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Memorandum

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Subject	**Determination of Thallium Ambient/Background Concentration at the Pacific Gas and Electric Company Topock Compressor Station, Needles, California**
Attention	Pacific Gas and Electric Company (PG&E)
From	Jacobs Engineering Group Inc. (Jacobs)
Date	August 13, 2019
Copies to	Curt Russell/PG&E Pam Innis/U.S. Department of the Interior (DOI) Aaron Yue/California Department of Toxic Substance Control (DTSC)

1. Introduction

This technical memorandum presents the approach and methodology Jacobs used to develop a soil ambient concentration for thallium at the PG&E Topock Compressor Station (TCS). PG&E is implementing the Remedy Soil Management Plan (Remedy SMP), Appendix L of the Construction/Remedial Action Work Plan (C/RAWP) (CH2M, 2015), as part of groundwater remedy construction. Table 2.4-1 of the Remedy SMP contains an interim screening level (ISL) for thallium of 0.78 milligram per kilogram (mg/kg) based on the U.S. Environmental Protection Agency (EPA) Residential Regional Screening Level (RSL), (EPA 2017). The ISL is significantly less than the concentrations of thallium found in certain soil samples collected to document baseline conditions prior to installation of remedy infrastructure in areas unimpacted by past PG&E TCS operations. Additionally, the RSL of 0.78 mg/kg is below the normal detection limit of most analytical techniques and therefore poses practicability issues. The Draft Soil Human Health and Ecological Risk Assessment Report specifies risk-based criteria used to determine the acceptability of soils for reuse at the site. Until that document is approved, compliance with the Remedy SMP would necessitate offsite disposal of soils with thallium concentrations exceeding the ISL. Therefore, PG&E calculated an ambient/background threshold value (BTV) of thallium to assist the agencies in making practical ambient/background soil management decisions.

As of June 2019, a total of 38 baseline soil samples have been collected a) outside of areas of concern (AOCs) and solid waste management units (SWMUs) associated with TCS operations and b) not in close proximity to the BNSF railroad track along National Trails Highway (Figure 1). Of these 38 samples, 4 were collected approximately 1 foot below the bottom of the pipeline and conduit trenches. The remaining samples were collected approximately 1 foot below ground surface (bgs). The samples were analyzed in accordance with the Remedy SMP.

2. Ambient/Background Threshold Value Determination

When conducting a compliance test using a BTV, two types of errors occur, namely a type-I error (a false positive) and a type-II error (a false negative). A false positive error occurs where one receives a positive result for a compliance test by incorrectly rejecting a true null hypothesis. This creates a false positive error for the compliance test, leading to an erroneous conclusion that a non-compliance has occurred. This is sometimes also called a false alarm. Similarly, a false negative error occurs when one erroneously receives a negative result for a compliance test by not rejecting a false null hypothesis, i.e. the obtained false negative result is wrong. While elimination of these errors is not possible, one seeks to minimize one or both errors. In most practical applications, a confidence coefficient (CC) of 0.95 is commonly used to provide a proper balance between false positives and false negatives. The upper limits are determined for a CC of 0.95 and a coverage probability of 0.95. Such upper limits (for example, 95 percent upper confidence limits [UCLs] of the 95th percentiles are also known as ambient/background threshold values (BTVs). It is expected that 95 percent of the observations (current and future) coming from the target ambient/background population will be less than that BTV estimate, with a specified CC of 0.95.

The BTVs are estimated using established data sets collected from ambient/background reference areas and unimpacted site-specific ambient/background areas representing the ambient/background population under consideration. The established ambient/background data set should be free from outliers and represent a single environmental ambient/background population. Based on the environmental literature review, one or more of the following statistical upper limits are used to estimate BTVs (EPA, 2015a):

- Upper percentiles (x0.95)
- Upper prediction limits (UPLs)
- Upper tolerance limits (UTLs)
- Upper simultaneous limits (USLs)

From these candidate upper limits, either the UTLs or the USLs are used to estimate BTVs. To provide a proper balance between false positives and false negatives, the ProUCL Technical Guide (EPA, 2015a) suggests using the 95th percentile upper simultaneous limits (USL95) to estimate BTVs. However, USL95 should be used only when the raw ambient/background data set represents a single environmental population without outliers, as inclusion of multiple populations and outliers tends to yield elevated values of USLs, which can result in undesirable false negatives. Therefore, the following stepwise procedure is used to estimate BTV values for a given ambient/background data set:

1) If the raw ambient/background data set is free from outliers, USL95 is used to determine BTV values. Otherwise, UTL95-95 representing a 95th percentile UCL of the 95th percentile of the ambient/background population data is used to estimate BTV values.
2) Further, based upon the distributional characteristics of the given ambient/background data set, two approaches, namely parametric and nonparametric procedures, are used to determine BTV values. If the ambient/background data can be characterized by a well-known distribution (for example, a normal, a lognormal, or a gamma), the parametric method is used to estimate BTVs; otherwise, a nonparametric method is used.

2.1 Parametric Upper Tolerance Limit

Parametric tolerance limits assume normality of the sample ambient/background data used to construct the limit. Validity of this assumption is essential to the applicability of the method, since a tolerance limit with high coverage can be viewed as an estimate of a quantile or percentile associated with the tail probability of the underlying distribution. If the ambient/background sample data do not fit a normal distribution, data are transformed using an appropriate transformation so that the transformed data fit a normal distribution. If a suitable transformation is found, the UTL is calculated using the transformed measurements and then back-transformed to the raw concentration scale.

2.1.1 Normal Upper Tolerance Limit

If sample ambient/background data are normally distributed or can be transformed to fit a normal distribution, then the normal UTL is calculated using the following equation (EPA, 2009, 2015a):

$$UTL = \overline{x} + K(n, \gamma, 1 - \alpha)s \quad \textbf{(1)}$$

Where:

$\bar{x}$ = The sample mean

K(n, γ, 1−α) = The one-sided normal tolerance factor associated with a sample size of n, coverage coefficient of γ, and confidence level of (1−α)

s = The sample standard deviation (SD)

2.1.2 Lognormal Upper Tolerance Limit

The procedure to compute UTLs for lognormally distributed data sets is similar to that for normally distributed data sets. In this case, the sample mean, $\bar{y}$, and SD, s_y, of the log-transformed data are computed, then the lognormal UTL is calculated using the following equation EPA (2009, 2015a):

$$UTL = \exp[\bar{y} + K(n, \gamma, 1-\alpha)s] \quad \textbf{(2)}$$

The K factor in Equation (2) is the same as the one used to compute the normal UTL.

2.1.3 Gamma Distribution Upper Tolerance Limit

The gamma distribution UTLs are estimated using the normal approximation to the gamma distributed data. There are two approximations that are used to transform gamma distributed data into approximate normally distributed data (EPA, 2009, 2015a):

- Wilson-Hilferty (WH) transformation: Wilson-Hilferty (EPA, 2015a) suggested that if a ambient/background data set fits the gamma distribution, then the transformation, $Y = X^{1/3}$ follows an approximate normal distribution. Using the WH approximation, the gamma UTL (in original scale, X), is given by:

$$UTL = max\left[0, \left(\bar{y} + K(n, \gamma, 1-\alpha)s_y\right)^3\right] \quad \textbf{(3)}$$

- Hawkins-Wixley (H-W) transformation: Hawkins-Wixley (EPA, 2015a) suggested that if a ambient/background data set fits the gamma distribution, then the transformation, $Y = X^{1/4}$ follows an approximate normal distribution.

$$UTL = \left(\bar{y} + K(n, \gamma, 1-\alpha)s_y\right)^4 \quad \textbf{(4)}$$

The K factor in Equations (3) and (4) is the same as the one used to compute the normal UTL.

2.2 Nonparametric Upper Tolerance Limit

If a suitable transformation is not found, then a nonparametric tolerance limit is considered. Unfortunately, nonparametric tolerance limits generally require a much larger number of observations to provide the same levels of coverage and confidence as a parametric limit. EPA guidance (2009) recommends that a parametric model be fit to the data if possible.

Unlike parametric tolerance intervals, the desired coverage (γ) or confidence level (1–α) cannot be pre-specified using a nonparametric limit. Instead, the achieved coverage and confidence level depends entirely on the ambient/background sample size (n) and the order statistic chosen as the UTL. For a nonparametric procedure, no distribution needs to be fitted to the ambient/background measurements. According to Guttman (EPA, 2009), the number of ambient/background samples should be chosen such that:

$$\sum_{i=m}^{n} \binom{n}{i} (1-\gamma)^i \gamma^{n-i} \geq 1-\propto \quad \textbf{(5)}$$

If the ambient/background maximum is selected as the UTL, the nonparametric UTL is defined in terms of the number of measurements, n as:

$$\gamma^n \leq \propto \quad \textbf{(6)}$$

Equation (6) can be written as:

$$n = \frac{\ln(\propto)}{\ln(\gamma)} \quad \textbf{(7)}$$

For a 95 percent confidence level and 95 percent coverage, n = 59 ambient/background measurements are required according to Equation (7). A nonparametric UTL is computed by first ranking the ambient/background data in ascending order and then choosing the lowest-ranked detected concentration that defines the 95th percentile with 95 percent confidence, such as the largest, the second largest, the third largest, and so on. The order, r of the statistic, x(r), used to compute a nonparametric UTL depends upon the sample size, n, coverage probability, γ, and the desired CC, (1 - α). Data sets with less than 59 observations, the definition of the 95 percentile, is not statistically possible with 95 percent confidence, even when the maximum concentration is assigned as the UTL. In this situation, the value of the lowest achievable coverage is reported.

For a given data set of size n, coverage probability γ, and CC $(1 - \alpha)$, the r^{th} order statistic can be determined using the normal approximation of the binomial distribution as (EPA, 2015a):

$$r = n\gamma + z_{(1-\propto)}\sqrt{n\gamma(1-\gamma)} + 0.5 \quad \textbf{(8)}$$

After determining the r^{th} order, the corresponding value of r^{th} order statistic x(r) is determined from the ranked data. As mentioned previously, for a given data set of size n, the r^{th} order statistic may or may not achieve the specified CC, (1 - α). ProUCL Guide (EPA, 2015a) suggests using the F-distribution $(F_{df1,df2})$ to compute the CC achieved by the UTL determined by the r^{th} order statistic as (EPA, 2015a):

$$CC_{Achieved} = Probability\left\{F_{[2(n-r+1),2r]} \leq \frac{r(1-\gamma)}{(n-r+1)\gamma}\right\} \quad \textbf{(9)}$$

As a cautionary note, outliers, when present, distort BTVs, which, in turn, may lead to incorrect remediation decisions that may not be cost-effective or protective of human health and the environment. Thus, the BTVs should be estimated by statistics representing the dominant ambient/background population represented by most of the data set. Upper limits computed by including a few low-probability high outliers (for example, coming from the far tails of data distribution) tend to represent locations with elevated concentrations rather than representing the main dominant ambient/background population. The minimum sample size needed to achieve a coverage probability γ, and CC (1 - α), can be calculated using the following equation suggested by Scheffe and Tukey (EPA, 2015a):

$$n_{needed} = 0.25\chi^2_{2m,(1-\alpha)}\left[\frac{(1+\gamma)}{(1-\gamma)} + \frac{(m-1)}{2}\right] \quad \textbf{(10)}$$

In Equation (10), m should follow the constraint:

$$1 \leq m \leq n$$

Where:

m = 1 when the largest value, x(n), is used to compute the UTL.

m = 2 when the second largest value, x(n-1) is used to compute a UTL.

m = n-r+1 when the r^{th} order statistic, x(r), is used to compute a UTL.

By construction, outliers in ambient/background can be a problem for nonparametric tolerance limits, especially if the ambient/background maximum is chosen as the upper limit. A limit based on a large, extreme outlier will result in a test having little power to detect increases in compliance samples.

Consequently, the ambient/background sample should be screened ahead of time for possible outliers. Confirmed outliers should be removed from the data set before setting the tolerance limit (EPA, 2009).

An important caveat to this advice is that almost all statistical outlier tests depend crucially on the ability to fit the remaining data (minus the suspected outliers) to a known statistical distribution. In those cases where a nonparametric tolerance limit is selected because of a large fraction of nondetects (NDs), fitting the data to a distributional model may be difficult or impossible, negating formal outlier tests. As an alternative, the nonparametric UTL could be set to a different order statistic in ambient/background (that is, other than the maximum) to provide some insurance against possible large outliers. This strategy will work, provided there are enough ambient/background measurements to allow for adequately high coverage and confidence in the resulting limit.

2.3 Parametric Upper Simultaneous Limit

An (1 – α) * 100 percent USL based upon an established ambient/background data set provides coverage for all observations simultaneously in the ambient/background data set. It is implicitly assumed that the data set comes from a single ambient/background population and is free of outliers (so is the established ambient/background data set). It is expected that observations coming from the ambient/background population will be less than or equal to the USL95 with a 95 percent CC.

2.3.1 Normal Upper Simultaneous Limit

If sample ambient/background data is normally distributed, then the normal USL providing coverage for 100 percent of the sample observations is given as follows:

$$USL = \overline{x} + d_{2\alpha}^{b} s \qquad \textbf{(11)}$$

Where:

$\overline{x}$ = The sample mean

$d_{2\alpha}^{b}$ = The critical value of the maximum Mahalanobis distance, Max (MDs), for a 2α level of significance (EPA, 2015a)

s = The sample SD

2.3.2 Lognormal Upper Simultaneous Limit

The procedure to compute USLs for lognormally distributed data sets is similar to that for normally distributed data sets. In this case, the sample mean, $\overline{y}$, and SD, s_y, of the log-transformed data are computed, then the lognormal USL is calculated using the following equation:

$$UTL = \exp[\overline{y} + d_{2\alpha}^{b} s] \qquad \textbf{(12)}$$

2.3.3 Gamma Distribution Upper Simultaneous Limit

The gamma distribution USLs are estimated using the normal approximation to the gamma distributed data. There are two approximations that are used to transform a gamma distributed data into an approximate normally distributed data (EPA, 2015a):

- WH transformation: Transform the ambient/background data using the transformation, $Y = X^{1/3}$, then the gamma USL in original scale is given as:

$$USL = max\left[0, \left(\overline{y} + d_{2\alpha}^{b} s_y\right)^3\right] \qquad \textbf{(13)}$$

- H-W transformation: Transform the ambient/background data using the transformation, $Y = X^{1/4}$, then the gamma USL in original scale is given as:

$$USL = \left(\overline{y} + d_{2\alpha}^{b} s_y\right)^4 \quad \textbf{(14)}$$

2.4 Nonparametric Upper Simultaneous Limit

When an assumption of normality cannot be justified, USL is determined using the nonparametric method. According to this method, the largest value, x(n), is used as the nonparametric USL. Just like a nonparametric UTL, a nonparametric USL may fail to provide the specified coverage, especially when the sample size is small (for example, less than 60). The confidence actually achieved by a USL can be computed using the same process as used for a nonparametric UTL described in the preceding section. Specifically, by substituting r = n in Equation (6), the confidence coefficient achieved by a USL can be computed, and by substituting m =1 in Equation (7), one can compute the sample size needed to achieve the desired confidence.

2.5 Ambient/background Threshold Value Estimation for Nondetect Data

NDs are inevitable in most environmental data sets. The following procedure is used to manage ND data:

1) For constituents composed of 100 percent NDs, the Double Quantification Rule (EPA, 2009) is used. According to this rule: “A confirmed exceedance is registered if a constituent exhibits quantified measurements (i.e., at or above the reporting limit).” Thus, for 100 percent NDs data, the reporting limit was used as the BTV.
2) For constituents exhibiting an ND frequency greater than 50 percent, a nonparametric BTV was computed.
3) For constituents exhibiting an ND frequency less than or equal to 50 percent, the Kaplan-Meier (KM) censored estimation technique was used to estimate the ambient/background mean and SD to determine the parametric BTV.

2.6 Assumptions

To estimate appropriate BTVs, the following assumptions must be satisfied by the ambient/background data:

- Parametric BTVs assume that the data follow a normal distribution. If a data set does not fit a normal distribution, then a suitable transformation is needed to normalize the measurements. The BTV should be computed using the transformed values and then back-transformation should be used to determine the final limit in the original scale.
- Nonparametric BTVs do not assume normality or any particular type of distributional form.
- The ambient/background data must be stationary. Thus, the temporal ambient/background data collected over a period of time must be free from any obvious trends or temporal patterns.
- The ambient/background data should be statistically independent i.e., it should have no auto-correlation. Thus, ambient/background samples collected over time should have enough temporal spacing between consecutive observations so that temporal independence can be assumed.
- Although nonparametric BTVs do not require an assumption of normality, other assumptions of BTVs apply equally to parametric and nonparametric methods. Specifically, the ambient/background data should be statistically independent and show no evidence of autocorrelation, trends, or seasonal effects.
- If a USL is used as the BTV, the original ambient/background data set should be free from outliers and represent a single environmental ambient/background population.
- If a UTL is used as the BTV, the confirmed outliers should be removed from the data set before estimating values of UTLs.

2.7 Preliminary Data Analysis

Table 1 presents basic statistics of the thallium ambient/background data.

Table 1. Basic Statistics of Thallium Ambient/background Data

Determination of Thallium Ambient/background Concentration at the Topock Compressor Station, Needles, California

General Statistics for Raw Dataset using Detected Data Only								
NumObs	**Min**	**Max**	**Mean**	**Median**	**Var**	**SD**	**Skewness**	**CV**
11	2.6	4.2	3.545	3.6	0.223	0.472	-0.635	0.133
General Statistics for Censored Datasets (with NDs) using KM Method								
NumObs	**NumDs**	**NumNDs**	**% NDs**	**Min ND**	**Max ND**	**KM Mean**	**KM SD**	**KM CV**
38	11	27	71.05	2	2.5	2.447	0.742	0.303

Notes:

% = percent

CV = coefficient of variation

Max = maximum

Min = minimum

NumDs = number of detects

NumNDs = number of nondetects

NumObs = number of observations

Based on these statistics, the following points are noted:

- The ambient/background data set consists of 38 observations. Among these observations 11 observations are detects and 27 observations are nondetects (NDs). Thus, there are about 71 percent NDs in the ambient/background data.
- The mean, SD, and CV values of the detected data are 3.545 milligrams per kilogram (mg/kg), 0.472 mg/kg, and 0.133, respectively.
- The mean, SD, and CV values of the censored data sets using the KM method are 2.447 mg/kg, 0.742 mg/kg, and 0.303, respectively.

To further investigate whether the ambient/background data complies with the required assumptions for estimating BTVs and selecting the most appropriate method, statistical independence, spatial stationarity, outliers, and normality characteristics are examined.

2.7.1 Identification of Outliers

Outliers are data that appear anomalous or outside the range of expected values. Outliers may indicate errors, may indicate data unrelated to the rest of the data set, or may be perfectly valid data that indicate contamination or unusual geochemical conditions. The goal of outlier identification is to properly analyze the data to determine which outliers are representative of valid data points and should be kept, and which outliers likely represent anomalous situations and should be removed from the data set. Data should not be ignored simply because they are identified as outliers. After identifying data points as potential outliers, further evaluation is conducted to determine the reason for their existence. Outliers should generally be kept as part of the data set unless there is reasonable evidence that they are the result of an error. Many statistical tests require that outliers resulting from an error be removed; some statistical tests may also require removal of valid but extreme outliers that are not representative of the general population. The presence of outliers may preclude the use of some statistical methods altogether, requiring, for example, a nonparametric alternative.

The box-whisker plot is a good tool for screening the data to identify possible outliers. Figure 1 presents time-series and box-whisker plots for observed thallium concentrations. The time-series plot shows the thallium concentrations with respect to sampling time. It shows two types of points: hollow and solid circles. The hollow circles are NDs; whereas, the solid circles are the detected observations. In the box-whisker plot, an outlier is defined as a value falling outside the first quartile (Q1) and the third quartile (Q3) range by more than 1.5 times the interquartile range (IQR = Q3-Q1). Based on the developed box-whisker and time-series plots (Figure 1), it appears that there are no outliers in the ambient/background data set.

For formal outlier assessment, the ND observations were replaced with half of their reporting limits. The obtained data was tested for normality and found that it does not comply with the normality assumption. Thus, the Rosner's test cannot be applied to test outliers. The nonparametric tests (for example, the IQR and median of absolute deviations [MAD] tests) were used instead. These tests are particularly useful for data sets that do not comply with normality assumptions.

Reviewing outlier results, the following points are noted:

- The IQR value is 1.825, indicating no outliers in the ambient/background data.
- The MAD value is 0.074, indicating no outliers in the ambient/background data.

2.7.2 Testing Normality

A normality assumption is not only needed for establishing a BTV (that is, a UTL or USL), but it is also needed for evaluating the ambient/background data for outliers using the parametric methods, as described. Therefore, data need to be examined for normality prior to performing the outlier tests. In most situations, probability plots are used as a screening tool for checking a data set's conformance to a normal distribution, and the Shapiro-Wilk test is used as a formal test of normality. To verify the normality of the raw data, histograms and Q-Q plots were developed, as shown on Figure 2.

Looking at the histogram and Q-Q plot of thallium raw ambient/background data, it is clear that the thallium concentration does not fit a normal distribution. Based on further analysis, it was observed that the thallium ambient/background data does not fit any well-known distribution (for example, lognormal, gamma,). However, using the detected data only, the Shapiro-Wilk normality test gives a p-value of 0.138, indicating that the detected data fits a normal distribution.

3. Ambient/Background Threshold Value Determination

After establishing the ambient/background data based on conducting various data exploratory analyses using R (R Core Team, 2016), the following step-by-step procedure was used by applying the ProUCL Statistical Software (EPA, 2015b) for determining ambient/background limits:

1) Both UTL95-95 and USL95 were computed as a candidate for BTV using the established ambient/background data set.
2) For constituents exhibiting an ND frequency greater than 50 percent, nonparametric UTL95-95 and USL95 were computed. Based on this guideline, the following UTL and USL values are obtained:
   - 95 percent UTL with 95 percent coverage = 4.2 mg/kg. The approximate actual confidence coefficient achieved by UTL is about 87 percent
   - 95 percent USL = 4.2 mg/kg
3) Based on the Unified Guidance (EPA, 2009) for constituents exhibiting an ND frequency less than or equal to 50 percent, the KM censored estimation technique is used to estimate the ambient/background mean and SD to estimate the parametric UTL95-95 and USL95. As the current ND frequency is 71 percent, the KM censored technique is not applicable in this particular case. This technique is still applied to determine the BTV value corresponding to 95 percent confidence, as applying the nonparametric method, only 86 percent confidence could be achieved. At least 59 observations are needed to achieve 95 percent confidence. Thus, using the KM censored technique, the following results are obtained:

- 95 percent UTL with 95 percent coverage = 4.03 mg/kg
- 95 percent USL = 4.56 mg/kg

4) Based on EPA (2015a) recommendations, if the raw ambient/background data set is free from outliers, USL95 must be selected as the BTV value. Otherwise, UTL95-95 representing a 95 percent UCL of the 95th percentile of the ambient/background population data is selected as the BTV value. Thus, the BTV values are given as:

   - Based on the nonparametric method = 4.2 mg/kg
   - Based on the parametric method = 4.56 mg/kg

4. References

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Soil Sample Location

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Baseline and Opportunistic Soil Sampling Locations

Monthly Progress Report
Groundwater Remedy Phase 1 Construction
PG&E Topock Compressor Station, Needles, California

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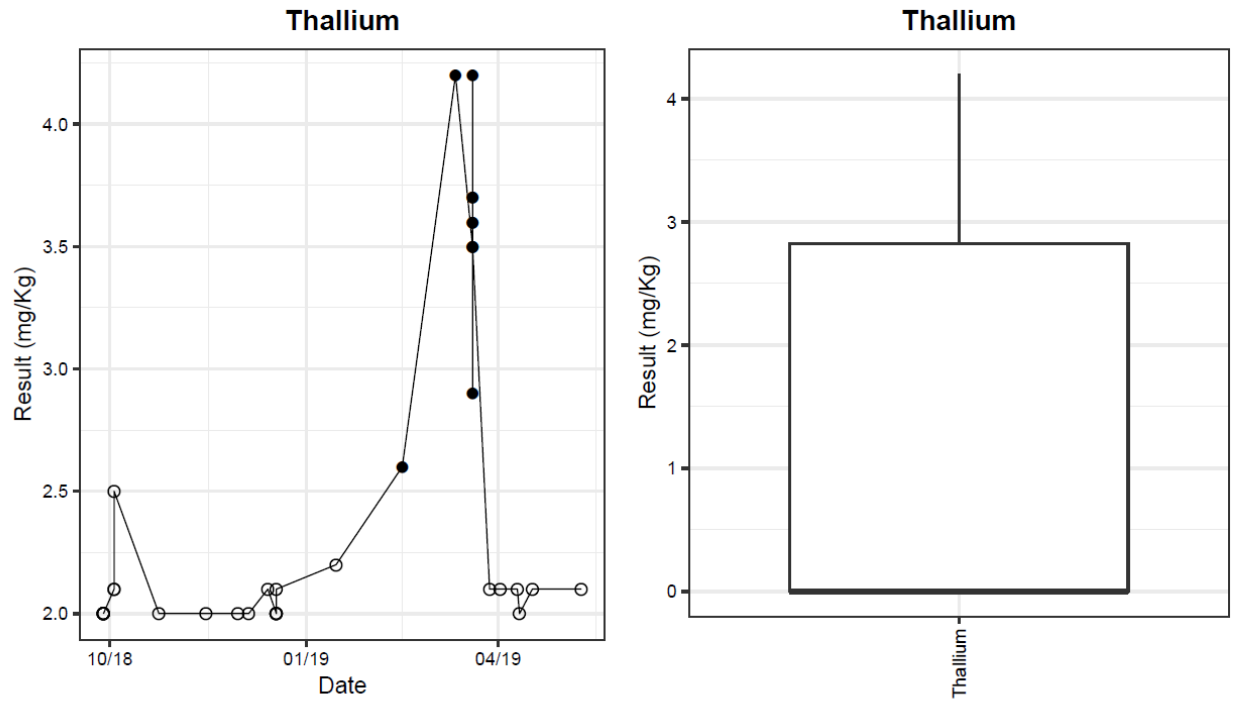

Figure 1. Time Series and Box-Whisker Plots for Thallium Concentration
Determination of Thallium Ambient/background Concentration at the Topock Compressor Station, Needles, California

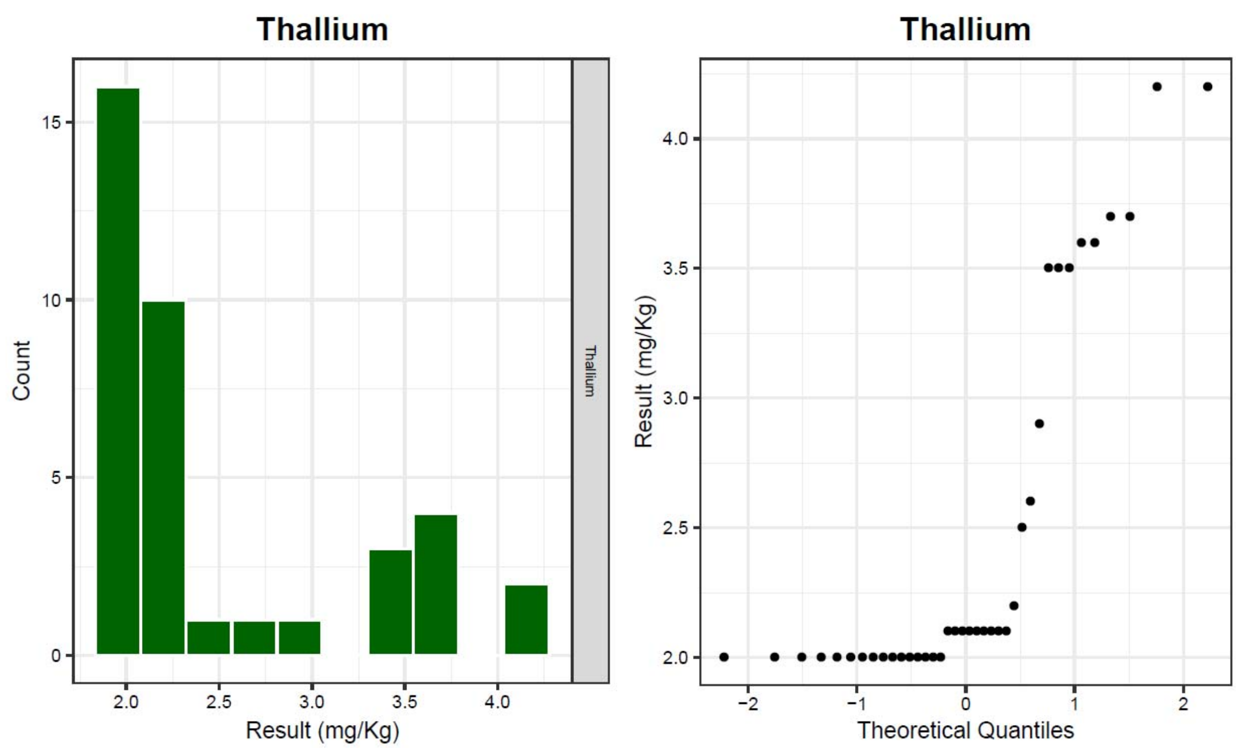

Figure 2. Histogram and Q-Q Normal Probability Plots for Thallium Concentration
Determination of Thallium Ambient/background Concentration at the Topock Compressor Station, Needles, California