans, nitrate, total lead and total arsenic in private domestic drinking water wells in the Lower Yakima Valley. Analytical results from the November 2019 and April 2021 sampling show there is a localized issue with one of the wells for dioxins. The drinking water standard was exceeded for nitrate in four wells, and there were no exceedances for lead or arsenic.

Dioxins

Dioxins were reliably detected in well ZIL-04 which was the only well where dioxins exceeded (not meeting) the drinking water standard during sampling events. Well ZIL-04 had detections in 3 of 8 samples collected, with 2 results exceeding the drinking water standard for dioxins of 30 pg/L. Results from this well were highly variable (as illustrated in Figures 3, A1 and A2).

Potential issues with the construction of well ZIL-04 were noted during the first round of sampling. Avery Richardson, a hydrogeologist and well inspector with Ecology's Water Resources Program conducted an inspection of this well in February 2021. Appendix C contains a description and images related to the integrity of well ZIL-04. Avery found the integrity of this well to be very poor, and does not meet current well construction standards. This well is located in a below-ground vault without an adequate surface seal; and the homeowner reports that the vault occasionally floods. A long-term backyard burn pile is located upgradient and adjacent to the vault. The well inspector and field staff conclude that the backyard burn pile is the most likely source of dioxins detected in this well.

Dioxins were detected at low levels in two other wells. Well MAB-08 had detection in 1 of 4 samples, with no results exceeding the drinking water standard (30 pg/L). The low concentrations of dioxins found in samples from MAB-08 along with the high variability from multiple samples at this site, suggest that sampling and analytical noise is a likely reason for detecting dioxins in one of the samples. Well SUN-21: detection in 1 of 3 samples, with no results exceeding the drinking water standard (30 pg/L). The low concentrations of dioxins found in samples from SUN-21, along with the high variability from multiple samples at this site, suggest that sampling and analytical noise is a likely reason for detecting dioxins in one of the samples.

This study did not find evidence that groundwater in the Lower Yakima Valley is contaminated with dioxins. Dioxins in drinking water are an isolated to one well, which appears to be related to poor well construction and backyard burning issues.

Nitrate

Nitrate concentrations in the private domestic wells sampled exceeded the drinking water standard of 10 mg/L in one well (7%) in November 2019 and three wells (21%) in April 2021.

Elevated nitrate in groundwater above the drinking water standard, is an issue in the Lower Yakima Valley. A groundwater management area was established in 2012 to address this issue. These efforts are ongoing.

The nitrate results found in this study are consistent with other studies previously conducted to determine the extent of nitrate in groundwater in the Lower Yakima Valley (Ecology, 2010), (GWAC, 2019), (USGS, 2018), (PGG, 2019).

Lead and Arsenic

There were no exceedances of the drinking water standard for total lead or total arsenic at any of the wells.

The reported arsenic concentrations are consistent with the natural background groundwater concentrations of 6.0 ug/L defined by Ecology, 2021.

Conclusions

- Dioxins were positively detected in only one well (ZIL-04). This well has serious well construction issues, and transport of dioxin from a nearby burn pile is the likely source.
- Dioxins were detected, but not reliably present, at low levels in 2 other wells: MAB-08 and SUN-21. The low concentrations of dioxins found in samples from these wells, along with the high variability from multiple samples at this site, suggest that sampling and analytical noise is the likely reason for detecting dioxin in one of multiple samples from each well.
- The drinking water standard of 10 mg/L for nitrate was exceeded in one well during the November 2019 sampling, and in 3 wells during the April 2021 sampling.
- There were no exceedances of the drinking water standard for total lead or total arsenic at any of the wells.
- Based on the analysis of the two sampling events, Ecology determined that a third round of sampling is not necessary.

Recommendations

- Advise the owners and residents of well ZIL-04, of the water quality results of this study. Confirm that residents are not drinking the water. Refer residents to Yakima Health District to discuss options for safe drinking water.
- Discuss the issue of poor well construction, lack of an adequate surface seal, and compromised well integrity. Recommend (1) discontinuing backyard burning adjacent to the well, (2) installing a new well in an alternate location and that this new well be protected from practices, which might introduce contamination.
- Advise all homeowners of their individual results, explain the implications, and discuss further actions that could assist with assuring safe drinking water.
- Conduct community outreach and education about backyard burning and potential consequences from the practice (e.g. air pollution, production and release of dioxins to air/land/water).
- Conduct community outreach on the importance of proper well construction to protect personal drinking water sources.
- Communicate results of this study to participants in this study, the community, and other interested groups.
- Continue efforts of the Lower Yakima Valley Groundwater Management Area (GWMA) to focus on holistic approaches to reduce nitrate contamination of groundwater.

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Appendices

Appendix A: Dioxin/Furan data

Table A1. TCDD-TEQ values for all samples from November 2019 (pg/L).

Sample Type	Date	Time	Sample ID	TCDD-TEQ, ND=DL/2
Well	11/5/19	13:15	GRA-14	0.854
Well	11/6/19	12:00	GRA-20	3.38
Well	11/5/19	9:00	MAB-08	7.15
Well	11/5/19	18:00	OUT-16	1.46
Well	11/5/19	19:00	OUT-18	2.03
Well	11/4/19	11:45	PRO-02	3.23
Well	11/5/19	9:45	PRO-10	4.51
Well	11/5/19	10:45	PRO-11	2.09
Well	11/5/19	14:30	SUN-15	0.835
Well	11/6/19	14:15	SUN-24	2.29
Well	11/4/19	10:30	ZIL-01	0.626
Well	11/6/19	10:30	ZIL-19	1.69
Well-Field Rep 1	11/5/19	11:30	PRO-12.1 *	4.44
Well-Field Rep 2	11/5/19	12:00	PRO-12.2 *	0.885
Well: Mean of Field Reps 1-2	-	-	*PRO-12.1:2 mean*	*2.66*
Well-Field Rep 3	11/6/19	13:00	SUN-21.1 *	4.59
Well-Field Rep 4	11/6/19	13:30	SUN-21.2 *	2.04
Well: Mean of Field Reps 3-4	-	-	*SUN-21.1:2 mean*	*3.32*
Well-Field Rep 5	11/4/19	13:30	ZIL-04.1 *	8.23
Well-Field Rep 6	11/4/19	14:00	ZIL-04.2 *	**93.2**
Well: Mean of Field Reps 5-6	-	-	*ZIL-04.1:2 mean*	***50.7***
Blank-lab, method blank 1	11/7/19	-	Blk-MB.1	0.907
Blank-lab, method blank 2	11/13/21	-	Blk-MB.2	2.33
Blank-lab, method blank 3	11/27/21	-	Blk-MB.3	3.15
Blank-lab: Mean of method blanks	-	-	*Blk-MB.1:3 mean*	*2.13*
Blank-lab, extra method blank A	11/7/19	9:00	Blk-Xlab.A	5.21
Blank-lab, extra method blank B	11/7/19	-	Blk-Xlab.B	1.25
Blank-lab: Mean of extra method blanks	-	-	*Blk-Xlab.A:B mean*	*3.23*
Blank-travel 1	11/4/19	12:00	Blk-Tvl.1	4.40
Blank-travel 2	11/5/19	8:00	Blk-Tvl.2	3.38
Blank-travel 3	11/5/19	17:00	Blk-Tvl.3	2.62
Blank-travel: Mean of travel blanks	-	-	*Blk-Tvl.1:3 mean*	*3.47*
Blank-transfer	11/6/19	12:30	Blk-Xfr	4.49
Blank-equipment	11/4/19	13:00	Blk-Eqp	2.63

Bold font indicates values which do not meet the drinking water standard.
* Wells also sampled in the private study

Table A2. TCDD-TEQ values for all samples from April 2021 (pg/L).

Sample Type	Date	Time	Sample ID	TCDD-TEQ, ND=DL/2
Well	4/27/21	9:35	GRA-14	5.89
Well	4/28/21	9:45	GRA-20	6.13
Well	4/28/21	11:05	OUT-16	4.99
Well	4/28/21	13:20	OUT-18	5.31
Well	4/27/21	13:45	PRO-10	5.74
Well	4/27/21	12:40	PRO-11	4.49
Well	4/27/21	23:40	PRO-12 *	6.07
Well	4/26/21	15:30	SUN-15	5.45
Well	4/28/21	12:20	SUN-21 *	10.1
Well	4/26/21	14:30	SUN-24	5.90
Well	4/26/21	9:50	ZIL-01	4.60
Well-Field Rep 7	4/27/21	10:25	MAB-08.a	3.63
Well-Field Rep 8	4/27/21	10:35	MAB-08.b	6.08
Well-Field Rep 9	4/27/21	10:45	MAB-08.c	4.17
Well: Mean of Field Reps 7-9	-	-	*MAB-08.a:c mean*	*4.63*
Well-Field Rep 1	4/26/21	10:45	ZIL-04.1a *	**68.6**
Well-Field Rep 2	4/26/21	10:55	ZIL-04.1b *	4.74
Well-Field Rep 3	4/26/21	11:05	ZIL-04.1c *	4.57
Well: Mean of Field Reps 1-3	-	-	*ZIL-04.1.a:c mean*	*26.0*
Well-Field Rep 4	4/28/21	8:30	ZIL-04.2a *	4.13
Well-Field Rep 5	4/28/21	8:40	ZIL-04.2b *	10.3
Well-Field Rep 6	4/28/21	8:50	ZIL-04.2c *	5.54
Well: Mean of Field Reps 4-6	-	-	*ZIL-04.2.a:c mean*	*6.66*
Well: Mean of Field Reps 1-6	-	-	*ZIL-04.1a:2c mean*	*16.3*
Well-Field Rep 10	4/26/21	12:10	ZIL-19.a *	5.54
Well-Field Rep 11	4/26/21	12:20	ZIL-19.b *	5.92
Well-Field Rep 12	4/26/21	12:30	ZIL-19.c *	6.83
Well: Mean of Field Reps 10-12	-	-	*ZIL-19.a:c mean*	*6.10*
Blank-lab, method blank a	5/3/21	-	Blk-MB.a	3.54
Blank-lab, method blank b	5/3/21	-	Blk-MB.b	3.68
Blank-lab, method blank c	5/20/21	-	Blk-MB.c	3.63
Blank-lab, method blank d	5/20/21	-	Blk-MB.d	2.42
Blank-lab: Mean of method blanks	-	-	*Blk-MB.a:d mean*	*3.32*
Blank-travel a	4/26/21	9:00	Blk-Tvl.a	2.95
Blank-travel b	4/27/21	9:00	Blk-Tvl.b	7.02
Blank-travel c	4/28/21	8:00	Blk-Tvl.c	5.67
Blank-lab: Mean of travel blanks	-	-	*Blk-Tvl.a:c mean*	*5.21*
Blank-transfer a	4/26/21	11:15	Blk-Xfr.a	4.59
Blank-transfer b	4/27/21	10:55	Blk-Xfr.b	2.38
Blank-transfer c	4/28/21	9:00	Blk-Xfr.c	5.14
Blank-lab: Mean of transfer blanks	-	-	*Blk-Xfr.a:c mean*	*4.04*

Bold font indicates values which do not meet the drinking water standard. * Wells also sampled in the private study

Figures A1 and A2 show results from well samples and quality assurance samples collected in November 2019, and April 2021, respectively. Results for most well samples were in the same range as the laboratory and field blanks, illustrating how dioxins in well samples cannot be distinguished from dioxins in blank water.

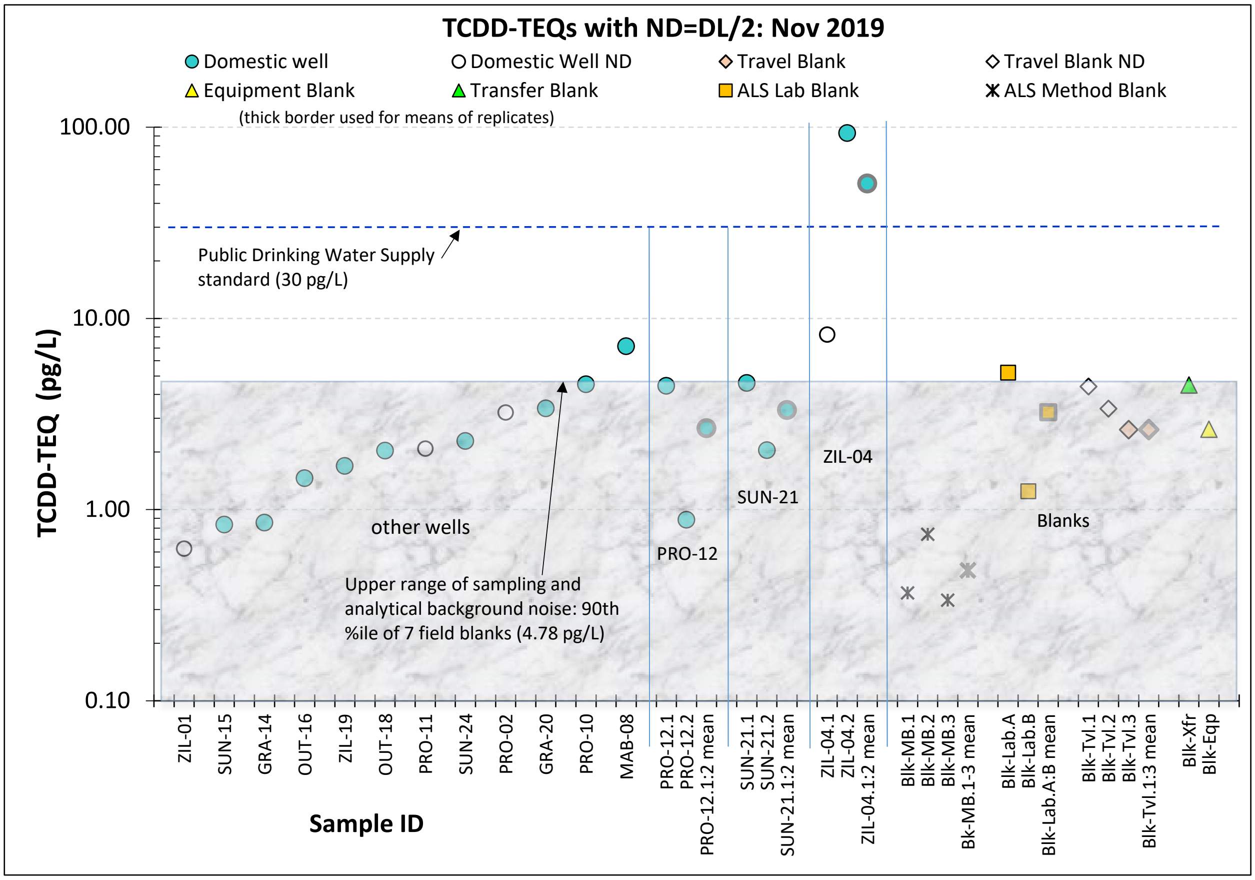

Figure A1. Sample results for wells, field replicates, and quality assurance blanks in 2019.

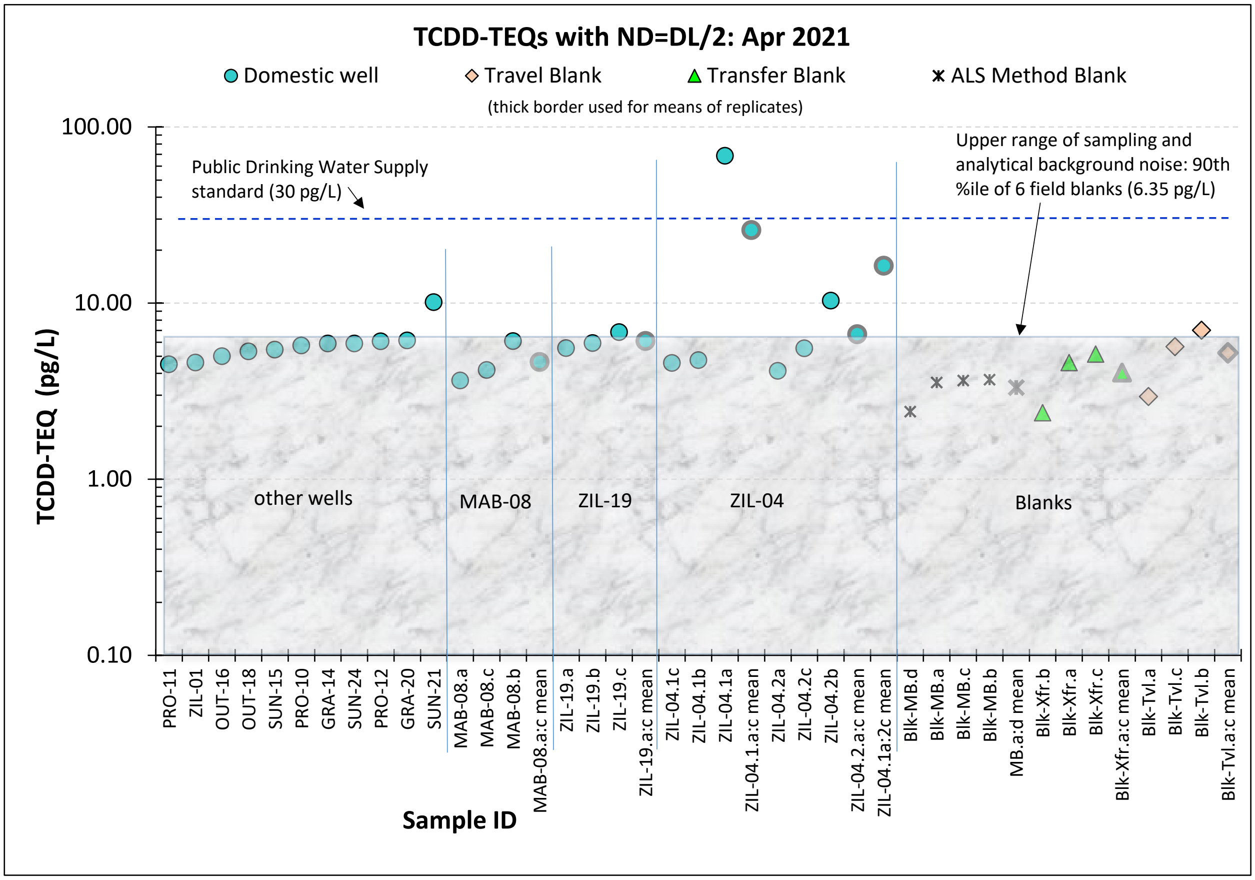

Figure A2. Sample results for wells, field replicates, and quality assurance blanks in 2021.

Appendix B: Inorganic data

Table B1. Inorganic data from Fall 2019 and Spring 2021 sampling.

	Drinking Water Standard													
	10 mg/L		15 ug/L		10 ug/L									
Sample ID	Nitrate (mg/L)	q	Lead (ug/L)	q	Arsenic (ug/L)	q	Turbidity (NTU)	q	Alkalinity (mg/L)	q	TOC (mg/L)	q	DOC (mg/L)	q
Fall 2019														
ZIL-01 *	1.3		0.22		4.8		0.5	U	148		0.5	U	0.5	U
PRO-02	0.1	U	0.28		4.2		10		225		0.5	U	0.5	U
ZIL-04	7.7		0.54		6.5		0.95		319		0.89		0.89	
MAB-08	3.79	J	0.04	J	4		0.5	U	225		0.5	U	0.5	U
PRO-10	8.03	J	0.13		3.6		0.5	U	248		2.01		1.96	
PRO-11	0.1	U	ND		1.6		14		219		0.5	U	0.5	U
PRO-12 *	0.1	U	0.255		1.2		0.5	U	206		2.08	U	0.5	U
GRA-14	4.07		0.05	J	3.1		0.5	U	165		0.5	U	0.5	U
SUN-15	8.33		0.12		3		3.1		110		0.619		0.61	
OUT-16	0.1	U	ND		3.5		13		156		0.5	U	0.5	U
OUT-18	5.29	J	0.09	J	8.3		0.8		239		0.784		0.79	
ZIL-19	3.49	J	0.05	J	8.6		0.5	U	205		0.5	U	0.5	U
GRA-20	5.48	J	0.04	J	5.7		0.5	U	250		0.735		0.73	
SUN-21 *	9.23	J	0.08	J	1.7		0.9		226		1.23		1.27	
SUN-24	25.9	J	0.04	J	3.2		0.5	U	334		1.89		1.83	
Spring 2021														
ZIL-01 *	1.43		1	U	4.88		0.5	U	145		0.5	U	0.5	U
PRO-02	not sampled													
ZIL-04	12.35		1		6.73		0.5		293		0.97		0.93	
MAB-08	4.07		1	U	3.97		0.5	U	230		0.5	U	0.5	U
PRO-10	10.2		1	U	3.79		0.5	U	243		1.78		1.75	
PRO-11	0.01	U	1	U	1.55		17		228		0.5	U	0.5	U
PRO-12 *	0.01	U	1	U	1.25		0.5	U	206		0.5	U	0.5	U
GRA-14	4.61		1	U	2.72		0.5	U	173		0.5	U	0.5	U
SUN-15	22.4		1	U	2.99		0.5	U	322		1.3		1.28	
OUT-16	0.01	U	1	U	3.06		6.3		148		0.5	U	0.5	U
OUT-18	4.93		1	U	8.03		0.5	U	243		0.821		0.84	
ZIL-19	3.11		1	U	9.18		0.5	U	210		0.5	U	0.5	U
GRA-20	7.86		1	U	5.57		0.5	U	233		0.776		0.75	
SUN-21 *	7.91		1	U	1.57		0.5	U	225		1.2		1.22	
SUN-24	7.69		1	U	2.95		6.9		113		0.576		0.59	

Bold indicates exceedance of a drinking water standard.
q = qualified
* Wells also sampled in the private study
Note that reporting limits varied for nitrate, lead, and arsenic.

Inorganic Quality Assurance Data

In 2019, several nitrate samples were analyzed past the hold time. The data was validated and reviewed. The nitrate results were determined by MEL to be acceptable as qualified (noted in Table B1). For all other samples in both 2019 and 2021, the laboratory performed the analysis within the specified hold times.

All samples for both 2019 and 2021 were received at the proper temperature, and were properly preserved. Laboratory calibration verification checks, control samples, r-values and standard residuals were within the acceptance limits. No analytically significant levels of analytes were detected in the method blanks. Laboratory replicates and matrix spikes were within the acceptance limits.

Field replicates for all inorganic parameters are compared in Table B2 using relative percent difference (RPD) to measure the precision of the data.

Method detection limits for lead, arsenic and nitrate varied from 2019 to 2021.

Table B2. Field replicate data for inorganic parameters

2019																
Field Station ID	**Nitrate (mg/L)**		**Nitrate RPD**	**Nitrate mean (mg/L)**	**Lead (ug/L)**		**Lead RPD**	**Lead mean (ug/L)**	**Arsenic (ug/L)**		**Arsenic RPD**	**Arsenic mean (ug/L)**				
ZIL-04	7.67		0.91	7.705	0.52		1.85	0.54	6.4		0.77	6.5				
ZIL-04	7.74				0.56				6.6							
PRO-12	0.1	U	0.00	0.1	0.24		2.94	0.255	1.2		0.00	1.2				
PRO-12	0.1	U			0.27				1.2							
SUN-21	9.02	J	4.44	9.225	0.08	J	0.00	0.08	1.7		0.00	1.7				
SUN-21	9.43	J			0.08	J			1.7							
Field Station ID	**Turbidity (NTU)**		**Turb RPD**	**Turb mean (NTU)**	**Alkalinity (mg/L)**		**Alk RPD**	**Alk mean (mg/L)**	**TOC (mg/L)**		**TOC RPD**	**TOC mean (mg/L)**	**DOC (mg/L)**		**DOC RPD**	**DOC mean (mg/L)**
ZIL-04	0.9		2.63	0.95	317		0.24	318.5	0.896		-0.37	0.8895	0.91		-1.12	0.89
ZIL-04	1				320				0.883				0.87			
PRO-12	0.5	U	0.00	0.5	207		-0.24	206	0.5	U	37.98	2.08	0.5	U	0.00	0.5
PRO-12	0.5	U			205				3.66				0.5	U		
SUN-21	0.9			N/A	226			N/A	1.23			N/A	1.27			N/A
SUN-21																
2021																
Field Station ID	**Nitrate (mg/L)**			**Nitrate mean (mg/L)**	**Lead (ug/L)**		**Lead RPD**	**Lead mean (ug/L)**	**Arsenic (ug/L)**		**Arsenic RPD**	**Arsenic mean (ug/L)**				
ZIL-04	**12.5**		0.00	12.5	1	U	0.00	1	6.74		1.05	6.885				
ZIL-04	**12.5**				1	U			7.03							
ZIL-04	**12.2**		0.82	12.25	1	U	0.00	1	6.72		0.04	6.725				
ZIL-04	**12.3**				1	U			6.73							
all ZIL-04				12.375				1				6.805				
MAB-08	4.07		0.00	4.07	1	U	0.00	1	3.97		0.25	3.99				
MAB-08	4.07				1	U			4.01							
ZIL-19	3.11		0.32	3.115	1	U	0.00	1	9.18		-0.16	9.15				
ZIL-19	3.12				1	U			9.12							
Field Station ID	**Turbidity (NTU)**		**Turb RPD**	**Turb mean (NTU)**	**Alkalinity (mg/L)**		**Alk RPD**	**Alk mean (mg/L)**	**TOC (mg/L)**		**TOC RPD**	**TOC mean (mg/L)**	**DOC (mg/L)**		**DOC RPD**	**DOC mean (mg/L)**
ZIL-04	0.5	U	0.00	0.5	289		0.09	289.5	0.963		-0.68	0.95	0.91		1.08	0.93
ZIL-04	0.5	U			290				0.937				0.95			
ZIL-04	0.5	U	0.00	0.5	297		-0.08	296.5	0.972		-1.21	0.949	0.94		0.00	0.94
ZIL-04	0.5	U			296				0.926				0.94			
all ZIL-04				0.5				293				0.9495				0.935
MAB-08	0.5	U	0.00	0.5	230		-0.22	229	0.5	U	0.00	0.5	0.5	U	0.00	0.5
MAB-08	0.5	U			228				0.5	U			0.5	U		
ZIL-19	0.5	U	0.00	0.5	210		-0.12	209.5	0.5	U	0.00	0.5	0.5	U	0.00	0.5
ZIL-19	0.5	U			209				0.5	U			0.5	U		

Appendix C: Evaluation of Domestic Water Well at Site ZIL-04.

ZIL-04 is the only well where dioxins were detected higher than (not meeting) the drinking water standard during both the 2019 and 2021 sampling events.

During the first round of sampling, Ecology staff noticed that there were potential issues with the well construction. Avery Richardson, Ecology's Water Resources Program, conducted an inspection of this well, and his assessment of this well dated 2/25/2021 are presented below.

> I was able to visit with the homeowner today and take a look at their well. After speaking with them and looking the site over I have a pretty good idea of the potential source of the dioxin.
> Their well is at least as old as 1968 and is in a underground vault structure. Wells in vaults are very prone to contamination. When the well construction act was passed in 1973, putting wells in vaults was outlawed because of this. I asked the homeowner if they had ever used a burn barrel to dispose of trash and they said they had for many years. They showed me where it had been and I was able to dig around the area and find many remnants of burnt garbage. The location was about 15 feet from where the well is. This is a very likely source of the dioxin. The soil had a high proportion of ash, charcoal like material, and garbage. I asked them if the vault where the well is had ever flooded. They said it had about three years ago when an underground pipe had been chewed through by a gopher. The damaged pipe was right next to the burn barrel location. The cap on the well was very old and likely not waterproof. The flood water overtopped the well and almost certainly leaked into the well bore. I asked them if they had problems with the pump running even when no water was being used, and they said they had. This can be the result of two things- a failed pressure tank or a hole rotted in the drop pipe. It turns out that was happening when Ecology took the water sample. The homeowner said that they had to replace the pressure tank shortly after the sample was taken and also said the drop pipe looked like it had blisters all over it the last time they pulled the pump (high degree of corrosion). It too is likely leaking (spraying) inside the well casing. When this happens it rapidly circulates the water in the well bore and can keep a high volume of materials in suspension. Basically this was a 'perfect storm' of things going wrong. They also said the well had failed a coliform bacteria, nitrate and arsenic test. Further evidence of materials leaking past the well cap and getting into the well bore when the vault flooded.
>
> The good news is that they only use the water for washing clothes, watering plants, and showering. They have bottled water for their source of drinking water.
>
> I told the homeowner that there really isn't a way to repair their well and bring it up to current construction and hygiene standards. The only option would be to construct a new well and decommission the existing one. That would likely cost >$25,000. This is a difficult situation, with no simple fix.

Figures 8 -14 are photos showing the condition of well ZIL-04.

Figure 8. Tarp covering the pit where well ZIL-04 is located.

Figure 9. Opening to pit for well ZIL-04.

Figure 10. View of pit, pressure tank, and wellhead for ZIL-04.

Figure 11. Wellhead for ZIL-04.

Figure 12. Site of backyard burn pile. Note soil darkened by ash.

Figure 13. View of ZIL-04 covering. Note site of burn pile in foreground.

Figure 14. Arial view of well ZIL-04 location.