Montana Dioxin Background Investigation Report

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ABSTRACT

In 2008, the Montana Department of Environmental Quality completed an effort to collect surface soil samples for dioxins and dibenzofurans statewide to quantify background concentrations of these compounds in surface soils in all regions of the state. Surface soils were collected using a stratified approach based on land use and were analyzed for polychlorinated dioxins and dibenzofurans. In all, DEQ collected 223 surface soil samples from locations that were not indicated to be impacted by point sources of dioxins. The data were then evaluated to establish background dioxin concentrations in Montana as a whole and in the stratified land use populations. The results of the investigation indicate Montana surface soils from unimpacted areas have dioxin concentrations below the Environmental Protection Agency's Regional Screening Level of 4.5 nanograms per kilogram (ng/kg). Montana's statewide background dioxin concentration was determined to be 3.7 ng/kg.

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ACRONYMS

ANOVA	analysis of variance
BCa	biased-corrected accelerated
BIR	background investigation report
CV	coefficient of variation
DEQ	Montana Department of Environmental Quality
EPA	U.S. Environmental Protection Agency
GC/MS	gas chromatograph/mass spectrometry
HpCDD	heptachlorinated dibenzo-p-dioxin
HpCDF	heptachlorinated dibenzofuran
HxCDD	hexachlorinated dibenzo-p-dioxin
HxCDF	hexachlorinated dibenzofurans
IQR	inter-quartile range
KM	Kaplan-Meier
LCS	laboratory control sample
MVUE	minimum variance unbiased estimator
ng/kg	nanograms per kilogram
OCDD	octachlorodibenzodioxin
OCDF	octachlorodibenzofuran
PCDD	polychlorinated dibenzodioxins
PCDE	polychlorinated diphenyl ethers
PCDF	polychlorinated dibenzofurans
PeCDD	pentachlorinated dibenzo-p-dioxin(s)
PeCDF	pentachlorinated dibenzofuran(s)
QA	quality assurance

QAPP	quality assurance project plan
QC	quality control
RSL	regional screening level
TCDD	tetrachlorodibenzo-p-dioxin(s)
TCDF	tetrachlorinated dibenzofuran(s)
TEF	toxicity equivalency factor
TEQ	toxicity equivalent quotient
UCL	upper confidence limit
UTL	upper tolerance limit

1. INTRODUCTION

The Montana Department of Environmental Quality (DEQ) manages or oversees activities at numerous sites in Montana where surface soils are evaluated for the presence of chlorinated dioxins and dibenzofurans (hereinafter collectively called *dioxin* or *dioxins*) because of past uses of these sites. This dioxin background investigation report (BIR) quantifies dioxin concentrations and corresponding toxicity equivalent quotients (TEQs) in Montana surface soils by region and by defined land uses. To support this effort, DEQ collected data throughout Montana in accordance with the *Montana Department of Environmental Quality, Quality Assurance Project Plan Montana Background Dioxin Investigation* (CDM 2007).

The results of the investigation indicate background dioxin concentrations in Montana are generally lower than the most conservative Environmental Protection Agency (EPA) risk-based regional screening level (RSL) of 4.5 nanograms per kilogram (ng/kg). This BIR was prepared to provide a full examination of the background dioxin data collected, and to quantify background dioxin concentrations statewide and regionally. The background information presented in this BIR does not preclude the collection of site-specific background dioxin samples. DEQ encourages those performing site characterization activities to perform site-specific background determinations whenever possible.

1.1 Project Description

Dioxins are known to be released to the environment from multiple sources, including incineration of medical and municipal waste, as by-products of chlorinated pesticide manufacturing, and combustion of coal and wood (EPA 2005). The primary mechanism for dioxins to contact and bind with soil is atmospheric deposition from natural and anthropogenic sources (EPA 2005), which has the potential to cause widespread, low-level ambient (or "background") concentrations in surface soil. Thus, elevated dioxin concentrations from point sources (for example, from wood treating operations or a burn pile) are expected to occur superposed on background concentrations (CDM 2007).

Dioxins have multiple anthropogenic and natural point and non-point sources, making it difficult to evaluate whether concentrations measured at a given site are the result of ambient background or other sources. Prior to this study, background dioxin concentrations in Montana surface soil were not documented, except on a limited site-by-site basis. The goals of the background investigation were to:

- Estimate the mean background concentrations of dioxins in surface soils (0–2-inch depth) by collecting samples at non-impacted sites (sites with no known dioxin point sources) across Montana and analyzing these samples for dioxin via EPA Method 8290 (EPA 2009a).
- Establish upper tolerance limits (UTLs) for individual dioxin and dibenzofuran isomers and congeners from statewide surface soil data
- Derive TEQ UTLs for various sample populations (for example, urban and rural) using measured dioxin concentrations.

This report provides a comprehensive summary of the statewide and regional dioxin concentrations and the TEQs derived from these data for all regions and environmental settings in Montana.

1.2 Description of Sampling

To evaluate statewide background levels for dioxins, surface soil samples were collected throughout Montana using a stratified sampling approach. As part of the planning for the investigation, it was anticipated that land use may have a direct impact on the concentrations of dioxins in a given setting. As a result, the state was categorized into two primary land-use areas: (1) rural and (2) urban. The rural and urban categories were further stratified into three secondary categories based on common Montana land uses. Table 1 summarizes both the primary and secondary land-use categories.

Table 1. Stratification of BIR sampling design by land use.

Primary Category	Secondary Category		
Rural	Agricultural	Open Space	Forest
Urban	Residential	Commercial	Industrial

The six secondary land-use categories are defined by the following:

- Agricultural—currently or previously (within past 50 years) tilled and used for crop production;
- Open Space—undeveloped or unimproved, barren, or in a natural state, including tundra, prairie, grassland, grazing land, etc;
- Forest—national forest, state forest, and treed lands;
- Residential—includes parks, greenbelts, trails, and any other open areas within or immediately adjacent to homes, excluding private yards;
- Commercial—includes shopping centers, restaurants, office buildings, and any other open areas; within or immediately adjacent to these kinds of businesses;
- Industrial— includes manufacturing, refining, warehousing, and transportation (garage) facilities, and any other open areas within or immediately adjacent to these areas, excluding those areas that are known or suspected dioxin sources.

In order to meet the data quality objective of providing geographic coverage, background sampling was conducted based on a systematic approach for each of the two primary land-use categories as follows:

- Rural—The state was divided into 20 approximately equally sized blocks. Three background dioxin samples were located in each of the 20 blocks from the associated secondary land-use categories.
- Urban—The seven major urban areas in Montana were divided into 20 approximately equally sized areas based on their relative population size. Three background dioxin samples were located in each of the 20 areas from the associated secondary land-use categories.

Table 2 provides a breakdown of the individual sampling areas evaluated in and around Montana's seven largest cities.

Table 2. Urban sampling areas – Montana's largest cities.

City Name	Billings	Bozeman	Butte	Great Falls	Helena	Kalispell	Missoula
Number of Sampling Areas	5	2	2	4	2	1	4

The number 20 was selected to achieve the data quality objective of having a sufficient sample size to allow statistical calculations on the smallest sample populations in this investigation. This quantity is an estimate based on best available information (primarily other similar studies) and was modified as the project proceeded. Figure 1 provides a site map of the locations of all rural surface soil samples collected in support of this BIR. Figure 3-1 of the quality assurance project plan (QAPP) for the Montana dioxin background investigation (CDM 2007) illustrates the 20 blocks established for the rural land-use category and is superimposed on a map of secondary land-use categories.

For each primary rural block or urban area, three sampling points were located in secondary land-use categories as follows:

1. If all three secondary land-use categories were present in a block/area, then one sample point was located in each of them;

2. If only two secondary land-use categories were present in a block/area, then two sample points were located in the largest (geographically) of the two, and one sample point was located in the smallest; and

3. If only one secondary land-use category was present in a block/area, then all three sample points were located in this category.

For the majority of the rural settings, the land-use-dictated sampling follows the scheme described in #1 above. Deviations from the planned sampling approach and instances where the first example could not be followed are discussed in Section 1.2.2, Sampling Deviations.

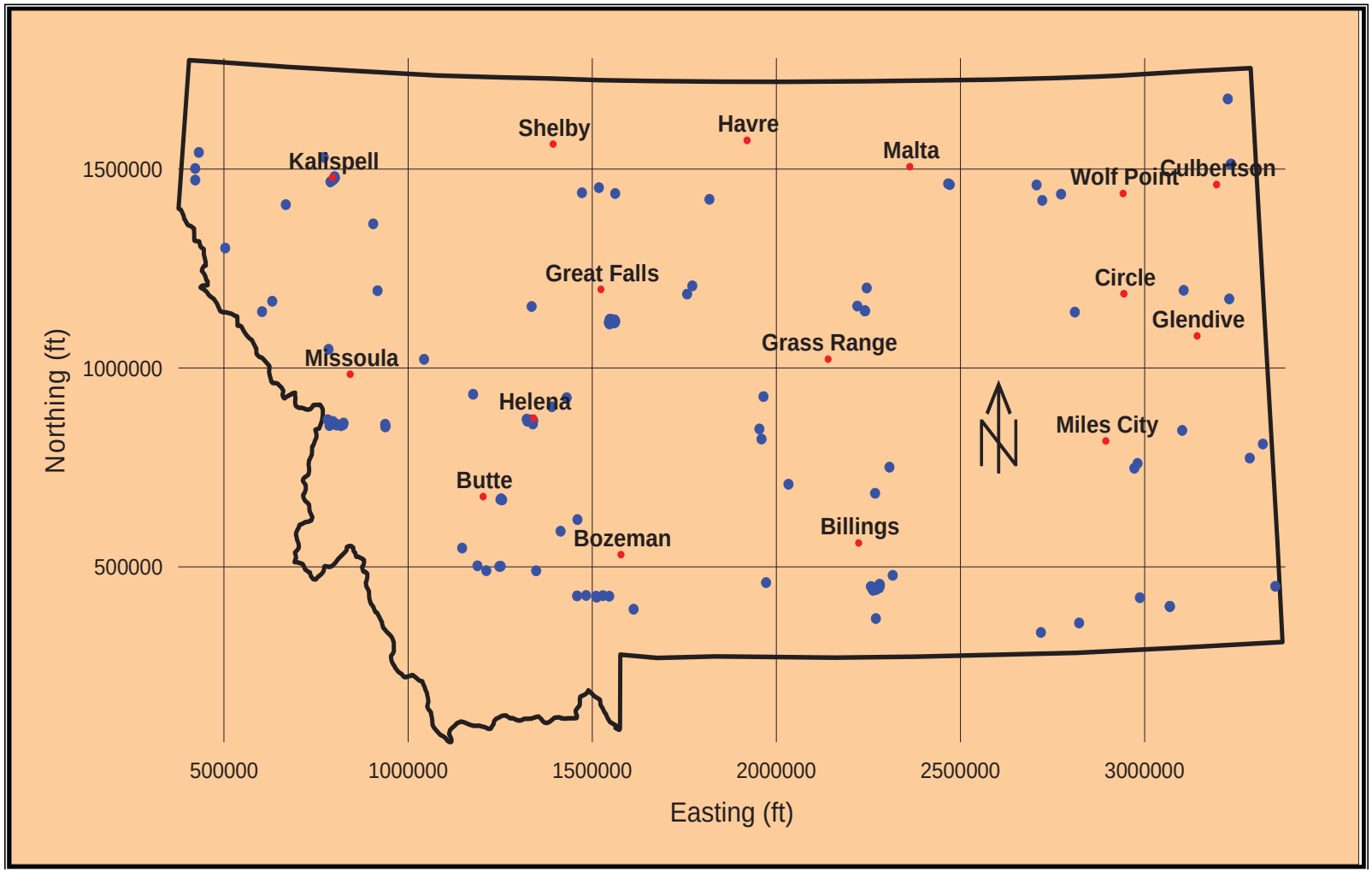

Figure 1. Sample location map of the Montana dioxin background investigation.

Note: Blue dots represent rural sample locations. Urban samples were collected in Billings, Bozeman, Butte, Helena, Missoula, Kalispell, and Great Falls. Additional cities and towns are shown for location reference. It should be noted that not all samples are distinguishable from one another on Figure 1.

1.2.1 Sample-Collection Procedure

Sampling was conducted in accordance with the provisions detailed in the QAPP for this investigation (CDM 2007). DEQ collected 30 of the 120 samples prior to contracting with Hydrometrics, Inc.; Hydrometrics subsequently completed the sampling efforts. The following summarizes sampling-related considerations:

- Compositing was used for all samples to minimize local variability in the soil media
- At each sample location, five surface-soil grab samples were collected as follows:
  - One grab sample was collected from the center point
  - One grab sample each was collected from approximately 20 ft north, 20 ft south, 20 ft east, and 20 ft west of the central point
- The five grab samples were composited into one sample.

Each grab sample was collected from 0 to 2 inches below ground surface using either stainless-steel or disposable plastic scoops and contained approximately 100 g of soil. Loose vegetation and rocks were removed prior to placing samples in containers. Once all were acquired, the five grab samples were combined in a large bowl or Ziploc® bag and mixed. The composite sample was then transferred to an amber-colored glass jar with a Teflon®-lined lid, placed in laboratory-provided bubble wrap, sealed, and placed into a cooler maintained at 4±2°C. All samples were analyzed for chlorinated dioxins and dibenzofurans by Pace Analytical Laboratory in accordance with EPA Method 8290 (EPA 2009a).

Each sample location was surveyed using a hand-held Global Positioning System device, and this data was recorded in the field logbook along with other field observations (soil texture, color, and other characteristics). The location information was incorporated into the project database along with the analytical results to aid in developing statewide maps and statistical analysis.

1.2.2 Sampling Deviations

Conditions in the field were generally as expected. As a result, limited deviations occurred from the planned sampling approach (Hydrometrics 2008). Some minor deviations from typical procedures were noted, but all fell within the provisions detailed in the QAPP. The following describes specific deviations from the planned approach:

- Sampling was initiated in early December 2007. However, because of statewide ground freeze, DEQ chose to suspend activities following completion of sampling in and around the Billings and Great Falls urban areas. Sampling resumed in April 2008 and was completed at the end of June 2008.
- The collection of rinsate blanks was required only for samples collected from the Billings urban area, because reusable stainless-steel spoons were used to acquire samples there. As required by the QAPP for this investigation, rinsate blanks were collected when sampling equipment was decontaminated. Disposable, single-use scoops were used at the remaining locations and, as a result, decontamination was not required between samples at other locations.

- Trip blanks supplied by Pace Laboratories were composed of pea gravel. The sample media for the majority of background samples consisted primarily of soil/sand. While they are a deviation from the QAPP, trip blanks are not a normal requirement for semivolatile organic compounds, such as dioxins, and were included in the sampling program only as a precautionary tool. All trip blanks were collected in accordance with the QAPP for this investigation.

- Sampling in the Missoula urban area was conducted on April 17, 2008. Industrial samples were not available for collection in urban Locations U19 and U20. In accordance with Section 3.4 of the QAPP, two residential samples were collected from Missoula urban Locations U19 and U20 in lieu of the industrial samples.

- With the assistance of the Montana Eastern Lands Office in Miles City, Hydrometrics identified two potential state lease land parcels located between Forsyth and Colstrip in rural sampling Block R-19 for collection of agricultural Sample R19-A01. On May 13, 2008, sampling was initiated in southeastern Montana. Upon inspection of the two parcels, they were found to fall into the open range classification, with no active or apparent history of agricultural activity. Additionally, both were posted with no-trespassing signs. After consultation with the Eastern Lands Office and local maps, and in accordance with the provisions of Section 3.4 of the QAPP, the approach was modified for Block R-19. The modification resulted in the collection of an additional open space sample as a substitute for the agricultural sample. Overall, two open space samples (R19-O01 and R19-O02) and one forest sample (R19-F01) were collected in rural Block 19. Notations of the change were made on the R19-002 field form.

1.3 Description of Statistical Methods

The primary purpose of this BIR is to quantify background concentrations for dioxins and corresponding TEQs for Montana surface soils. To support this purpose, surface-soil data were grouped as follows and examined to compare the possible sample populations:

- Statewide by combining all urban and rural data

- Urban only data

- Rural only data

- Each of the six secondary categories.

This approach provides data users with dioxin background concentrations for nearly all settings in Montana. In addition, this BIR provides a comprehensive data assessment that includes summary statistics and plots for the various data groupings. The data assessment also examines the data distribution for each setting and identifies outliers for each. When identified, outliers are both included and excluded from the summary statistics, allowing data users to examine the effect the outlier(s) has on the background concentration. The following sections provide a description of the statistical approach and background computations performed on the dioxin data gathered for Montana.

1.3.1 Data Analysis Techniques

The following sections summarize the statistical tools and techniques used to evaluate statewide dioxin data and to compute the background concentrations and TEQs for the various regions and settings

in Montana. It is important to note that, for computation of TEQ values, DEQ requires one-half the method detection limit to be substituted for any non-detected congeners (DEQ 2011). Statistical analysis was then performed on these computed TEQ values. However, for statistical analysis of individual congeners, it is appropriate to use the actual method detection limits (not half the method detection limits).

1.3.1.1 ***Mean.*** One measure of primary interest is the center of the data. The average ($\overline{x}$), or the mean, is the most commonly used measure of the central tendency of the data. However, it can be heavily influenced by outliers and by asymmetric data. The mean is calculated using Equation (1):

$$\overline{x} = \frac{\sum_{i=1}^{n} x_i}{n} \quad (1)$$

Where:

$\overline{x}$ = mean

n = number of observations

x_i = i^{th} observation.

1.3.1.2 ***Standard Deviation.*** Another quantity of interest is the spread of the data. The standard deviation(s) is the most commonly used measure of spread, because it is easily interpreted and is used in many other statistical methods. Because it is calculated using the average, it is also sensitive to outliers and affected by data that are not symmetric. The standard deviation is calculated using Equation (2):

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^2}{n-1}} \quad (2)$$

Where:

s = standard deviation

n = number of observations

x_i = i^{th} observation

$\overline{x}$ = mean of the observations.

1.3.1.3 ***Coefficient of Variation.*** The coefficient of variation (CV) is a relative measure of variation in the sample data. The CV measures the standard deviation relative to the mean. The CV is expressed as a percentage and provides a method for directly comparing the standard deviations of two different data sets. It is important to note the mean of the data may be very close to or very far away from zero, and the spread may be independent of the distance from the mean to zero. Therefore, no firm guidelines have

been established for interpreting the CV. The CV was calculated for each detected analyte in each data grouping using Equation (3):

$$CV = \frac{s}{\overline{X}} \times 100\% \quad (3)$$

Where:

s = standard deviation

$\bar{x}$ = mean of the observations.

1.3.1.4 ***Upper Confidence Limit and Upper Tolerance Limit.*** An upper confidence limit (UCL) was computed for each dioxin congener when a sufficient number of positive (detected) results were available. The UCL provides a maximum expected value for the true mean concentration. The 95% UCL provides a value greater than the true population mean with 95% confidence. Therefore, the 95% UCL is a conservative estimate of the mean, allowing data evaluation to be completed to ensure protectiveness of human health and the environment. UTLs were also calculated for the Montana dioxin data. The UTL provides an upper bound on the individual concentrations in the population such that the majority of the highest background dioxin concentrations should be less than the UTL. More detailed discussions of UCL and UTL are provided in Sections 2.5 and 2.6.

1.3.1.5 ***Visual Tools.*** It is difficult to review numerical summary statistics and identify the degree of symmetry or normality of data without the aid of visual tools. In completing the statistical analysis for the Montana BIR, a number of statistical plots were developed. They include histograms, box plots, and normal-quantile plots.

1.3.1.5.1 ***Histograms—***Histograms exhibit the distribution and symmetry of the data. The data are displayed in such a way that deviations from normality can be easily observed. Outliers are also often identifiable in a histogram. Histograms for this BIR were generated using both nondetects and detected results. For nondetects, the detection limit was plotted to identify the data point(s). Figure 2 is an example histogram of rural dioxin data collected for this investigation. It plots the rural 2,3,7,8-tetrachlorinated dibenzofuran (2,3,7,8-TCDF) values (ng/kg) versus the number of rural measurements. This figure is provided here to illustrate data distribution using a histogram. All of the histograms used to examine the Montana dioxin background data are provided in Attachments 1–3.

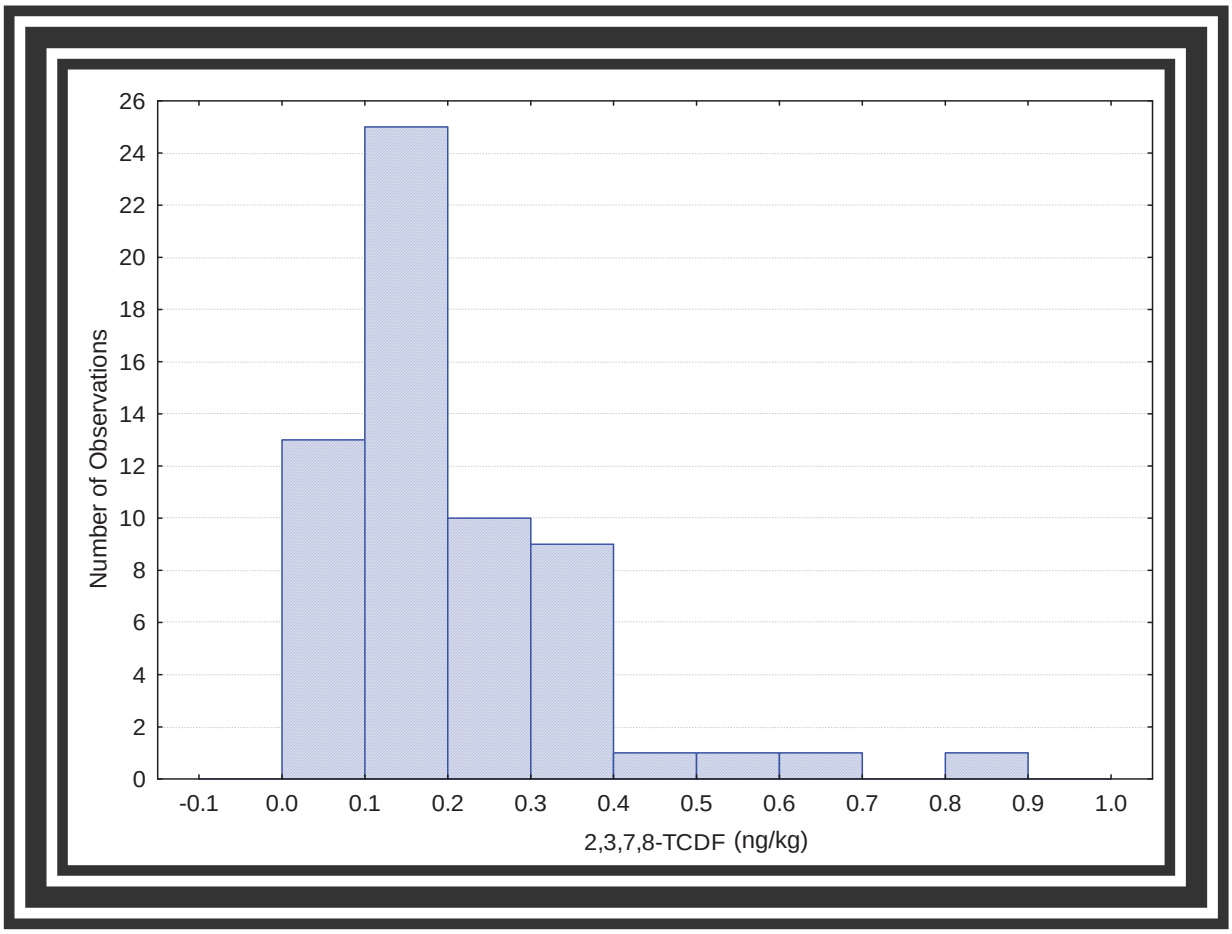

Figure 2. Histogram of rural dioxins.

1.3.1.5.2 ***Box Plots.*** Box plots provide a visual method for viewing the symmetry of the data. The plots consist of a central box, a line inside the box, and two lines extending beyond the ends in either direction. Inside, the line represents the median, the edges represent the two quartiles, and the extreme ends of the lines typically represent the largest and smallest observations. Data points outside of this range are identified by point markers. Circles reflect results greater than 1.5 times the interquantile range (IQR) and asterisks represent data points greater than 3 times the IQR. Box plots were also generated using both nondetects and detected values; for nondetects, the detection limit was used to plot the values. Using the same data presented in Figure 2, Figure 3 plots the rural 2,3,7,8-TCDF values (ng/kg) versus the number of rural measurements and is provided here to illustrate data distribution using a box plot. All of the box plots used to examine the Montana dioxin background data are provided in Attachments 1–3.

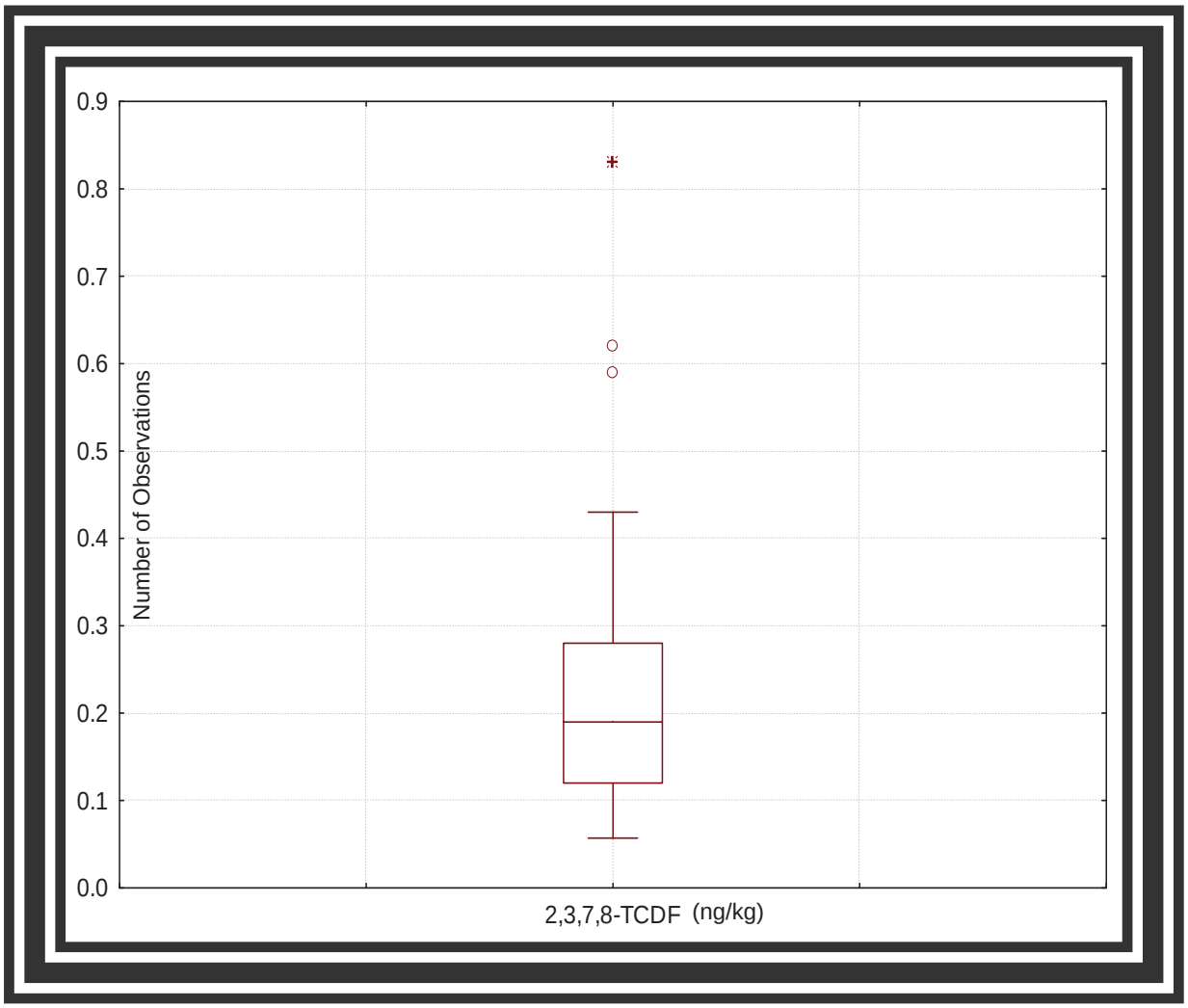

Figure 3. Box plot for rural dioxins.

1.3.1.5.3 ***Normal-Quantile Plots.*** A normal-quantile plot is a graphical tool used to assess the normality of data. When the data follow a normal distribution, the points on the graph lie along a straight line. Any deviations from a straight line are indicative of deviations from normality. It is important to note that no real-world data set is perfectly normal, so a certain amount of deviation from the line is to be expected even in data that are sufficiently normal to construct a reliable UCL. Normal-quantile plots in this document were generated using both nondetects and detected values; for nondetects, the detection limit was used to plot a value. Figure 4 uses the same rural data used to develop Figures 2 and 3 by plotting the rural 2,3,7,8-TCDF values (ng/kg) versus the number of rural measurements. All of the normal-quantile plots used to examine the Montana dioxin background data are provided in Attachments 1–3.

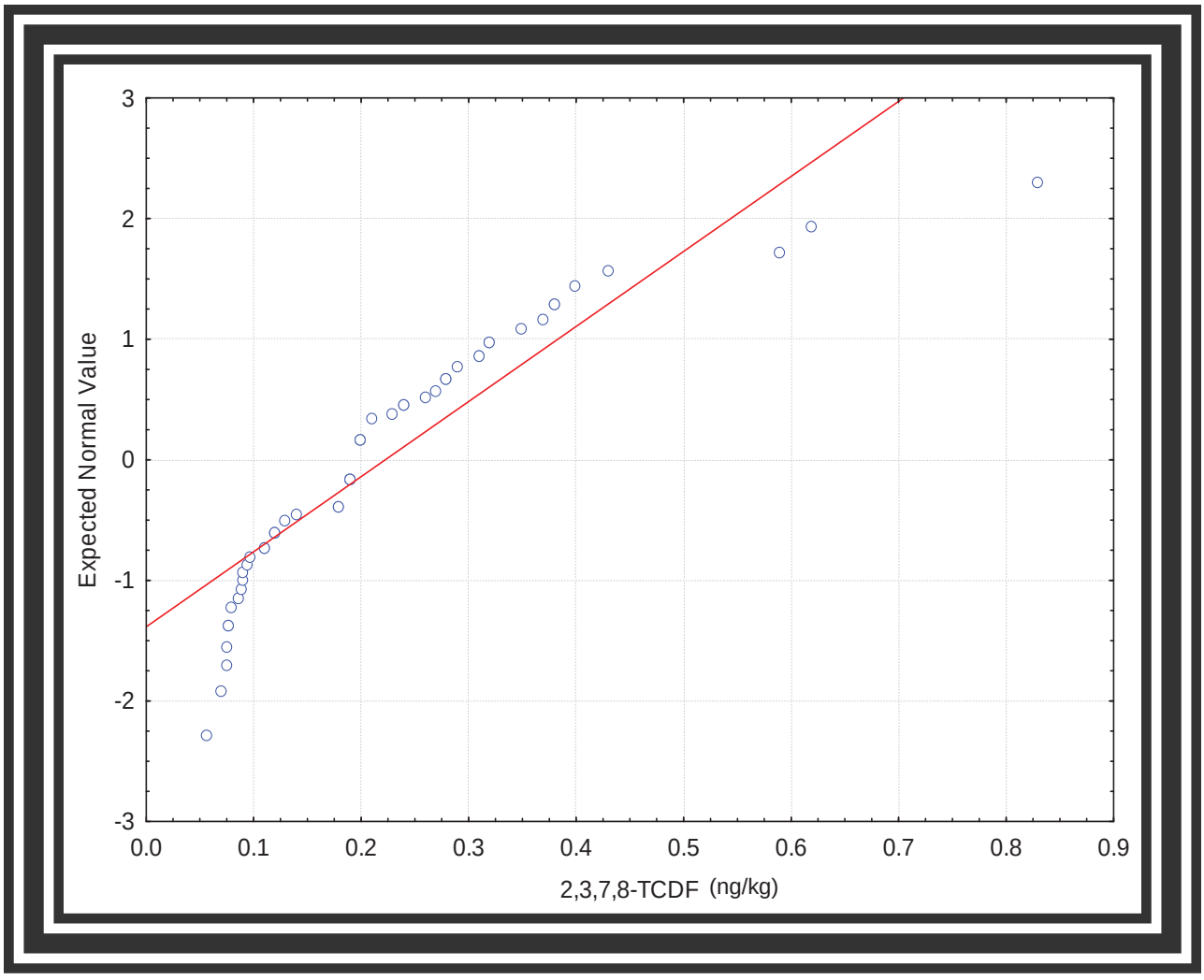

Figure 4. Normal quantile plot for rural dioxins.

1.3.2 Treatment of Outliers

Outliers are data points that are notably larger or smaller than the rest of the data set and may indicate a problem with the data point or the data set as a whole. Examples that may be indicative of outliers include (a) a misreported or erroneous concentration, (b) analytical error(s), or (c) natural variations in soil concentrations. As prescribed in the QAPP for this investigation (CDM 2007), strict quality assurance/quality control (QA/QC) procedures were followed during sample collection and analysis, and all data were validated, with the objective of limiting the potential for outliers due to (a) and (b). All the outliers in this investigation had a high bias, which was likely due to natural variability in background dioxin concentrations.

Outliers are generally not omitted from project data simply because they are outliers. Rather, the result is examined individually or by project to ensure the outlier does not represent an erroneous result or another concern warranting either additional sampling or omission of the outlier from the data analysis. There are reasonable situations when it is appropriate to remove outliers. For example, if outliers that represent exceedingly low concentrations are used to compute background concentrations, the outliers may result in background levels that are too conservative and unachievable for cleanup. Conversely, use of excessively high outlier concentrations to compute background levels may result in an overestimation of background concentrations, resulting in residual contaminant levels at a site that are not protective of human health or the environment.

Outliers were identified in the Montana dioxin background data set. In all cases, summary statistics were computed both with and without the outliers to demonstrate their effect on the statistical quantities. Outliers were identified using visual inspection of the histograms, box plots, and normal-quantile plots for each subgroup. None of the outliers were the result of errors in the data, in analytical method error, or that occurred during laboratory reporting. Therefore, the outliers in this investigation likely represent variations resulting from sample variability.

Some of the data points identified as outliers for individual subgroups were not outliers when considered with the larger urban or rural group. This occurred when a data point was unusually high relative to the other data in an individual subgroup but was within the normal range of data for the overall urban or rural data set. All identified outliers were high outliers. Outliers are discussed in more detail in Section 2.

1.3.3 Treatment of Nondetects

Nondetect values are common in environmental data. When present in data sets, nondetects produce difficulties in computing statistical metrics, because reliable values cannot be assigned. Substituting a value such as the detection limit or one-half of the detection limit as a concentration is a common practice. However, use of the detection limit or one-half of the detection limit can produce unstable or unreliable results (EPA 2009b). Statistical methods, such as Kaplan-Meier (Helsel 2004), can be used to appropriately evaluate data sets containing significant quantities of nondetects by producing estimates of the survival probability function for nondetects. These estimates can then be used to compute summary statistics on the data set. However, Kaplan-Meier does not perform well if more than 70% of the results are nondetects or if fewer than eight detections are available for evaluation.

The dioxin data acquired to support this BIR contain numerous nondetects. As a result, Kaplan-Meier was used to compute means, standard deviations, UCLs, and UTLs for data groups and subgroups containing less than 70% nondetects. For those groups/subgroups where more than 70% of the results were nondetect, the mean, standard deviation, UCL, and UTL could not be computed. In these cases, the

maximum detected value is considered the UTL (EPA 2009b). More traditional statistical methods (Section 1.3.1) were used when a higher proportion of detections were noted (> 30%). Appendix A details the data subgroups where the maximum concentration was used for the UTL.

1.3.4 Toxicity Equivalent Quotients

The general term "dioxin" refers to a related group of 17 halogenated aromatic compounds that can create health effects to humans, birds, and fish when exposed to these compounds for prolonged periods. The 17 dioxin compounds are divided into two general classes: (1) polychlorinated dibenzodioxins (PCDDs) consisting of seven isomers and congeners; and (2) polychlorinated dibenzofurans (PCDFs) consisting of 10 isomers and congeners. The relative toxicity of a particular congener is related to the most toxic, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD or TCDD), by normalizing each isomer/congener to TCDD through toxicity equivalency factors (TEFs). TEQ is an overall expression of isomer and congener concentrations normalized to TCDD determined by multiplying all isomers and congener concentrations by their corresponding TEF. The TEQs provide important information about the overall toxicity of all dioxins found at a site. TEQs for the Montana dioxin background data were computed using Equation (4) below.

$$TEQ = \sum_{i=1}^{n} (c_i \times TEF_i) \tag{4}$$

Where:

c_i = concentration

TEF_i = TEF

i^{th} = congener

n = total number of congeners.

In addition to the summary statistics for individual isomers and congeners presented herein, a statistical summary of surface soil TEQs has also been computed and is presented for each of the land-use categories. As of the date of this BIR, DEQ guidance requires the use of the 2005 World Health Organization TEFs for calculation of TEQs (DEQ 2011). Because the TEQ calculation is not statistical in nature, it is not possible to use Kaplan-Meier to aid in the calculation. Therefore, one-half the detection limit was used in place of nondetect values for TEQ determinations. DEQ requires the use of one-half the detection limit in TEQ calculations to be consistent with EPA and Montana risk assessment guidance (EPA 1991, DEQ 2011).

In addition to the summary statistics for individual isomers and congeners presented herein, a statistical summary of surface soil TEQs has also been computed and is presented for each of the land-use categories. Because the TEQ calculation is not statistical in nature, it is not possible to use Kaplan-Meier to aid in the calculation. Therefore, one-half the detection limit was used in place of nondetect values for TEQ determinations. The DEQ requires the use of one-half the detection limit in TEQ calculations in order to be consistent with EPA and Montana risk assessment guidance.

2. ANALYSIS OF SURFACE SOIL BACKGROUND DATA

This section contains the technical analysis of the Montana dioxin background data for surface soils. Included are a discussion of overall data quality and a presentation of summary statistics. The discussion of data quality is included for the entire data set. Summary statistics are presented for each of the major data categories and each subcategory.

2.1 Data Quality

The data for dioxins was acquired in accordance with EPA SW-846 Method 8290, PCDDs and PCDFs by high-resolution gas chromatography/high-resolution mass spectrometry (EPA 2009a). Method 8290 is designated as the "low-level method" for measuring dioxins, providing extreme sensitivity for chlorinated compounds.

The background data were validated to Level III by Portage, Inc. (Portage 2009a, 2009b, 2009c, 2009d, 2009e, 2009f), in accordance with the EPA *National Functional Guidelines for Chlorinated Dioxin/Furan Data Review* (EPA 2002). As part of this effort, results were evaluated versus the various quality control (QC) indicators used to denote the effectiveness of the analytical method. When QC indicators failed to meet the prescribed requirements, data validation qualifiers were assigned to affected results. While developing background dioxin concentrations, qualifications noted in the data validation reports were closely examined to assess their impact on usability. Attachment 4 contains all of the data validation results for the Montana dioxin background study.

2.2 Data Validation Summary

In keeping with EPA data validation guidance, the QA/QC indicators reviewed for the Montana dioxin background data set include those listed immediately below. Specific QA/QC issues relative to analytical performance are presented in text following the listed items. Data were qualified as appropriate.

1. Holding times and sample preservation
2. Gas chromatograph/mass spectrometry (GC/MS) calibration and resolution
3. Window-defining mix check
4. Chromatographic resolution
5. Instrument stability
6. High-resolution GC/MS initial calibration
7. High-resolution GC/MS calibration verification
8. Identification criteria
9. Method blanks
10. Laboratory control samples
11. Toxicity equivalent factor and isomer specificity

12. Second column confirmation

13. Detection/quantitation limits

14. Surrogate recoveries.

Octachlorodibenzodioxin (OCDD) and octachlorodibenzofuran (OCDF) results in Samples MBDS-U09-R01, MBDS-U09-C01, MBDS-U09-I01, MBDS-U08-I01, MBDS-U08-R01, and MBDS-U08-C01 were qualified with a "J+" validation flag to denote the reported concentrations may be overestimated based on high laboratory control sample (LCS) recovery (Portage 2009a). The LCS and duplicate LCS percent recoveries (144 and 131%, respectively) were also outside their 70–130% limits. Multiple PCDD and PCDF congeners reported at estimated maximum possible concentrations in several samples were qualified with a "J+" validation flag (estimated with potential high bias), because the reported results are likely overestimated due to interference in the sample (Portage 2009b, 2009c, 2009d, 2009e, 2009f, 2009g). While the results qualified with a "J+" validation flag are considered to contain a high bias, they were retained in the overall data set. However, each was closely evaluated as an outlier during the statistical analysis.

OCDF and OCDD results in Sample MBDS-U17-I01 and total heptachlorinated dibenzofuran (HpCDF) in Sample MBDS-R17-F01 were qualified with a "J-" validation flag to denote the reported concentration is likely underestimated (biased low) due to low internal standard recovery. These results were also retained in the overall data set but were closely evaluated as outliers during the statistical analyses.

During validation, instances were noted when determinations of certain PCDD or PCDF congeners were severely impacted by interference. Sample results reported under these conditions were rejected during data validation and assigned "R" validation qualifiers. Specifically, the reported results for 1,2,3,7,8- pentachlorinated dibenzofuran (PeCDF) in Samples MBDS-U09-R01, MBDS-U09-C01, MBDS-U09-I01, MBDS-U08-I01, MBDS-U08-R01, MBDS-U08-C01 (Portage 2009a), MBDS-U17-I01, MBDS-U17-C01, MBDS-U19-R02, MBDS-U19-C01, MBDS-U20-R01, MBDS-U20-C01, MBDS-U18-R01, MBDS-U18-I01, and MBDS-U18-C01 (Portage 2009h) were qualified as rejected because of interference from polychlorinated diphenyl ethers (PCDE). In Samples MBDS-R13-A01 (Portage 2009c), MBDS-U06-C01, and MBDS-U06-R01 (Portage 2009d), 1,2,3,4,6,7,8-HpCDF was reported at an estimated maximum possible concentration and also qualified as rejected because of interference from PCDE. The result reported for 1,2,3,6,7,8- hexachlorinated dibenzofurans (HxCDF) in Sample MBDS-U07-I01 was reported at an estimated maximum possible concentration and was qualified as rejected because of PCDE interference (Portage 2009d). These data were removed from the data set(s) prior to computing background concentrations to avoid introducing a high bias to the calculated background concentrations.

During validation, low-level, positive detections were noted for PCDD or PCDF congeners in laboratory method blanks and trip blanks (Portage 2009a, 2009b, 2009c, 2009d, 2009e, 2009f, 2009g, 2009h). In these instances, the sample results were evaluated versus blank concentrations. Samples whose measured PCDD or PCDF concentrations were less than five times the level measured in the blank were qualified with either a "U" (nondetect) or "UJ" (nondetect, estimated) qualifier. These data are considered false positives and were treated as nondetects in the statistical analyses. All of the remaining validation qualifiers assigned were "J" flags to denote that the reported results were estimates with an undetermined bias. Neither severe quality control discrepancies nor uncommon interferences for a soil matrix were noted in any of these cases, and the impact of the "J" validation flags on data usability is minimal.

Field QA samples (equipment rinsate blanks, trip blanks, and field duplicates) were collected in accordance with the QAPP (CDM 2007). Field blanks were assessed during data validation, and data qualification flags were assigned based on positive detections. Six locations were collected as co-located field duplicates. Of the results reported, only those with validated detections in both samples were evaluated for precision. Thirty-three validated data points were evaluated for precision based on values that were detected in both samples. Of those, 82% of the data met the 35% target relative percent difference.

2.3 Comparison of Data Subgroups

Samples were collected from two primary subgroups of data and from six secondary subgroups (Table 1). A nested analysis of variance (ANOVA) test was used in developing summary statistics to determine whether the data from the two main settings (rural or urban) are different from one another or whether statewide data represent one large dioxin population. The nested ANOVA also determines whether any of the rural subgroups differ from one another and whether the urban subgroups differ from one another. However, the nested ANOVA can only determine whether any difference exists in the subgroups; the test will not identify where there are differences. Therefore, a one-way ANOVA evaluation was completed on the overall urban and overall rural data sets to clarify any detected differences in the subgroups. This ANOVA analysis differs from the examination of the complete data sets (rural versus urban) in that it examined only the urban data and its subgroups, and then a separate ANOVA was performed to examine only the rural data and its subgroups. Table 3 provides the results of the nested ANOVA and both one-way ANOVA evaluations for Montana BIR results.

Table 3. Nested and one-way ANOVA results for Montana dioxin background data as TEQ.

Nested ANOVA

	Degrees of Freedom	Sum of Squares	Mean Squared Error	F-Value	P-Value
Rural/Urban	2	44.3515	22.17573	6.796558	0.0016271
Subgroups	6	2.693	0.44897	0.137602	0.9910454
Residuals	114	371.958	3.26279		
Total	122	419.0025			

One-way ANOVA for Urban Subgroups

	Degrees of Freedom	Sum of Squares	Mean Squared Error	F-Value	P-Value
Urban Subgroups	2	1.505	0.7525	0.12579	0.882033
Residuals	59	352.9331	5.9819		
Total	61	354.4381			

One-way ANOVA for Rural Subgroups

	Degrees of Freedom	Sum of Squares	Mean Squared Error	F-Value	P-Value
Rural Subgroups	2	0.04918	0.02459	0.0661	0.936109
Residuals	58	21.57672	0.37201		
Total	60	21.6259			

The ANOVA evaluation examined the mean concentrations determined for complete urban and rural data sets (including all subgroups) to determine whether significant differences were present between urban and rural settings. Sum of squares, mean squared errors, F-statistics, and P-values were developed for each data set to perform the ANOVA evaluation. The P-value is used to determine whether significant differences exist between major groups and/or subgroups. If the P-value is greater than or equal to 0.05, then it can be assumed that the subunits come from the same population. If the P-value is less than 0.05, then the groups are considered statistically different from one another.

2.3.1 Overall Urban versus Overall Rural

The ANOVA evaluation revealed a P-value of 0.0016 when the overall urban and overall rural data sets were compared. This indicates that the urban and rural areas have significantly different levels of dioxins and therefore each represents a separate population. The nested ANOVA also shows that the subgroups have a P-value of 0.991. This indicates that (a) the rural subgroups do not differ from each other and therefore do not represent separate populations, and (b) that the urban subgroups do not differ and therefore do not represent different populations. It is sufficient to distinguish data as urban or rural. One-way ANOVAs were run on urban subgroups and rural subgroups to provide further clarification. Figure 5 shows a visual representation of the differences in TEQ between the rural and urban groups.

2.3.2 Overall Urban versus Individual Urban Subgroups

The ANOVA evaluation revealed a P-value of 0.882 when the overall urban data set was compared with individual urban subgroups. This indicates a relatively high level of agreement between all data sets and all urban subgroups, supporting the idea that statewide urban dioxins represent a single population. Figure 6 illustrates some differences between the urban subgroups, but this difference is not sufficient to support establishing separate urban subgroups

2.3.3 Overall Rural versus Individual Rural Subgroups

The ANOVA evaluation revealed a P-value of 0.936 when the overall rural data set was compared with individual rural subgroups. This indicates a relatively high level of agreement between all rural subgroups and statewide rural dioxins present in a single population. Figure 7 provides a visual representation of the ANOVA analysis for rural data.

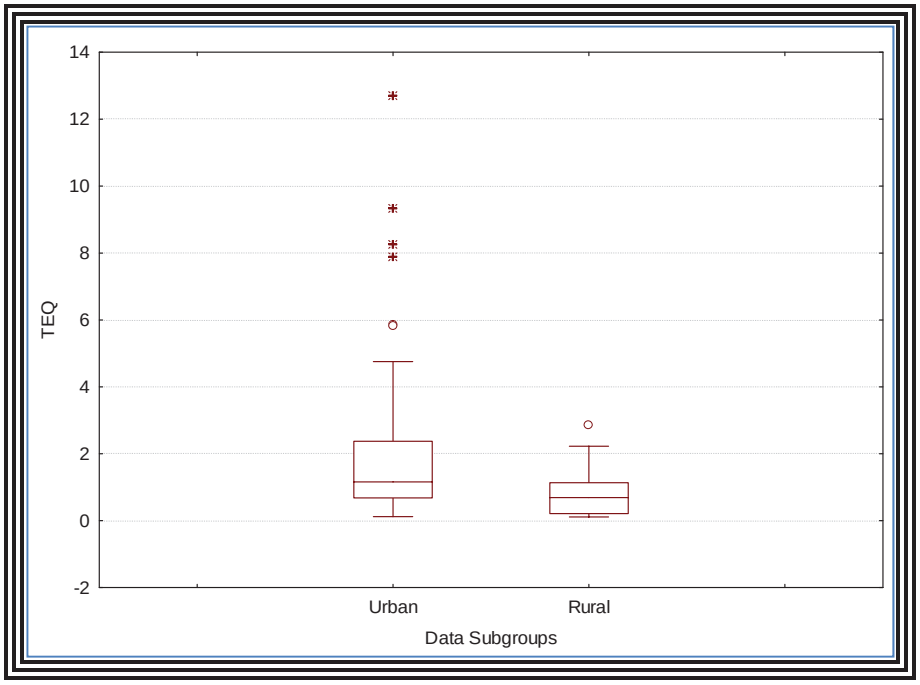

Figure 5. ANOVA – Montana urban versus rural dioxin/dibenzofuran results.

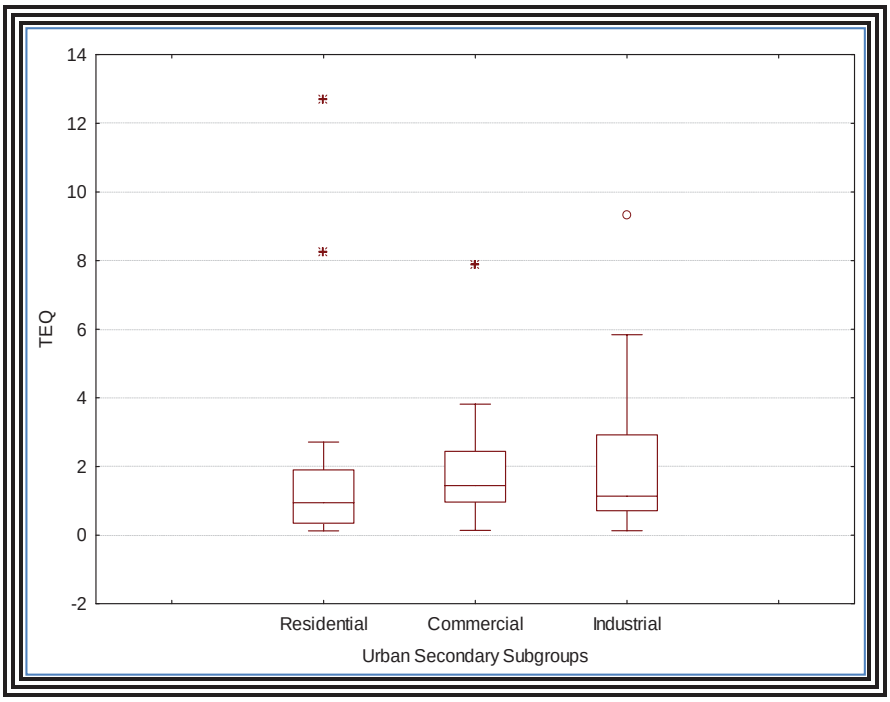

Figure 6. ANOVA – Montana urban subgroup dioxin/dibenzofuran results.

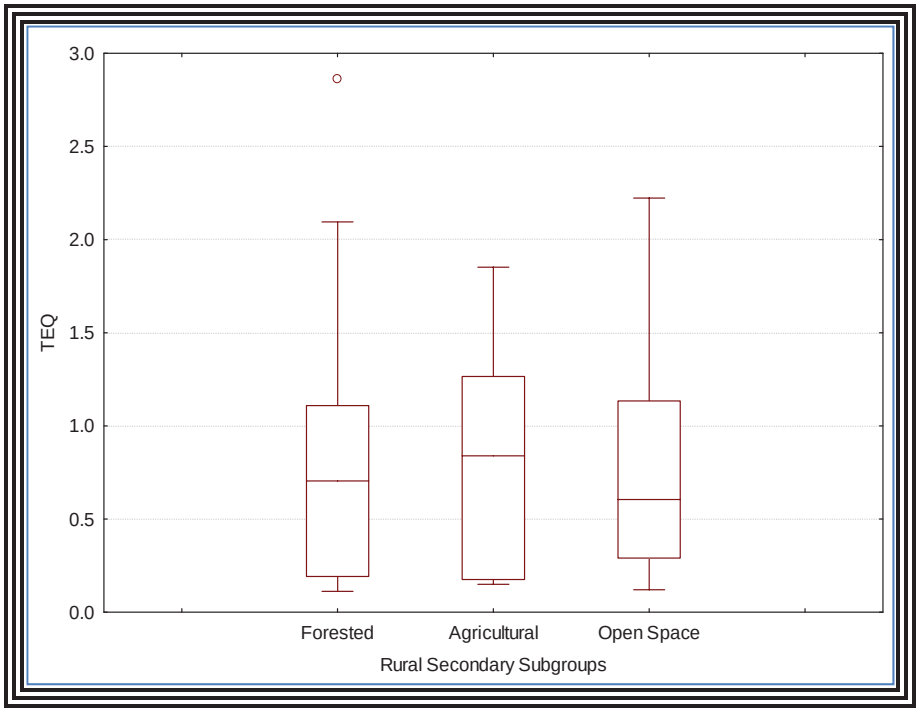

Figure 7. ANOVA – Montana rural subgroup dioxin/dibenzofuran results.

2.4 Summary Statistics

This section contains the summary statistics and data analysis for the complete Montana background dioxin data set. Data were examined for outliers, and summary statistics are presented both with outliers and without outliers to aid data users in understanding their effect. Summary statistics include the maximum and minimum detected values, range of detection limits (when applicable), percentage of detected data, mean, standard deviation, CV, UCL, and UTL. The background UTLs are presented in Section 2.6. Tables B-1 through B-9 (in Appendix B) (provide the summary statistics for each of the major land-use types and their corresponding subgroups. Histograms, box plots, and normal-quantile plots are presented in Attachments 1–3. Methods used to compute UCLs and UTLs are listed in Appendix A.

When examining Montana background dioxin data, outliers were evaluated for any trends. As noted previously, outliers were both included and excluded from data sets. The tables contained in Appendix B present statistical results including and excluding the outliers. The following summarizes specifics concerning outliers in the background data set:

- The highest concentration for TCDD or TCDF congeners noted in an outlier was in Sample MBDS-U20-C01. Sample MBDS-U20-C01 was collected from Lion's Park in Missoula. The TEQ for this sample was 7.860.

- The majority of target compounds found to have outliers were identified in the urban industrial data set in Sample MBDS-U04-I01. This sample was collected on the east side of BBWA Canal north of King Avenue in Billings. The TEQ for this sample was 9.336.

- Two other samples in the urban industrial data set had outliers originating from Samples MBDS-U18-I01 and MBDS-U14-I01. MBDS-U18-I01was collected from an open space/trail near Loyola Sacred Heart in Missoula, and Sample MBDS-U14-I01 was collected from batch fields or Centennial Park in Helena. The TEQ values for these two samples were 5.840 and 5.804, respectively.

- Outliers for the urban residential data set primarily came from Sample MBDS-U19-R01 and MBDS-U18-R01. MBDS-U19-R01was collected from Boyd Park in Missoula, and MBDS-U18-R01 was collected from Northside Park in Missoula. The TEQ values for these samples were 12.69 and 8.226, respectively.

- The rural agricultural data had three congeners that were outliers: MBDS-R10-A01 and MBDS-R02-A01. MBDS-R10-A01 was collected near Freezeout Lake near Fairfield, and MBDS-R02-A01 was collected at the north end of Kuhn's Wildlife Management Area in agricultural fields near Whitefish. The TEQ values for these samples were 1.224 and 1.852, respectively.

- All of the outliers in the rural forested data were in two samples: MBDS-R10-F01 and MBDS-R02-F01. MBDS-R10-F01 was collected from the Trout Creek trailhead in the Helena National Forest, and MBDS-R02-F01 was collected from Lone Pine State Park near Kalispell. The TEQ values for these samples were 2.095 and 2.859, respectively.

- The majority of the outliers noted for the rural open data originated from Samples MBDS-R11-001 and MBDS-R02-O01. MBDS-R11-O01 was collected 5 miles west of Buffalo, while MBDS-R02-O01 was collected between Lake Elwell and Road 366 in Section 36 in Flathead National Forest. The TEQ values for these samples were 1.405 and 2.223, respectively.

It is not surprising the outliers are clustered to certain samples. Often, when a sample exhibits higher concentrations of one congener, it may also show higher concentrations of other congeners. This is the case with the majority of the outliers noted in the Montana dioxin background data set.

It is also worth noting that none of the outliers observed in the statewide data set resulted from laboratory reporting errors. However, several of the outliers did result from inadequate quantitation at the time of analysis, resulting in QC issues that rendered these results unusable. In these cases, results were qualified as "R" (rejected) during data validation due to the extremely low confidence in the reported concentrations. In all cases, the rejected results were omitted from the data set so as not to bias background concentrations high. Section 2.2 discusses the specific issues and samples impacted by analytical difficulties. None of the samples mentioned in the above bulleted list contained R-flagged data.

2.5 Upper Confidence Limits

UCLs provide important information about the data mean while providing helpful estimates of the population mean. A one-sample *t*-test can be performed by comparing the UCL to a regulatory threshold that is based on what the mean concentration of an analyte may be. However, UCLs *cannot* be compared with each other to perform any type of statistical test.

The UCLs presented in this BIR were computed for each congener, overall TEQ, and each data group and subgroup. The UCLs in this document have a level of confidence of 95% (i.e., 95% UCL), meaning that if all possible data sets of samples of size *n* were collected from Montana surface soils and a

sample mean and UCL were computed, 95% of the UCLs would be greater than the true population mean concentration. All UCLs found in this BIR were computed using ProUCL Version 4.00.04 (EPA 2009c).

2.6 Upper Tolerance Limits

A UTL is designed to be an upper bound on possible values that may be found in the background population. As with the UCL, UTLs require a very specific type of comparison. The appropriate comparison for a UTL is to compare all detected sample concentrations (most of the time these concentrations will be TEQs) from a site to the appropriate background dioxin UTL. If the maximum TEQ value from a site is less than the appropriate background UTL, it can be concluded that the dioxin concentration for that site does not exceed background levels. If one or more TEQ value exceeds the calculated background concentration, it is likely that site dioxin levels are greater than background. This comparison may also be performed with individual dioxin congeners in some circumstances. Table 4 presents summary statistics for TEQ values.

A UTL does not capture 100% of possible background values but rather captures a large percentage of those values with a specified degree of confidence. The UTLs used in this document are designed to capture 95% of the background population concentrations with 90% confidence. This means that 5% of the background values are expected to be larger than the UTL. Because of this, it is possible for the maximum detected concentration at a site to exceed the calculated background concentration even if site concentrations do not exceed background concentrations. This is particularly likely if a large number of samples (more than 20) are collected. Therefore, for large data sets, additional statistical analysis may be needed to determine whether background levels have indeed been exceeded.

In general, the UTLs for the urban and rural data sets are less than the UTLs for the combined (statewide) data set. This also occurred for the rural data UTLs when compared with the rural subgroups. The difference in UTLs occurs because the broader data sets (urban and rural) were computed using more samples than their associated subgroups. The corresponding error portion of the formula is divided by the square root of N, which results in a decrease in the error as the sample size increases. The UTLs for the total data set are greater than the subgroups, because the variation in the data is much larger for the statewide data set than the variance observed within the subgroups. Appendix A provides a complete examination for the intra-group and statewide comparisons.

The UTLs presented in this BIR are for informational purposes; they are not intended to represent regulatory values. The background information presented in this BIR does not preclude the collection of site-specific background dioxin samples. DEQ encourages those performing site characterization activities to perform site-specific background determinations whenever possible.

Table 4. Summary statistics for TEQ values.

	N	Number of Detects	Percentage of Detects (%)	Minimum Detected Value (ng/kg)	Maximum Detected Value (ng/kg)	Detection Limit (ng/kg)	Mean (ng/kg)	Standard Deviation (ng/kg)	Coefficient of Variation (%)	Upper Confidence Limit (ng/kg)	Upper Tolerance Limit (ng/kg)
All Data (Urban + Rural)	**123**	**NA**	**NA**	**0.112**	**12.69**	**NA**	**1.386**	**1.853**	**134%**	**2.43**	**2.43**
All Rural Data	**61**	**61**	**100**	**0.112**	**2.859**	**NA**	**0.79**	**0.6**	**76%**	**1.125**	**1.817**
Rural-Open (outliers removed)	20	20	100	0.12	1.405	NA	0.678	0.43	63%	0.844	1.266
Rural-Agricultural	20	20	100	0.149	1.852	NA	0.811	0.57	70%	1.366	1.503
Rural-Forested (outliers removed)	18	18	100	0.112	1.203	NA	0.626	0.432	69%	0.891	1.203
All Urban Data	**62**	**62**	**100**	**0.124**	**12.69**	**NA**	**1.972**	**2.41**	**122%**	**3.306**	**7.456**
Urban-Residential (outliers removed)	21	21	100	0.124	2.71	NA	0.982	0.756	77%	1.375	2.556
Urban-Commercial (outlier removed)	18	18	100	0.14	3.818	NA	1.627	1.054	65%	2.059	3.818
Urban-Industrial	20	20	100	0.13	9.336	NA	2.18	2.427	111%	4.545	5.84

3. CONCLUSIONS

As the background UTLs and the ANOVA evaluation illustrate, there are definite patterns in the background values for Montana surface soils. Figure 8 provides a visual representation of background dioxin distribution statewide.

Figure 8 reveals that rural areas, which dominate the central and eastern portions of Montana, show little or no background concentrations of dioxins in surface soils. The exception to this would be a geographical area south/southeast of Billings. This is a reasonable finding, given the heavy industrial production related to oil and agricultural products that takes place in this area. It is also reasonable to conclude the noted area may be considered part of the Billings urban area.

Conversely, urban areas in and around six of the seven largest cities (excluding Great Falls) show elevated concentrations of dioxins relative to rural areas. This result was not unexpected, given the long history of mining, wood products, agriculture, and other heavy industrial activities that have taken place in and around these cities for many years.

As preceding sections note, the levels of dioxins in the urban and rural settings differ at levels that are statistically significant. The overall Montana TEQ background UTL was computed to be 3.7 ng/kg, while the urban TEQ was 7.5 ng/kg and the rural TEQ was 1.8 ng/kg. In comparison, the EPA's risk-based Regional Screening Level (RSL) is 4.5 ng/kg for residential soil and 18 ng/kg for industrial soils (EPA 2010). In conclusion, none of the Montana background dioxin TEQs exceed the applicable risk-based RSLs (based on specific land use).

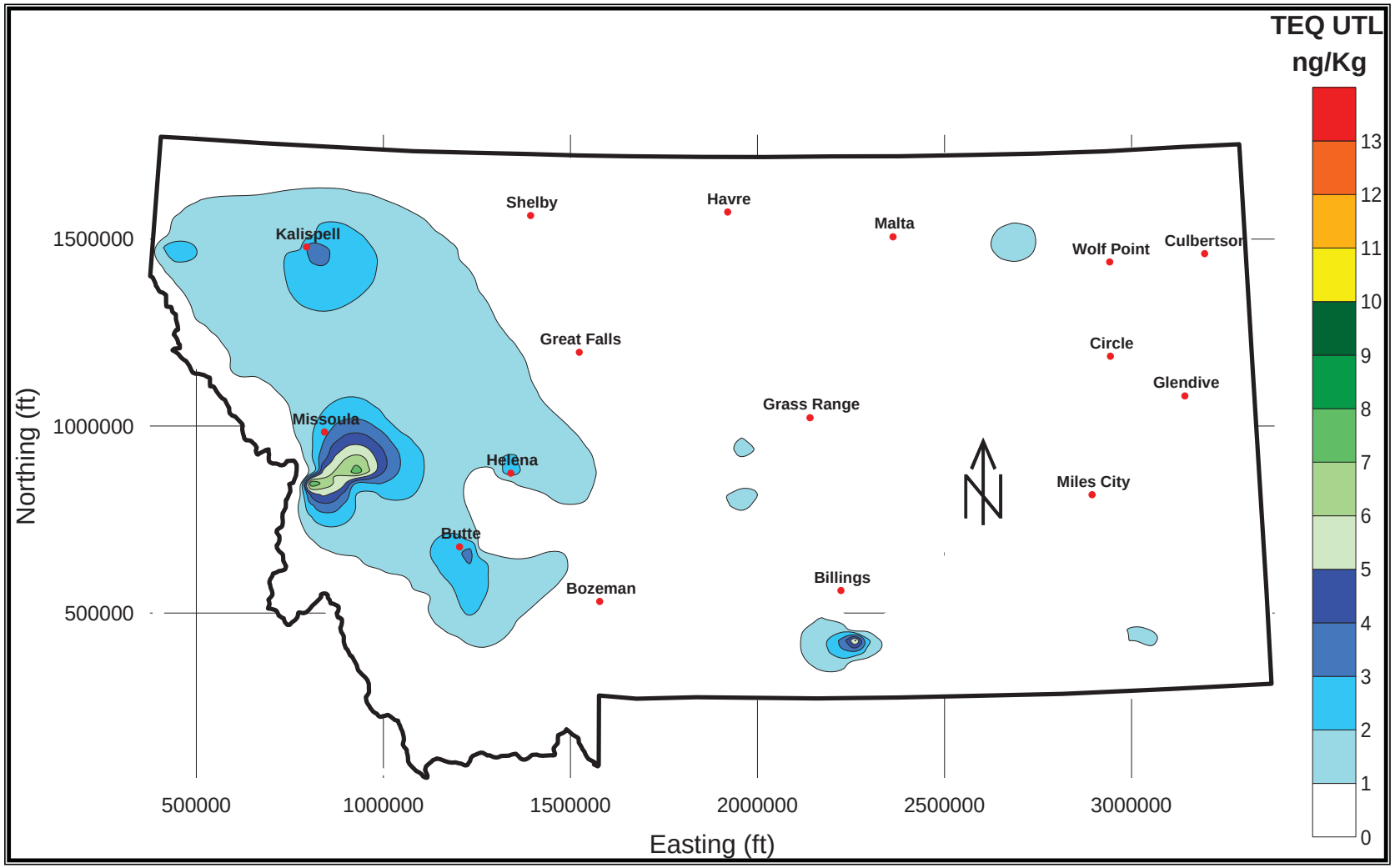

Figure 8. Distribution of dioxins and dibenzofurans in Montana.

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