HAWAIIAN ISLANDS SOIL METAL BACKGROUND EVALUATION REPORT

Hawai'i Department of Health Hazard Evaluation and Emergency Response 919 Ala Moana Blvd., Room 206 Honolulu, HI 96814

May 2012

AECOM

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Prepared for:

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ACRONYMS AND ABBREVIATIONS

| 0/ | nercont |
|----------|---|
| % | percent |
| Ag | silver |
| Al | aluminum |
| As | arsenic |
| Ва | barium |
| Be | beryllium |
| BTV | background threshold value |
| Са | calcium |
| Cd | cadmium |
| Со | cobalt |
| Cr | chromium |
| Cu | copper |
| EAL | environmental action level |
| EBA | environmental background analysis |
| EPA | Environmental Protection Agency, United States |
| Fe | iron |
| HDOH | Hawai'i Department of Health |
| Hg | mercury |
| HQ | hazard quotient |
| J | detected, estimated concentration (data qualifier) |
| K | potassium |
| Mg | magnesium |
| mg/kg | milligram per kilogram |
| Mn | manganese |
| Мо | molybdenum |
| Na | sodium |
| Ni | nickel |
| NRCS | Natural Resources Conservation Service |
| Р | phosphorus |
| PARCCS | precision, accuracy, representativeness, completeness, comparability, and sensitivity |
| Pb | lead |
| r | correlation coefficient |
| Sb | antimony |
| Se | selenium |
| Sn | tin |
| Sr | strontium |
| Ti | titanium |
| TI | thallium |
| U | non-detect concentration (data qualifier) |
| UBC | upper bound concentration |
| UCL | upper confidence limit |
| U.S. | United States |
| USCS | Unified Soil Classification System |
| UTL | upper tolerance limit |
| V | vanadium |
| Ŵ | tungsten |
| Zn | zinc |
| <u>-</u> | |



1.0 INTRODUCTION

This report presents the results of environmental background analysis (EBA) to develop estimates of background concentration ranges for target elements in soils of the seven main Hawaiian islands (Kaua'i, O'ahu, Moloka'i, Lana'i, Maui, Kaho'olawe, and Hawai'i island). The following 29 target elements (26 metals, 2 metalloids, and 1 non-metal) are evaluated:

Metals:

- Aluminum (AI) ٠
- Barium (Ba)
- Beryllium (Be)
- Cadmium (Cd)
- Calcium (Ca)
- Chromium (Cr)
- Cobalt (Co)
- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Magnesium (Mg)
- Manganese (Mn)
 - Mercury (Hg)
- Metalloids:
 - Antimony (Sb)
 - Arsenic (As)

Non-Metal:

Phosphorus (P) •

Concentration data and soil characteristics reported for soil samples collected on the main Hawaiian islands were evaluated to estimate background concentration ranges based on evidence including the spatial distribution of the data, population distribution characteristics, and geochemical association relationships. This EBA report was prepared for the Hawai'i Department of Health (HDOH) Office of Hazard Evaluation and Emergency Response.

1.1 **OBJECTIVES**

The objectives of the Hawai'i Soil EBA are as follows:

- Estimate the background concentration range for each target element.
- Identify potential data and information needs to provide a more comprehensive and • representative dataset for further refinement of the estimated background concentration range for each target element.

Most of the data compiled and used for the analysis represent soil in "non-impacted areas," with some data points included from literature studies representing potentially "impacted areas." The



- Molybdenum (Mo)
- Nickel (Ni) ٠
- Potassium (K)
- Selenium (Se) •
- Strontium (Sr) Silver (Ag)

Sodium (Na)

Thallium (TI)

Titanium (Ti)

٠

٠

٠

•

1

٠ Tungsten (W)

Tin (Sn)

- Zinc (Zn) .
- Vanadium (V) •

background analysis methods presented in the Navy guidance document *Guidance for Environmental Background Analysis Volume I: Soil* (NFESC 2002) were used to evaluate the data and develop the estimated background ranges. The background range for each element was first estimated by evaluating the evidence provided by a combined plot consisting of a cumulative probability plot (representing the distribution of the data population) and a series of univariate plots (representing the spatial distribution of the data). If the combined plot analysis did not provide conclusive evidence to support a background estimate for a particular target element, then a geochemical correlation plot was constructed to further evaluate background for the element of concern.

2.0 SOILS IN THE HAWAIIAN ISLANDS

Major factors contributing to soil formation in Hawai'i produced the diversity in types and characteristics of Hawaiian soils. These factors include the different types of parent rock, the different geologic ages of the islands, and the wide range of climatic conditions that occur throughout the islands. These factors affect elemental concentrations in soil due to differences in concentrations present in the primary (rock-forming) minerals within the parent rock, and the physical and chemical weathering processes that result in formation of different soil horizons and secondary minerals.

The United States (U.S.) Department of Agriculture soil order classification system (USDA 1999) provides a general system for differentiating soil types present in Hawai'i based on measurable properties. Soils throughout the world can be classified into twelve soil orders. Due to the variety of climates present in Hawai'i and varying degrees of weathering, 10 of the 12 soil orders are present in Hawai'i. Figure 1 through Figure 5 present soil order distribution maps for each of the main Hawaiian islands, and depict the soil sampling locations corresponding to the data used in the EBA. Deenik & McClellan (2007) provides a detailed discussion of the general types of soils that occur in Hawai'i. The ten soil orders that occur in Hawai'i are described in Table 1.

| Soil Order | Description | |
|-------------|---|--|
| Andisols | Soils derived from volcanic ejecta (e.g., ash, cinder). Most extensive soil type present in Hawai'i. Weathered clay minerals in Andisols have high AI and Fe contents with strong capacity to adsorb P. Low bulk density (0.4–0.8 g/cm ³). High organic content. More fertile in areas with rainfall < 60 inches per year; in areas of higher rainfall Andisols are depleted in nutrients (Ca and K). | |
| Histosols | Organic soils (> 50% organic matter). Typically formed on recent lava flows from materials derived from decaying vegetation. Slightly acidic to neutral in areas of moderate rainfall with high Ca and K contents; more acidic in areas of high rainfall with less Ca and K content due to leaching. | |
| Oxisols | Product of weathering of basaltic lava. Highly weathered and low fertility due to leaching of most minerals (e.g., silicate clays); high iron and aluminum oxides. | |
| Mollisols | Nutrient-rich soils found typically on grass lands. Typically reddish in colors due to high iron content. Neutral to slightly alkaline; high Ca, Mg and K content; clay minerals do not adsorb P very well. | |
| Inceptisols | Young soils; very diverse in characteristics depending on location of formation. Formed from alluvium in river valleys with high nutrient content. In older and/or wetter landscapes, very acidic with low nutrient content and high levels of Al and Mn. | |
| Ultisols | Weathered soils rich in kaolinite (silicate clay). Present in mountainous areas. Acidic to strongly acidic, deficient in plant nutrients (Ca, K, P), high Al content binding P in soil. | |
| Aridisols | Desert soils found in coastal areas on leeward sides with low rainfall and prolonged dry periods. High salt conte due to lack of weathering and leaching. | |
| Entisols | Poorly developed soils that are either very young or old soils that have not undergone significant soil formation processes. Sandy soils formed from coral limestone in coastal areas are deficient in nutrients (P and K). Near intermittent streams, Entisols can develop into organic rich sandy soil from alluvial volcanic ash with high Ca, K, and Mg contents. | |
| Vertisols | Clay-rich soils, neutral to alkaline in Ph, typically present in dry environments in lowland regions. Low organic matter; unstable soil due to significant shrink-swell behavior during dry-wet conditions, respectively. Low organic content. | |
| Spodosol | Formed under forest vegetation in moist to wet areas. Generally acidic, infertile soils. Limited to Kaua'i, Moloka'i, and Lana'i. | |



3.0 ENVIRONMENTAL BACKGROUND ANALYSIS METHODS AND PROCEDURES

This section provides a summary of the dataset, methods, and procedures used to develop estimates of background concentration ranges for the 29 target elements identified for the Hawai'i Soil EBA.

3.1 DATASET

The Hawai'i Soil EBA database includes concentration data representing a total of 187 soil samples collected throughout the main Hawaiian islands (i.e., Kaua'i, O'ahu, Moloka'i, Lana'i, Maui, Kaho'olawe, and Hawai'i island). The database was compiled from data provided by the HDOH, the Natural Resources Conservation Service (NRCS), and available literature reports. The database includes analytical results representing concentrations of 29 elements in surface soil. Figure 6 illustrates the soil sampling locations and distributions of the data used for the EBA.

The 29 target elements were divided into three categories for the EBA:

• Target elements with established HDOH (2011) environmental action levels (EALs):

| Antimony (Sb) | Mercury (Hg) |
|----------------|-----------------|
| Arsenic (As) | Molybdenum (Mo) |
| Barium (Ba) | Nickel (Ni) |
| Beryllium (Be) | Selenium (Se) |
| Cadmium (Cd) | Silver (Ag) |
| Chromium (Cr) | Thallium (TI) |
| Cobalt (Co) | Vanadium (V) |
| Copper (Cu) | Zinc (Zn) |
| Lead (Pb) | |

• Target elements with no established HDOH EALs:

| Aluminum (Al) | Strontium (Sr) |
|----------------|----------------|
| Calcium (Ca) | Tin (Sn) |
| Iron (Fe) | Titanium (Ti) |
| Manganese (Mn) | Tungsten (W) |

• Additional target elements:

| Magnesium (Mg) | Potassium (K) |
|----------------|---------------|
| Phosphorus | Sodium (Na) |

The Hawai'i Soil EBA concentration database was compiled from several data sources:

- The HDOH provided data representing 67 surface soil samples collected at 47 locations throughout the main Hawaiian islands. Eleven of the samples were collected as part of site inspections/site investigations performed by the U.S. Environmental Protection Agency (EPA) and HDOH from 2002 through 2006 (HDOH 2002, Weston 2004, TEC 2006, and HDOH and Tetra Tech 2006). The remaining samples were collected by the HDOH in 2010 as part of the effort to provide additional data to support the Hawai'i Soil EBA.
- Data representing concentrations of the target elements reported for 59 surface soil samples collected from all seven main Hawaiian islands were obtained from the NRCS National Cooperative Soil Characterization Database (http://ssldata.nrcs.usda.gov). Based on the available sampling date records, the NRCS soil data were collected from 1982 to 2008.
- Additional data were obtained from previous research studies documented in the literature. 41 samples were collected as part of studies of chromium distribution (Nakamura and Sherman 1958) and vanadium content of Hawaiian island soils (Nakamura and Sherman 1961). Arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver



concentration data reported for five surface soil samples were obtained from Brownfields Community Assessment studies conducted by EPA on Kaua'i (ERM 2006a,b). Arsenic, cadmium, cobalt, and copper concentration data reported for 15 surface soil samples were obtained from a study of the abundance and distribution of arsenic in Hawaiian soils and sediments conducted by a University of Hawai'i student (deGelleke 2007).

Figure 6 illustrates the spatial distribution of sampling locations represented in the database compared to the land use zone intended for the area, and lists the number of data points available for each island. The numbers of samples represented in the datasets for Kaua'i (38), O'ahu (58), and Hawai'i island (40) are relatively large, while the Moloka'i (9), Lana'i (2), and Kaho'olawe (8) datasets are relatively small. In general, most of the data were collected in relatively undisturbed areas. Although some of the samples were collected in residential and industrial areas, most of the data represent surface soil samples collected from range/farm (agricultural) lands and forest lands. The sampling locations tend to be more concentrated along the perimeter of the islands (which are relatively accessible), and less concentrated in the interior, mountainous areas where access is limited and the soil formations are not well developed. The sampling locations are generally distributed relatively equally on both the leeward and windward sides of the islands, except for Hawai'i island, where there is a distinct lack of data on the southwest portion of the island (South Kona District).

All data including those potentially collected from impacted areas will be part of the analysis to provide a larger dataset for the background analysis. In addition, the combined plots analysis technique (as detailed in Section 3.2.1) is designed to identify multiple populations present in the dataset. Therefore, data from impacted areas will be isolated and will not affect the estimated upper range of background concentration.

3.1.1 Data Quality

The data obtained from the NRCS database are considered to be of sufficient quality for use in this study, and most likely represent non-impacted or minimally impacted soil given that NRCS pedon sampling locations are carefully limited to lands that are generally undisturbed or minimally disturbed.

Data representing the 43 soil samples collected by the HDOH for the Hawai'i Soil EBA were evaluated against the precision, accuracy, representativeness, completeness, comparability, and sensitivity (PARCCS) criteria for data quality and usability. The data quality assessment is presented as a separate report, attached in Appendix A. The data quality assessment concluded that there were no rejected data based on the evaluation against the PARCCS criteria, and the data are considered suitable for use in the EBA. Data obtained from other sources are also considered to be of sufficient quality and representative for EBA.

3.2 ENVIRONMENTAL BACKGROUND ANALYSIS APPROACHES

The background concentration range for each target element was estimated by evaluating cumulative probability plots and spatial univariate plots, in addition to multiple other lines of evidence. The plots were evaluated to determine if the dataset for the target element may represent more than one distinct concentration population. If a single population was identified for the target element, then the data were evaluated to confirm that they most likely represent background conditions. If two or more populations were identified for the target element, detailed spatial analysis, elemental association, and geochemical analysis were used to distinguish between concentrations representing background conditions and elevated concentrations that may represent contamination.

3.2.1 Combined Plots Analysis

For each target element, a combined plot consisting of a cumulative probability plot and a series of univariate plots was constructed to distinguish between data representing separate concentration



populations. A *probability plot* is a graph of concentration values vs. their cumulative probabilities. Probability plots are useful to graphically:

- Illustrate how well the data fit a particular distribution (e.g., log-normal or normal).
- Identify outliers (e.g., natural or contamination).
- Identify inflection points or other discontinuities that may define thresholds associated with the upper or lower bounds of separate concentration populations.

Linear-scale and log-scale probability plots were constructed for each target element because concentrations of naturally occurring elements typically fit either a normal or log-normal distribution. A normally distributed dataset will plot as a straight-line on a linear-scale probability plot, whereas a log-normally distributed data set will plot as a straight line on a log-scale plot.

Probability plots can be used to estimate background concentration ranges by eliminating outliers representing potential contamination, and identifying inflection points or other discontinuities representing the boundaries between separate populations (e.g., data representing the background concentration range vs. elevated concentrations potentially associated with a site-related release). Data points that plot on or near a straight line and form a continuous distribution are likely to represent a single population and similar geochemical conditions. The presence of multiple populations in a dataset results in a segmented probability plot, i.e., data that fall along more than one straight line. Data points representing elevated or lower concentrations that do not fit a continuous distribution are considered outliers. By identifying the outliers and re-plotting the dataset, a clearer picture of the underlying distribution can be obtained.

The probability plotting method for background analysis typically involves one or more of the following cases:

- *Single Populations*: A non-segmented probability plot with no inflection points indicates a single population (e.g., the background population).
- Background Delimiters: Segmented probability plots or probability plots with inflection points suggest the existence of multiple subpopulations. An inflection point in which the slope increases or a break between segments with a gradual slope followed by a segment with a steeper slope represents the delimiter between a lower concentration subpopulation and a higher concentration subpopulation. The inflection point could represent the break between background concentrations and concentrations attributable to a chemical release, or it could represent two different mineralogical or geochemical conditions (both of which are background).
- Multiple Inflection Points: The background range may be composed of multiple natural or anthropogenic subpopulations. In this situation, the data set will yield segmented probability plots with multiple inflection points, and the lowest inflection point will not always represent the upper bound of the background range. Evaluation of univariate plots may help to identify the inflection point that represents the background delimiter.
- Non-delimiting Inflection Points: Not all inflection points can be considered background delimiters. Specifically, if the subpopulation above an inflection point forms a segment with a more gradual slope than the lower subpopulation, then the inflection point should not be considered a background delimiter. In most cases, both segments are treated as part of the same population unless evidence indicating the presence of more than one separate data population is revealed by the associated univariate plots.

Univariate plots are used to graphically segregate the concentration data into subsets corresponding to spatial characteristics (e.g., sampling location, sampling depth, soil type) and plot the concentration range for each subset with respect to a single numeric axis, the y-axis. Four types of univariate plots were constructed for each target element evaluated for the Hawai'i Soil EBA:



- A *sampling location univariate plot* to depict concentration ranges corresponding to the different islands.
- A *data source univariate plot* to depict concentration ranges corresponding to the various data sources.
- A *data qualifier univariate plot* to classify the individual data points according to their reliability and usability as evidence for estimating the background range.
- A *soil order univariate plot* to depict the concentration ranges corresponding to different types of soil as indicted by the soil order classifications.

Different soil orders have different characteristics such as parent rock type, clay content, and organic carbon content. Metals tend to adsorb strongly to clay and organic material; therefore, concentrations of naturally occurring metals tend to be highest in fine-grained soils that contain high percentages of clay or organic particles (NFESC 2002). Hawaiian soils derived from volcanic parent rocks (e.g., basalts) generally have higher concentrations of metals compared to soil derived from sedimentary parent rocks (e.g., coralline limestones).

Table 2 summarizes the laboratory data qualifiers used in this analysis. All data are included and presented on the combined plots; however, only NQ (no qualifier) and J (estimated) values were used in the analysis to estimate background concentration range for each target element. The complete set of qualified data from the HDOH 2010 sampling event is presented in Appendix A, Attachment 1. The complete set of qualified data used in the combined plots is presented in Appendix B, Table B-1.

| Qualifier | Definition | Explanation |
|-----------|-------------------------|--|
| NQ | Not qualified | All quality control criteria associated with the analytical result were within acceptance criteria and the concentration was quantified at a value above the laboratory reporting limit. |
| J | Estimated concentration | The associated concentration value is an estimated quantity. |

Table 2: Data Qualifiers Used in the Analysis

Note: Complete qualified data based on third party validation are available in Appendix A, Attachment 1. The complete set of qualified data used in the combined plots is presented in Appendix B, Table B-1.

The background range for each target element was estimated by evaluating the spatial and soil type distribution patterns demonstrated by the univariate plots in conjunction with the population characteristics displayed by the probability plot. Multiple lines of evidence were thus used to estimate the background range for each target element. The combined plot analysis process is summarized in Table 3.



| Evaluation Criterion | | Conclusions |
|----------------------|--|---|
| 1. | Does the probability plot show an inflection point or discontinuity that could differentiate between the background population and a population that represents potential contamination? | An inflection point marking an increase in slope may correspond to the threshold value separating a background population from a higher concentration population that represents natural outliers or potential anthropogenic contamination. A break (discontinuity) between segments may indicate two separate populations, e.g., the background population and a population representing potential contamination. If a low-concentration segment plots near a relatively straight line on a linear-scale probability plot, the segment is likely to represent a normally distributed background population. If a low-concentration segment plots near a relatively straight line on a log-scale probability plot, the segment is likely to represent a log-normally distributed background population. |
| 2. | Does the soil type univariate plot indicate that relatively high concentrations tend to occur only in certain types of soil? | If the concentration ranges for a given target element vary significantly according to soil type, the distribution of that element is more likely to reflect natural geochemical processes than contamination. If enrichment is due to natural geochemical processes, metal concentrations tend to be high in fine-grained soils such as clays and silts, and low in coarse-grained soils, such as sands and gravels. A chemical release can impact any type of soil; therefore, if elevated concentration ranges occur across different types of soil at a site, contamination should be suspected. |
| 3. | Does the sampling location univariate plot indicate that relatively high concentrations occur only on particular islands? | In addition to site-related contaminant releases, anthropogenic effects attributable to different current and historical land use practices and population densities may result in different concentration ranges for the individual islands. If a target element shows only small concentration differences among islands, the concentrations are likely to represent naturally occurring background levels as opposed to contamination or anthropogenic background. However, different islands have different geologic ages; therefore the rock and soil formations on each island have experienced varying amounts of physical and chemical weathering. These differences may result in different background concentration ranges for the individual islands. |

3.2.2 Geochemical Analysis

Geochemical analysis is used (1) when results of the combined univariate and cumulative probability plot analysis are inconclusive, (2) when there are strong associations between each target element, or (3) to support the background range estimates indicated by the combined univariate and cumulative probability plots. The distribution of metals and other elements in soil is controlled by several mechanisms, including geochemical, biological, chemical, physical processes, as well as by contaminant releases to the environment. Natural processes are important in controlling elemental distributions and associations. In contrast, site releases may disrupt the natural elemental associations. Therefore, potential contaminants may be identified by examining the relationships between elements in soils.

The strength of association for element pairs is initially determined by evaluating a matrix of correlation coefficients (*r* values) as shown in Table 4. Aluminum and iron are typically used as reference metals in geochemical association analysis to estimate background concentrations of target elements or metals of potential concern. Both aluminum and iron strongly correlate with a number of target elements in the dataset and are suitable to serve as reference metals for the analysis. Pairs of target elements can also be analyzed in the same manner if they are strongly correlated.

Reference and target element pairs with r values greater than 0.5 were evaluated further to determine whether geochemical correlation can be used to evaluate or support background concentration estimates. Data representing the target element and reference element were plotted on a log-log scatter plot and visually inspected to determine whether clear association is present or can be revealed by removing outliers that may represent elevated concentrations attributable to contamination. Data representing strongly associated pairs of elements tend to plot along a straight line on the log-log scatter plot. The strength of the association is quantified by fitting a straight-line through the data points using least squares regression analysis. The upper bound of the background concentration range is estimated by calculating the 95% prediction interval, which is the range within which the target element concentration (plotted with respect to the y-axis) corresponding to the reference element concentration (plotted with respect to the x-axis) is predicted to occur 95% of the



time. The upper bound of the background concentration range is estimated as the highest concentration of the target element that falls within the 95% prediction interval.

4.0 HAWAIIAN ISLANDS SOIL METAL EBA RESULTS

Results of the EBA are presented in this section. The combined cumulative probability and univariate plots are used to determine the following parameters for each target element:

- *Outlier:* data points with concentrations that are much higher or lower compared to the rest of the dataset and do not fit a continuous distribution. Outliers can be attributed to either natural enrichment processes, anthropogenic contribution or related to site contamination.
- Background threshold value (BTV): the maximum concentration that can be attributed to background conditions, which may or may not include natural outliers.
- Upper bound concentration (UBC): the upper limit of the range of background concentrations that fit a relatively continuous distribution and do not include any of the natural outliers. UBC is estimated based on inflection points and/or gaps in the data distribution from the combined cumulative probability and univariate plots.

Concentration distribution and combined plot analysis results are discussed for each target element. Elements with established HDOH (2011) risk-based EALs are the primary target elements, followed by elements with no established risk-based EALs, and additional major elements that occur in Hawaiian soils.

For each of the target element, three sets of combined plots are presented in each figure: (a) combined univariate and probability plots with all data included; (b) combined univariate and probability plots with only filtered data (non-qualified and/or J-flagged data only with potential outliers retained; (c) combined univariate and probability plots with filtered data and outliers removed. For some target element, the figures may be repetitive due to absence of any non-detects and/or outliers; however, the three sets of figures are maintained to provide consistency in the steps taken for the analysis.

4.1 DESCRIPTIVE STATISTICS

Table 5 presents descriptive statistics for the dataset used for this study. The 187 samples represented by the dataset were not analyzed for the same suites of chemicals; therefore, the sample quantities and number of associated data points varies for the different elements. The background dataset is compared to the HDOH (2011) risk-based EALs (Table I-1, Unrestricted Direct Exposure Soil Action Levels (non-carcinogens, hazard quotient [HQ] = 1).

4.2 RESULTS: ELEMENTS WITH ESTABLISHED EALS

4.2.1 Antimony (Sb)

Figure 7 shows the distribution of sampling locations and Sb concentrations in the dataset. Sb has the highest percentage of non-detect concentrations of all the elements included in the dataset with 81 of the total 121 data points representing non-detect (U-flagged) concentrations. Three samples have Sb concentration above the HDOH risk-based EAL for Sb (8.2 milligrams per kilogram [mg/kg]); however, they are all non-detect values and therefore are considered to be outliers and are excluded from the analysis. The highest detection reported as an estimated (J-flagged) concentration of 2.4 mg/kg representing a sample collected along the west coast of Kaua'i.



Table 4: Correlation Coefficient Matrix of 29 Target Elements

| | AI | Sb | As | Ва | Be | Cd | Ca | Cr | Co | Cu | Fe | Pb | Mg | Mn | Hg | Мо | Ni | Р | к | Se | Sr | Ag | Na | ті | Sn | Ti | w | v | Zn |
|----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|-------|----------|
| AI | 1.00 | | | | _ | | | _ | | | - | | 3 | | 5 | | | | | | | 5 | | | - | | | | |
| Sb | -0.23 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| As | 0.09 | 0.01 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Ва | 0.20 | 0.21 | -0.12 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | | |
| Be | 0.25 | 0.22 | -0.09 | 0.70 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | | |
| Cd | 0.00 | 0.02 | 0.17 | 0.25 | 0.00 | 1.00 | | | | | | | | | | | | | | | | | | | | | | | |
| Ca | 0.21 | 0.11 | 0.11 | 0.34 | 0.20 | 0.25 | 1.00 | | | | | | | | | | | | | | | | | | | | | | |
| Cr | 0.42 | -0.22 | 0.04 | -0.18 | -0.19 | -0.02 | -0.16 | 1.00 | | | | | | | | | | | | | | | | | | | | | |
| Со | 0.34 | 0.01 | 0.10 | 0.38 | 0.51 | 0.20 | 0.31 | 0.05 | 1.00 | | | | | | | | | | | | | | | | | | | | |
| Cu | 0.46 | -0.13 | 0.20 | -0.12 | -0.14 | 0.35 | 0.12 | 0.23 | 0.22 | 1.00 | | | | | | | | | | | | | | | | | | | |
| Fe | 0.72 | -0.03 | 0.03 | 0.00 | 0.12 | -0.14 | -0.02 | 0.69 | 0.09 | 0.22 | 1.00 | | | | | | | | | | | | | | | | | | |
| Pb | 0.19 | 0.11 | 0.04 | 0.12 | 0.05 | 0.19 | 0.33 | 0.14 | -0.04 | 0.08 | 0.09 | 1.00 | | | | | | | | | | | | | | | | | |
| Mg | 0.27 | -0.14 | 0.34 | 0.25 | 0.17 | 0.36 | 0.67 | 0.02 | 0.44 | 0.19 | 0.12 | 0.20 | 1.00 | | | | | | | | | | | | | | | | |
| Mn | 0.66 | -0.13 | 0.07 | 0.58 | 0.53 | 0.22 | 0.37 | 0.04 | 0.60 | 0.32 | 0.37 | 0.21 | 0.37 | 1.00 | | | | | | | | | | | | | | | |
| Hg | -0.14 | 0.03 | -0.01 | -0.17 | -0.17 | 0.06 | -0.31 | 0.16 | -0.35 | -0.28 | 0.29 | 0.12 | -0.26 | -0.20 | 1.00 | | | | | | | | | | | | | | |
| Мо | -0.32 | 0.18 | -0.09 | 0.10 | -0.05 | -0.02 | 0.08 | 0.04 | -0.09 | -0.18 | -0.38 | 0.32 | 0.14 | -0.07 | 0.06 | 1.00 | | | | | | | | | | | | | |
| Ni | 0.36 | -0.20 | 0.17 | 0.03 | 0.00 | 0.15 | 0.21 | 0.33 | 0.54 | 0.42 | 0.16 | -0.08 | 0.51 | 0.27 | -0.33 | -0.13 | 1.00 | | | | | | | | | | | | |
| Р | 0.26 | 0.34 | 0.06 | 0.66 | 0.44 | 0.25 | 0.24 | 0.03 | 0.21 | -0.06 | 0.08 | 0.27 | 0.20 | 0.49 | -0.01 | 0.10 | -0.03 | 1.00 | | | | | | | | | | | |
| к | 0.31 | -0.19 | -0.12 | 0.57 | 0.48 | -0.08 | 0.27 | -0.06 | 0.11 | -0.13 | 0.33 | 0.46 | 0.26 | 0.49 | 0.20 | 0.03 | -0.06 | 0.28 | 1.00 | | | | | | | | | | |
| Se | -0.14 | 0.34 | 0.03 | 0.03 | -0.31 | 0.66 | -0.11 | 0.16 | -0.25 | -0.22 | -0.06 | 0.20 | -0.03 | -0.23 | 0.31 | 0.20 | -0.20 | -0.13 | -0.13 | 1.00 | | | | | | | | | 1 |
| Sr | 0.30 | 0.03 | -0.04 | 0.61 | 0.43 | 0.06 | 0.87 | -0.07 | 0.34 | 0.07 | 0.08 | 0.46 | 0.55 | 0.42 | -0.28 | 0.10 | 0.18 | 0.45 | 0.49 | -0.20 | 1.00 | | | | | | | | 1 |
| Ag | -0.30 | 0.32 | 0.06 | 0.22 | 0.02 | 0.90 | -0.07 | -0.01 | 0.00 | -0.16 | -0.13 | 0.16 | 0.08 | -0.23 | 0.10 | 0.15 | -0.03 | -0.09 | -0.28 | 0.72 | -0.20 | 1.00 | | | | | | | |
| Na | 0.17 | 0.00 | -0.01 | 0.61 | 0.45 | 0.14 | 0.80 | -0.21 | 0.37 | 0.01 | -0.05 | 0.29 | 0.64 | 0.41 | -0.35 | 0.17 | 0.16 | 0.32 | 0.51 | -0.23 | 0.88 | -0.13 | 1.00 | | | | | | <u> </u> |
| ТІ | -0.02 | 0.89 | -0.06 | 0.43 | 0.47 | 0.09 | -0.05 | -0.20 | 0.21 | -0.10 | 0.47 | 0.06 | -0.06 | 0.06 | 0.10 | 0.10 | -0.18 | 0.08 | -0.10 | 0.51 | -0.02 | 0.37 | -0.03 | 1.00 | | | | | <u> </u> |
| Sn | -0.33 | 0.13 | -0.01 | -0.08 | -0.09 | -0.15 | -0.11 | -0.04 | -0.16 | 0.02 | -0.29 | -0.02 | -0.19 | -0.29 | 0.06 | 0.13 | -0.11 | -0.16 | -0.20 | 0.12 | -0.12 | -0.08 | -0.12 | -0.07 | 1.00 | | | | <u> </u> |
| Ti | 0.41 | -0.31 | -0.13 | -0.15 | 0.03 | -0.34 | -0.27 | 0.58 | -0.11 | 0.00 | 0.83 | 0.08 | -0.20 | 0.10 | 0.40 | -0.18 | -0.10 | -0.09 | 0.22 | 0.12 | -0.13 | -0.07 | -0.26 | 0.01 | -0.20 | 1.00 | | | ļ |
| w | 0.26 | 0.85 | 0.41 | 0.00 | 0.16 | 0.10 | -0.16 | 0.20 | 0.27 | -0.20 | 0.10 | -0.04 | -0.13 | 0.08 | -0.22 | 0.63 | 0.08 | 0.12 | -0.51 | -0.08 | 0.95 | -0.35 | -0.28 | N/A | 0.31 | -0.02 | 1.00 | | ļ |
| v | 0.24 | -0.11 | 0.10 | -0.14 | -0.02 | -0.11 | -0.08 | 0.70 | 0.08 | 0.11 | 0.55 | 0.13 | 0.03 | 0.07 | 0.19 | 0.35 | 0.11 | -0.06 | -0.08 | 0.18 | -0.08 | 0.14 | -0.17 | 0.00 | -0.02 | 0.52 | 0.70 | 1.00 | ļ |
| Zn | 0.11 | 0.14 | 0.00 | 0.24 | 0.17 | 0.14 | 0.08 | -0.13 | 0.09 | -0.01 | 0.01 | 0.15 | 0.05 | 0.24 | -0.07 | 0.01 | -0.07 | 0.25 | 0.15 | -0.10 | 0.16 | -0.08 | 0.13 | 0.11 | -0.06 | -0.09 | 0.69 | -0.06 | 1.0 |

Note:Shaded, bolded valuesdenote correlations (r) greater than 0.50.N/Ainsufficient data to calculate correlation coefficient.



| | | | | Concentration (mg/kg) | | | | | | | | | |
|----------------|----------------------|----------------------|--------------------|-----------------------|------------|-----------|-----------|-----------------------|--|--|--|--|--|
| Element | Number of Samples | Number of Detects | EAL ^a | Min | Max | Mean | Median | Standard Deviation | | | | | |
| Target Elemer | ts with Establ | ished EALs | | | | | | | | | | | |
| Antimony | 121 | 40 | 8.2 | 0.004 | 31.5U | 1.22 | 0.25 | 4.08 | | | | | |
| Arsenic | 139 | 137 | 23 | 0.3 | 283.78 | 11.80 | 3.90 | 28.03 | | | | | |
| Barium | 125 | 124 | 15,000 | 4.5 | 926.00 | 175.15 | 93.59 | 192.49 | | | | | |
| Beryllium | 120 | 119 | 160 | 0.05 | 3.82 | 1.00 | 0.64 | 0.85 | | | | | |
| Cadmium | 135 | 102 | 70 | 0.02 | 17.00 | 1.08 | 0.41 | 2.53 | | | | | |
| Chromium | 147 | 147 | 1,145 ^b | 8.52 | 3,180.00 | 374.83 | 250.00 | 420.72 | | | | | |
| Cobalt | 139 | 139 | 23 | 0.69 | 113.49 | 35.07 | 31.11 | 22.64 | | | | | |
| Copper | 139 | 139 | 3,100 | 2.38 | 450.00 | 93.86 | 80.92 | 71.96 | | | | | |
| Lead | 138 | 132 | 200 | 0.76 | 380.00 | 19.11 | 8.65 | 36.87 | | | | | |
| Mercury | 115 | 105 | 23.0 | 0.017U | 1.40 | 0.24 | 0.14 | 0.26 | | | | | |
| Molybdenum | 108 | 74 | 390 | 0.06 | 4.00 | 0.69 | 0.49 | 0.69 | | | | | |
| Nickel | 124 | 124 | 3,800 | 2.1 | 767.18 | 154.33 | 103.70 | 141.65 | | | | | |
| Selenium | 113 | 105 | 390 | 0.24 | 12.20 | 2.30 | 1.10 | 2.62 | | | | | |
| Silver | 121 | 78 | 390 | 0.02 | 5.00 | 0.59 | 0.25 | 1.06 | | | | | |
| Thallium | 61 | 4 | 0.78 | 0.25U | 15.05J | 0.77 | 0.25 | 2.46 | | | | | |
| Vanadium | 141 | 141 | 390 | 0.25 | 1,090 | 230.73 | 174.11 | 190.61 | | | | | |
| Zinc | 125 | 125 | 23,000 | 3.57 | 1,200 | 132.47 | 98.00 | 139.12 | | | | | |
| Target Elemer | ts with No Es | tablished EAL | .s | | - <u>P</u> | | | | | | | | |
| Aluminum | 92 | 92 | N/A | 2,500 | 166,138 | 48,974.39 | 34,644.50 | 43,245.46 | | | | | |
| Calcium | 92 | 83 | N/A | 31 | 77,208 | 7,307.58 | 2,033.00 | 11,889.34 | | | | | |
| Iron | 104 | 104 | N/A | 1,713 | 260,082 | 95,549.46 | 79,231.00 | 63,348.87 | | | | | |
| Manganese | 92 | 92 | N/A | 13 | 4,880 | 1,058.46 | 769.50 | 979.57 | | | | | |
| Strontium | 77 | 65 | N/A | 2U | 1,094 | 93.93 | 22.00 | 188.82 | | | | | |
| Tin | 107 | 73 | N/A | 0.6 | 150 | 12.43 | 4.50 | 20.20 | | | | | |
| Titanium | 92 | 92 | N/A | 3,809 | 53,032 | 21,112.46 | 19,085.50 | 10,356.53 | | | | | |
| Tungsten | 50 | 21 | N/A | 0.002 | 5.43 | 1.18 | 0.10 | 1.74 | | | | | |
| Additional Tar | get Elements | | | • | | | | | | | | | |
| Magnesium | 92 | 80 | N/A | 25U | 68,611 | 9,364.25 | 3,571.50 | 14,678.07 | | | | | |
| Phosphorus | 92 | 92 | N/A | 170 | 10,178.00 | 1,992.51 | 1,450.00 | 1,695.49 | | | | | |
| Potassium | 92 | 92 | N/A | 37 | 10,850 | 2,524.95 | 1,684.50 | 2,229.00 | | | | | |
| Sodium | 92 | 88 | N/A | 63U | 18,078 | 1,991.52 | 835.00 | 2,923.46 | | | | | |

Table 5: Descriptive Statistics for all Chemical Elements Represented in the Dataset

J detect, estimated concentration

mg/kg milligram per kilogram

N/A not enough detection data to calculate background concentration ranges for thallium

U non-detect concentration, reporting limit value presented.

^a HDOH (2011) EAL: Table I-1, Unrestricted Direct Exposure Soil Action Levels (non carcinogens, HQ = 1)

^b Direct Exposure Soil Action Level is defined only for chromium III and VI, not total chromium.

4.2.1.1 SOURCES AND GEOCHEMISTRY

Mafic rocks, which are the primary parent rock material for soils in Hawai'i, tend to have the highest Sb concentrations, from 0.2–1.0 mg/kg. The geochemical characteristics of Sb are closely related to those of arsenic (As). Sb minerals and compounds are moderately soluble, but tend to be readily adsorbed and immobilized in soils containing clays, iron (Fe) and manganese (Mn) hydroxides, and



organic matter (Alloway 1990). This combination of relatively high solubility and strong sorption can lead to significant enrichment in soil, and strong correlation with grain size and organic content. The typical Sb concentration range in natural surface soil is 0.05–4.0 mg/kg (Kabata-Pendias 2001). A study of road-deposited sediment in an urban drainage basin in Honolulu reported Sb concentrations up to 3 mg/kg in roadside soils, and suggested that the elevated Sb concentrations in urban areas are associated with Sb use in vehicle brake pads (Sutherland and Tolosa 2000). In addition, Sb levels up to 100 mg/kg have been reported for phosphates; therefore, fertilizer application could be associated with elevated anthropogenic background concentrations in agricultural areas (Alloway 1990). Another potentially significant anthropogenic source of Sb includes ammunition such as lead shot pellets, which typically contain over 90% Pb, 1–7% Sb, <2% As, and <0.5% Ni (Rooney 2005).

4.2.1.2 COMBINED PLOTS

The cumulative probability plot for the full dataset (Figure 8a) show discontinuity between detect and non-detect values. Removing these non-detects and re-plotting the cumulative probability plot (Figure 8b and Figure 8c) show discontinuities in the data distribution at 0.17 mg/kg and at 1.5 mg/kg; however, the data appear to be log-normally distributed, falling along a segment with consistent slope despite the discontinuities. The highest concentrations reported are determined to be outliers due to the non-detect qualifier (U) assigned to samples, potentially due to elevated detection limit. The initial discontinuity is likely due to the limited number of available data points with sufficiently low detection limits to adequately represent background concentrations near the lower end of the range. Based on the available data, the maximum detected concentration of 2.4 mg/kg is estimated for the BTV and the UBC for Sb in Hawai'i soils.

4.2.2 Arsenic (As)

The As concentration range in the dataset is 3-238.78 mg/kg (n = 139), with a mean concentration of 11.92 mg/kg. Only two of the data points represent non-detect values. Elevated concentrations above the risk-based EAL (23 mg/kg) were reported for sampling locations on O'ahu, Maui, and Hawai'i island (Figure 9). The maximum As concentration represents a surface soil sample collected on the Hamakua coast on the windward side of Hawai'i island, where the land was historically used for sugarcane cultivation.

4.2.2.1 SOURCES AND GEOCHEMISTRY

As concentrations in mafic rocks generally can range up to 2 mg/kg (Kabata-Pendias 2001). Ascontaining minerals and compounds are relatively soluble; therefore, As is readily released from the primary rock-forming minerals during weathering. However, dissolved As is quickly and strongly adsorbed to clays, hydroxides, and organic matter. This combination of relatively high solubility and strong sorptive tendency often leads to significant enrichment in the soil. As concentration range for uncontaminated soils of the United States and other countries is very broad, ranging from < 0.1 mg/kg up to approximately 95 mg/kg. As is a common contaminant in agricultural and urban areas. Anthropogenic background sources of As, such as arsenical pesticides, herbicides, fungicides, and rodenticides, can significantly affect background concentrations in surface soils, particularly in agricultural areas (e.g., former sugarcane land). De Carlo and Anthony (2002) note that agricultural activities are likely to be responsible for anthropogenic As enrichment in O'ahu soils. Hawaiian soils often have relatively high As concentrations due to volcanic sources, adsorption of As from natural and anthropogenic background sources to clay, hydroxide, and organic particles.

4.2.2.2 COMBINED PLOTS ANALYSIS

Combined plots for As are presented in Figure 10. Only 2 of the 139 data points are non-detect values. Figure 10a and Figure 10b show the maximum concentration detected of 238.78 mg/kg that is isolated above the rest of the data distribution. This data point is clearly an outlier due to site contamination. The data point belongs to a sample collected from an area known for agricultural use on the Hamakua coast of Hawai'i island, and therefore likely impacted by arsenic use for current agriculture use. The rest of the data has a fairly continuous log-normal distribution up to 100 mg/kg, with potential for slight inflection at 23.8 mg/kg. On consultation with HDOH, it was decided that the



BTV for As is defined at 50 mg/kg based on observations of discrete sample concentrations in the 40–50 mg/kg range in non-impacted areas (R. Brewer, HDOH, pers. comm. 2011). Concentrations above the BTV are therefore considered as outliers potentially related to site contamination due to arsenical pesticide use. For the dataset, data points with concentrations above the BTV are primarily located along the Hamakua Coast of Hawai'i island, where historical and current land use includes extensive agriculture.

Cumulative probability plots with the outlier values removed (Figure 10c) for As indicate a log-normal distribution with confirmed inflection point at 23.8 mg/kg corresponding to a discontinuity in the data distribution. Six data points with concentrations above 23.8 mg/kg are located in clusters on the islands of O'ahu, Maui, and Hawai'i. The elevated concentrations are not distributed uniformly throughout all the soil orders and primarily limited to Andisols, Aridisols, Inceptisols and Mollisols. These soil types are typically not associated with high organic and clay content which leads to As enrichment in soil. Therefore, 23.8 mg/kg represents a reasonable estimate of the UBC for As in Hawai'i soil. The concentrations near or above the UBC may represent mixture of naturally occurring background and anthropogenic contribution.

4.2.3 Barium (Ba)

The Ba concentration range in the dataset is 4.5-926 mg/kg, with a mean of 175.15 mg/kg (n = 125). Only one of the data points represents a non-detect value. No data points are present above the risk-based EAL for Ba of 15,000 mg/kg. The two maximum data points with concentrations of 926 and 775 mg/kg correspond to sampling locations on the Kohala coast of of Hawai'i island and along the northeastern coastline of Kaua'i (Figure 11).

4.2.3.1 SOURCES AND GEOCHEMISTRY

Ba concentrations show significant correlation with rock type, with concentration ranges of 250 mg/kg to 400 mg/kg and up to 1,200 mg/kg for acidic rocks (e.g., granites and rhyolites) (Kabata-Pendias 2001). Concentration near 800 mg/kg was detected in a sample collected on O'ahu from a basaltic sample, suggesting that Ba concentrations in Hawaiian basalt extend to higher levels (Earth Tech 2006). Ba shows a strong affinity for clays; therefore, increased concentrations in soil relative to the parent rock could be attributable to natural enrichment. Ba is usually associated with potassium due to the similar ionic radii of the two elements, and therefore occurs in minerals such as alkali feldspar and biotite. Potential anthropogenic background Ba sources include atmospheric fallout from industrial facilities as well as from agricultural impact from the use of phosphate fertilizers.

4.2.3.2 COMBINED PLOTS ANALYSIS

Combined plots for Ba are presented in Figure 12. Although the cumulative probability plot for Ba shows a discontinuity at 450 mg/kg, all data points fall along a relatively straight segment on the log-scale plot, indicating a single log-normally distributed population likely representing background conditions. A second gap in the data distribution is present at 693.9 mg/kg, corresponding to a potential slight inflection point. The two data points above this discontinuity (775 and 926 mg/kg) do not fall significantly away from the main distribution, and therefore are not considered as contamination-related outliers, but likely from natural geochemical enrichment. The maximum concentration reported therefore is estimated to represent the BTV, and the UBC is defined as the value at 693.9 mg/kg.

4.2.4 Beryllium (Be)

The Be concentration range in the dataset is 0.05-3.82 mg/kg, with a mean of 1.00 mg/kg (n = 120) Only one non-detect value is included in the dataset. Figure 13 shows the spatial distribution of Be concentrations included in the dataset. All concentrations represented in the dataset are below the risk-based EAL for Be (160 mg/kg).



4.2.4.1 SOURCES AND GEOCHEMISTRY

The Be concentration range in volcanic rocks is 2.0–6.5 mg/kg for acidic rocks (e.g., granite), 0.3– 1.0 mg/kg for mafic rocks, and 0.2–2.0 mg/kg in limestone. Similar to Al in geochemical characteristics, Be may be concentrated in soil after weathering due to its limited mobility. High concentrations of Be can also be present in soils rich in organic matter due to the affinity of Be for organic carbon. Anthropogenic background sources for Be are dominated by fossil fuel combustion emissions (Kabata-Pendias 2001).

4.2.4.2 COMBINED PLOTS ANALYSIS

Combined plots for the full dataset and detected concentrations only dataset for Be are presented in Figure 14a and Figure 14b, respectively. The cumulative probability plots for Be show a relatively continuous log-normal distribution, represented by the straight-line segment in the log-scale plot. An inflection point coupled with a slight data gap in the distribution is present at 3.0 mg/kg. Two data points with concentrations above 3.0 do not fall along the same segment. These two data represent samples from Kaho'olawe and Hawai'i island. Based on the concentration distribution ranges for these two islands indicated on the sampling location univariate plots, these two data points are relatively isolated from the rest of the data distribution for each of the islands, therefore are potential outliers. However, the maximum data point (3.82 mg/kg) is collected from a soil sample with a very fine sandy loam which is likely to have high organic content that may concentrate Be due to its affinity for organic carbon. Therefore, the maximum concentration (3.82 mg/kg) reported is assumed to be a natural outlier, and estimated to be the BTV for Be in Hawai'i soils.

Removing the two data points and recalculating and re-plotting the cumulative probability as shown in Figure 14c shows a well-defined continuous single population distribution likely attributed to background conditions. Therefore, the UBC of the background concentration range is estimated at approximately 3 mg/kg.

4.2.5 Cadmium (Cd)

The Cd concentration range in the dataset is 0.02–17 mg/kg, with a mean of 1.08 mg/kg. Of the 135 data points in the dataset, 33 represent non-detect concentrations. All concentrations fall below the risk-based EAL for Cd of 70 mg/kg. The spatial distribution of Cd concentration is shown on the map in Figure 15; the highest concentrations of Cd in the dataset are located on the island of Kaua'i.

4.2.5.1 SOURCES AND GEOCHEMISTRY

The Cd concentration range in basalts and other mafic rocks is typically approximately 0.13–0.22 mg/kg (Kabata-Pendias 2001). Cd is mobile during weathering due to the relatively high solubility of Cd-containing minerals; therefore, enrichment can be a significant factor in the soil environment. Although Cd concentrations tend to increase with the clay content of soil, Cd shows stronger correlation with Fe, Mn, and organic matter. Anthropogenic Cd tends to accumulate in surface soils due to atmospheric deposition (from fossil fuel combustion and certain industrial activities) and application of fertilizers (e.g., manure and phosphate fertilizers) to agricultural land. Cd concentrations in soil along highways in the United States can range up to 10 mg/kg, while concentrations in sludged, irrigated, or fertilized agricultural soils in the United States range up to 8.3 mg/kg (Kabata-Pendias 2001).

4.2.5.2 COMBINED PLOTS ANALYSIS

Combined cumulative probability and univariate plots for Cd are presented in Figure 16. The cumulative probability plot for the full dataset (Figure 16a) shows a wide data gap and an inflection point in the lower end of the concentration range, likely due to the effect of the large number of non-detects included in the population. Removing non-detects from the plots (Figure 16b) removes the initial discontinuity and reveals a continuous log-normal population distribution with an inflection point at 2.29 mg/kg. Cumulative probability plot shown in Figure 16b identifies five data points with elevated concentrations that are isolated well beyond the rest of the data distribution, therefore



representing potential outliers. These five data points represent samples collected from the Island of Kaua'i as part of an EPA Brownfields Assessment Program (ERM 2006a,b) at two sites previously used as sugarcane lands. However, the study found no significant impact to surface soils from chemicals identified at the site; therefore these concentrations are not related to site contamination. However, as discussed in the previous section, Cd can accumulate from application of fertilizers in agricultural lands; therefore, these concentrations can be related to background anthropogenic impact due to agricultural lands. The BTV for Cd, therefore, is estimated to be at the maximum concentration reported (17 mg/kg).

The five data points were removed from the dataset and the combined plots were re-plotted (Figure 16c). The cumulative probability plot shows multiple discontinuities, however, all of the data fit along the same trend, therefore representing a single population related to background conditions. The UBC for the background Cd in Hawai'i soils is estimated to be 2.29 mg/kg.

4.2.6 Chromium (Cr)

The Cr (as total chromium) concentration range in the Hawai'i Soil EBA database is 8.52–3,180 mg/kg, with a mean of 374.83 (n = 147). The Cr dataset contains no U- or J-flagged values. No risk-based EAL is established for total Cr, only for certain species of Cr (Cr III and Cr VI). The maximum Cr concentration in the dataset represents a sample from the leeward coast of Kaua'i (Figure 17).

4.2.6.1 SOURCES AND GEOCHEMISTRY

The typical Cr concentration range in surface soils is 1–1,100 mg/kg (Kabata-Pendias 2001). O'ahu basalts contain relatively high Cr concentrations (Bishop Museum 2003) indicating that Hawaiian basalts represent substantial natural Cr sources. The upper tolerance limits (UTLs) reported for Cr concentrations in O'ahu basalts are 1,061 mg/kg for the Ko'olau Volcanics, 870 mg/kg for the Waianae Volcanics, and 600 mg/kg for the Honolulu Volcanics (Bishop Museum 2003). Hawaiian volcanic rocks therefore represent substantial natural Cr sources. Although Cr concentrations in Some soils may increase with increasing clay fraction, Cr concentrations in O'ahu soils have been found to be highest in the coarse-grained fractions because they contain more primary igneous minerals (e.g., olivine and pyroxene) (De Carlo and Anthony 2002, De Carlo et al. 2004). The information and data therefore indicate that parent rock type is the most important factor controlling natural background conditions for Cr. Therefore, soils developed on ultramafic and mafic rocks are likely to have relatively high Cr concentrations.

4.2.6.2 COMBINED PLOTS ANALYSIS

Combined plots for Cr are presented in Figure 18. The log-scale cumulative probability plot indicates a continuous log-normally distributed Cr population up to an inflection point at 1,145 mg/kg. Four samples have concentrations above 1,145 mg/kg; all four of these samples were collected on the island of Kaua'i. These data points fall along a segment with different slope compared to the lower concentrations, therefore likely represent different geochemical conditions. These four data points were collected as part of a study of Cr distribution in the Latosols of the Hawaiian islands (Nakamura & Sherman 1958). The study concluded that highly weathered Latosols from which the samples were collected have concentrated Cr to elevated levels; therefore, these data points represent high concentrations of localized, natural enrichment of Cr in highly weathered soils that are considered part of the background population. The BTV for Cr, therefore, is defined as the maximum concentration of 3,180 mg/kg.

Figure 18c shows the combined cumulative plots with the upper elevated segment removed. 1,145 mg/kg represents the upper range of the continuous concentration distribution for the data representing Hawai'i island and the data for Andisols (soils derived from volcanic fragments). The soil and parent rock data suggest that Cr concentrations up to approximately 1,145 mg/kg may occur in Hawaiian soils derived from weathering of basaltic parent rocks. Therefore, 1,145 mg/kg represents a reasonable estimate of the UBC for background range of Cr for Hawai'i soils.



4.2.7 Cobalt (Co)

The range of Co concentrations in the database is 0.69-113.49 mg/kg, with a mean of 35.07 mg/kg (n = 139). The Co dataset contains no U- or J-flagged values. 90 samples in the dataset have concentrations above the risk-based EAL of 23 mg/kg; these samples were collected at locations distributed throughout all the islands with the exception of Lana'i, for which no Co data are available (Figure 19). The maximum concentration represents a sample collected on Kaho'olawe, and is potentially an outlier not consistent with the background population (due to the military training operations and ordnance testing conducted on this island).

4.2.7.1 SOURCES AND GEOCHEMISTRY

Co is strongly correlated with rock type, with higher concentrations reported for mafic rocks (35– 50 mg/kg) and ultramafic rocks (100–200 mg/kg) (Kabata-Pendias 2001). Concentrations of up to 194 mg/kg have been reported for samples representing the Honolulu Volcanics (Bishop Museum 2003). Although there are no common rock-forming Co minerals, Co is geochemically similar to Fe and substitutes for Fe in rock-forming minerals. During weathering, Co is mobile in oxidizing environments; however, because it adsorbs strongly to clay and Fe/Mn oxides, Co is relatively immobile once deposited in most soils. DeCarlo and Anthony (2002) note that although Co concentrations may be elevated in some areas, concentrations generally reflect greater contributions from natural sources than from anthropogenic sources, with higher concentrations occurring in the sand fractions rather than the clay/silt fractions of soil samples.

4.2.7.2 COMBINED PLOTS ANALYSIS

Combined plots for Co are presented in Figure 20. The cumulative probability plot shows a lognormal distribution with data discontinuity at 80.35 mg/kg. Four data points representing samples from four separate islands (O'ahu, Maui, Kaho'olawe, and Hawai'i) have concentrations above this potential threshold. The data points from O'ahu and Kaho'olawe are fairly isolated from the rest of the data distribution for each respective island, and therefore represent potential outliers. The maximum concentration reported of 113.49 mg/kg is still within the range of maximum concentrations reported for volcanic rocks that are primary parent rock material for Hawai'i soils, however. Therefore, it is likely that the four data points represent natural outliers due to localized enrichment of Co from parent material enriched in Co, and through weathering process. Two of the data points have soil texture data available, which indicate that the samples were collected from clay soil, where Co tends to strongly adsorb. Therefore, the maximum concentration reported of 113.49 is considered to represent the BTV for Co in Hawai'i soils.

Removing the four natural outliers from the dataset and re-plotting the cumulative probability plot (Figure 20c) presents a relatively straight, continuous, single log-normal population, which most likely corresponds to natural background Co concentration range. Therefore, 80.35 mg/kg represents a reasonable estimate of the UBC of the background Co for Hawaiian soils.

4.2.8 Copper (Cu)

The Cu dataset contains 139 data points, all of which are detected concentrations or detected, estimated concentrations (J-flagged). The Cu concentration range is 2.38–450 mg/kg, with a mean of 35.07 mg/kg. None of the data points included in the dataset exceeds the risk-based EAL for Cu. Distribution of Cu concentrations included in the EBA is presented in Figure 21. The maximum concentration reported is from a sample located on the island of O'ahu.

4.2.8.1 SOURCES AND GEOCHEMISTRY

Cu concentrations are correlated to rock type; mafic rocks such as Hawaiian basalts typically have relatively high Cu concentrations (60–120 mg/kg). The Cu concentration range is 40–60 mg/kg in argillaceous sediments, and 2–10 mg/kg in limestones. The background copper concentration in surface soils is typically 1–140 mg/kg (Kabata-Pendias 2001). Cu concentrations of up to 431 mg/kg were reported for rocks of the Waianae Volcanic series (Bishop Museum 2003). Although Cu is



readily released during weathering, it reacts quickly with organic and mineral components, precipitating as secondary minerals and thereby remaining relatively immobile in the soil. Cu also tends to sorb to clay particles, Fe, Al, and Mn oxides. Primary anthropogenic sources of Cu include fertilizers, industrial emissions, and auto-related sources (Kabata-Pendias 2001).

4.2.8.2 COMBINED PLOTS ANALYSIS

The cumulative probability plots for Cu presented in Figure 22 indicate a continuous, log-normally distributed population with three potential outliers with concentrations of 289, 333, and 450 mg/kg. These data points were collected from Kaua'i and O'ahu, and are relatively isolated from the rest of the data distribution. The maximum concentration of 450 mg/kg was collected from the island of O'ahu. High concentrations of Cu have been reported in volcanic rocks which are primary parent source material for soils in Hawai'i. In addition, given the maximum concentration is found in O'ahu, there is potential for contribution from background anthropogenic sources (e.g., automobile emissions). Therefore, it is determined that the maximum reported concentration (450 mg/kg) represents elevated background concentrations due to natural and potentially background anthropogenic source, and determined to represent the BTV for Cu in Hawai'i soils.

Removing the three natural outliers and re-plotting the data as shown in Figure 22c indicates a single, continuous log-normal distribution associated with background conditions up to 252 mg/kg. This value represents a reasonable estimate of the UBC of the background Cu concentration range for Hawaiian soils.

4.2.9 Lead (Pb)

The Pb dataset contains 138 data points with only 6 non-detect values. The Pb concentration range in the dataset is 0.76–380 mg/kg, with a mean of 19.11 mg/kg. The one data point with a concentration above the risk-based EAL (200 mg/kg) corresponds to a sampling location on the southeast coast of the island of Kaua'i (Figure 23).

4.2.9.1 SOURCES AND GEOCHEMISTRY

Pb concentrations show strong correlation with rock type with higher concentration ranges in more acidic rocks (e.g., granites). The typically Pb concentration range in basalts and other mafic rocks is 3–8 mg/kg. In sedimentary rocks, the Pb concentration range is 20–40 mg/kg for argillaceous sediments, and 3–10 mg/kg in limestone (Kabata-Pendias 2001). Pb content in soil is inherited from parent rocks; however, its strong tendency to adsorb to clay and organic particles, Mn oxides and Fe/Al hydroxides leads to Pb enrichment in loamy and clayey soils. Natural Pb sources are relatively minor when compared to contributions from anthropogenic sources. Natural Pb concentrations in soils in the United States are typically 10–70 mg/kg for loamy and clay soils and 10–30 mg/kg for silty soils. However, Pb concentrations up to 900 mg/kg have been reported for urban soil on the island of O'ahu due to contributions from anthropogenic background sources (De Carlo et al. 2004).

4.2.9.2 COMBINED PLOTS ANALYSIS

Combined plots for the full Pb dataset are presented in Figure 24a. The log-scale cumulative probability plot shows a log-normal distribution with a one data point at a concentration (380 mg/kg) isolated from the rest of the data distribution, and therefore not likely to be associated with background conditions. Based on discussions with HDOH, the BTV for Pb is assumed to be equivalent to a value of 73 mg/kg based on professional judgment (Roger Brewer, HDOH, pers. comm. 2011). Three data points are present in the dataset with concentrations above the BTV, and therefore are removed from further analysis.

Figure 24c shows the revised combined plots with the outliers removed. The cumulative probability plot of the dataset without the outlier shows a single continuous data distribution up to the BTV concentration; therefore, the BTV value (72.8 mg/kg) is assumed to be equivalent to the UBC for soils in Hawai'i.



4.2.10 Mercury (Hg)

The Hg dataset contains 115 data points with a concentration range of 0.017U (non-detect concentration)–105 mg/kg and a mean of 0.24 mg/kg. Ten non-detect values are included in the dataset. All concentrations included in the dataset are well below the risk-based EAL for Hg (23 mg/kg). Figure 25 presents the spatial distribution of Hg concentrations throughout the Hawaiian islands.

4.2.10.1 SOURCES AND GEOCHEMISTRY

Hg concentrations in most magmatic rocks are relatively low (less than 0.1 mg/kg), and relatively higher in sedimentary rocks (up to 0.4 mg/kg). Hg is relatively immobile during weathering, with limited sorption to clay particles. However, Hg has strong affinity for organic matter and therefore tends to accumulate in surface soil with high organic content. Kabata-Pendias (2001) note that background concentrations are difficult to estimate due to widespread anthropogenic contributions of Hg. In soils formerly or currently used for agriculture, anthropogenic background concentrations can be significantly higher than natural background levels.

4.2.10.2 COMBINED PLOTS ANALYSIS

The combined plots presented in Figure 26 show a relatively continuous log-normal distribution for Hg. There are no distinct outliers that can be discerned from the data distribution, therefore the maximum reported concentration of 1.4 mg/kg represents the BTV for Hg in Hawai'i soils. The slope of the population segment appears to flatten with a slight inflection point at 0.72 mg/kg. The five data points with concentrations above the inflection point represent samples collected on Kaua'i, Maui, and Hawai'i island, likely from areas formerly or currently used for agricultural purposes. Removing these elevated concentration values and re-plotting the combined plots shows a continuous single population distribution (Figure 26c). Based on evaluation of the combined plots, the UBC of the background range for Hg in Hawai'i soils is estimated at 0.72 mg/kg.

4.2.11 Molybdenum (Mo)

The Mo dataset contains 108 data points, including 34 non-detect values; the concentration range is 0.06–4 mg/kg, with a mean of 0.69 mg/kg. All concentrations of Mo in the dataset are below the risk-based EAL (390 mg/kg). Spatial distribution of Mo concentrations is presented in Figure 27.

4.2.11.1 SOURCES AND GEOCHEMISTRY

According to Kabata-Pendias (2001), Mo concentrations tend to show strong correlation with rock type. For magmatic rocks, Mo concentration ranges tend to be higher in more acidic rocks (e.g., granite) compared to mafic rocks (e.g., basalt). The Mo concentration range in mafic rocks such as basalts is approximately 1.0–1.5 mg/kg. In sedimentary rocks, the Mo concentration range is 2.0–2.6 mg/kg in argillaceous sediments, and 0.16–0.4 mg/kg in limestone.

4.2.11.2 COMBINED PLOTS ANALYSIS

The combined plots constructed for Mo are presented in Figure 28. The data indicate that Mo concentrations fit a log-normally distributed population, as shown by the relatively straight segment in the log-scale cumulative probability plot. Although there is an apparent discontinuity in the distribution at 1.6 mg/kg, the data points above the discontinuity fall along the same slope as the data segment below the discontinuity, and therefore likely represent data from the same population.

Based on the combined plots analysis, all concentrations in the dataset represent background population, therefore the maximum reported concentration (4 mg/kg) represents both the BTV and UBC of background concentrations for Mo in Hawai'i soils.



4.2.12 Nickel (Ni)

The Ni dataset contains 124 data points with no non-detect values. The concentration range is 2.1–767.18 mg/kg, with a mean of 154.33 mg/kg. The maximum concentration of 767.18 mg/kg represents a sample collected from the island of O'ahu. All concentrations are below the risk-based EAL for Ni (3,800 mg/kg). The spatial distribution of Ni in the dataset throughout the Hawaiian islands is presented in Figure 29.

4.2.12.1 SOURCES AND GEOCHEMISTRY

The typical Ni concentration range in basalts is 45–410 mg/kg (Alloway 1990). However, higher concentrations in Hawaiian basalts have been observed, i.e., up to 1,524 mg/kg for the Ko'olau Volcanics of O'ahu (Bishop Museum 2003), indicating that basaltic rocks in Hawai'i represent substantial natural Ni sources. Ni is easily mobilized during weathering, co-precipitating with Fe and Mn oxides thereby showing strong association to Fe and Mn in soils. Ni can be released from the rock-forming minerals and incorporated into secondary minerals (e.g., clays) due to weathering. However, De Carlo and Anthony (2002) suggest that the Ni content of soils and sediments on O'ahu is controlled by the Ni content of the primary minerals in the parent rock; therefore, coarse-grained O'ahu soils may have higher Ni concentrations than fine grained soils.

4.2.12.2 COMBINED PLOTS ANALYSIS

Figure 30 presents combined plots for the Ni dataset. The log-scale cumulative probability plot for the full dataset presents a relatively log-normal data distribution with a discontinuity in at 410 mg/kg. Five data points have concentrations greater than 410 mg/kg. Four of the data points are collected from the island of Hawai'i, and one from Kaua'i. Comparison to the data distribution for each island as presented in the sampling location univariate plot indicate that these data points are higher in concentration and isolated from the data distribution of their respective island source, and therefore not likely associated with natural background conditions. Therefore, the UBC for background Ni concentration reported of 767.18 mg/kg is well within the upper limit of reported concentration of Ni in volcanic parent rocks (1,524 mg/kg), and therefore may represent geochemical enrichment from parent rock with high Ni content and thus can be part of the background population. The BTV for Ni, therefore, is estimated at 770 mg/kg.

4.2.13 Selenium (Se)

The Se dataset contains 113 data points, including eight non-detect values. The Se concentration range is 0.0240–12.20 mg/kg, with a mean of 2.3 mg/kg. No data points exceed the risk-based EAL for Se (390 mg/kg). Spatial distribution of Se concentrations in the dataset is illustrated in Figure 31.

4.2.13.1 SOURCES AND GEOCHEMISTRY

Alloway (1990) reports that the mean concentrations of Se in Hawaiian volcanic rocks can range as high as 2.0 mg/kg. For sedimentary rocks, Se concentrations are as high as 0.6 mg/kg in argillaceous rocks and approximately 0.1 mg/kg in limestones (Kabata-Pendias 2001). Se is a chalcophilic element (affinity for sulfur), and therefore substitutes for sulfur in sulfide minerals. Se is relatively mobile, particularly under oxidizing conditions at elevated pH; however, it is relatively immobile due to sorption to clay and organic particles in soil, leading to enrichment in clay-rich and organic-rich soils. Concentrations up to 1.9 mg/kg have been reported for loamy and clay soils (Kabata-Pendias 2001). Anthropogenic sources of Se include previous use of Se-containing pesticides (Alloway 1990). High levels of Se have been reported for Hawai'i soils, with concentrations up to 15 mg/kg (NRC 1983).

4.2.13.2 COMBINED PLOTS ANALYSIS

Figure 32a presents the combined plots for the full Se dataset. Combined plots for dataset including only detected concentrations are presented in Figure 32b. The log-scale cumulative probability plot



shows a log-normal distribution with a data discontinuity at 7.14 mg/kg. Six data points that are located in Kaua'i and Hawai'i islands have concentrations above 7.14 mg/kg. Based on the sampling location univariate plot, all six data points are separated from the rest of the dataset for each island and may represent potential outliers not associated with background conditions. Five of the data points, including the maximum concentration (12.2 mg/kg) collected as part of the EPA Brownfields Assessment Program (ERM 2006a,b) from two sites previously used as sugarcane lands. The study found no significant impacts from chemicals identified from soil samples at the site. Therefore, the five data points may still be part of the background population from localized enrichment due to natural or anthropogenic contribution. Therefore, the BTV for Se is estimated at 12.2 mg/kg.

Cumulative probability plots with the six data points removed are shown in Figure 32c. The cumulative probability plot shows an initial non-delimiting inflection point (likely associated with detection limits) followed by a continuous log-normal data distribution up to 7.14 mg/kg. Therefore, the 7.14 mg/kg concentration represents reasonable estimate for the UBC of the background concentration range for Se in Hawai'i soils.

4.2.14 Silver (Ag)

The Ag dataset contains 121 data points, including 43 non-detect concentrations. The Ag concentration range is 0.02–5.0 mg/kg, with a mean of 0.59 mg/kg. All concentrations included in the Ag dataset are below the risk-based EAL (390 mg/kg). Figure 33 presents the spatial distribution of Ag concentrations included in the dataset.

4.2.14.1 SOURCES AND GEOCHEMISTRY

Ag shows slight correlation with rock types in nature, with mafic rocks having the highest concentrations among the magmatic rocks (up to approximately 0.1 mg/kg). The Ag concentration range is approximately 0.07-0.1 mg/kg in shales, and up to about 0.15 mg/kg in limestone. Concentrations of Ag in streambed sediment samples indicate a continuous concentration range up to 1.5 mg/kg detected concentration (USGS 1998). The Ag concentration range in most soils is approximately 0.03-0.4 mg/kg, although higher concentrations of up to 5 mg/kg have been reported for organic-rich soils. The geochemical characteristics of Ag in soil are similar to those of Cu. Although readily available due to weathering, Ag quickly precipitates in neutral and alkaline soils due to low solubility in those types of conditions. Ag also sorbs readily to MnO₂ and forms complexes with humic substances in the soil (Kabata-Pendias 2001). Ag concentrations are strongly correlated with the organic carbon content of the soil (Alloway 1990). The geochemical characteristics of Ag therefore indicate that Ag can be significantly concentrated during weathering and soil formation processes. No anthropogenic sources relevant to background conditions have been identified in Hawai'i (Earth Tech 2006). Therefore, although literature data indicate low concentrations of Ag in the parent material source for Hawai'i soils, the geochemical characteristics of Ag indicate potential for enrichment of Ag in soils compared to the basaltic source rocks.

4.2.14.2 COMBINED PLOTS ANALYSIS

Combined plots for the full Ag dataset are presented in Figure 34a. The cumulative probability plot shows multiple discontinuities in the data distribution. The initial (low concentration) discontinuity is likely due to the limited number of available data points with sufficiently low detection limits to adequately represent background concentrations near the lower end of the range. The combined plots of only the detected values presented in Figure 34b reveal a more continuous log-normal data distribution, with a discontinuity corresponding to an inflection point at 1.5 mg/kg. The single data point with concentration above 1.5 mg/kg represents a sample collected on Maui; this data point is separated from the rest of the Maui data population and is therefore not likely to be associated with natural background conditions. Therefore, 1.5 mg/kg represents a reasonable estimate of the UBC of the background Ag concentration for Hawaiian soils. The single potential outlier (2.9 mg/kg) represents a sample collected from a soil in Maui with silt loam texture. As discussed in the previous section, Ag is strongly correlated with organic carbon content of the soil; therefore, the data point may represent natural enrichment through soil formation process that developed an organic carbon-



rich soil in the form of the silt loam. The BTV for Ag in soil therefore is estimated at the maximum reported concentration in the dataset of 2.9 mg/kg.

4.2.15 Thallium (TI)

The dataset for TI is limited to 61 data points, and includes only four detected concentrations. The TI concentration range in the dataset is 0.25U (non-detect concentration)–15.05J (estimated concentration) mg/kg. Two of the four detected concentrations exceed the risk-based EAL (0.78 mg/kg), both from samples collected on Maui. Spatial distribution of TI concentrations is shown in Figure 35.

4.2.15.1 SOURCES AND GEOCHEMISTRY

TI shows strong correlation with rock type, increasing in concentration with increasing acidity in magmatic rocks (Kabata-Pendias 2001). Concentrations are typically 0.05–0.4 mg/kg in mafic rocks, and 0.01–0.14 mg/kg in sedimentary rocks. TI is readily mobilized but quickly adsorbed to clays, and Mn or Fe oxides. Concentration of TI in most soils are generally less than 1 mg/kg (Alloway 1990). Anthropogenic sources of TI include combustion of coal, smelting of heavy metals, production of cement and various refining processes (Kabata-Pendias 2001).

4.2.15.2 COMBINED PLOTS ANALYSIS

Combined plots for TI are presented in Figure 36. There are not enough data representing detected concentrations to determine the data distribution and conduct the combined plot analysis; therefore, no background concentration can be estimated. However, all four detected concentrations are well above the EALs, and are therefore not likely to represent the background population. The UBC for TI is estimated at 0.25 mg/kg, and the BTV is estimated at 15 mg/kg (maximum detected concentration in the dataset).

4.2.16 Vanadium (V)

The V dataset contains 141 data points, with no non-detect values. The concentration range is 0.25–1,090 mg/kg, with a mean of 230.7 mg/kg. The dataset includes 18 data points with concentrations above the risk-based EAL (390 mg/kg). Concentrations above the EAL were detected in soil samples from all islands except for Kaho'olawe, as shown on the concentration distribution map in Figure 37.

4.2.16.1 SOURCES AND GEOCHEMISTRY

V is strongly correlated to rock type. The typical V concentration range in magmatic rocks approximately 200–250 mg/kg in mafic rocks, and 40–90 mg/kg in acidic rocks. For sedimentary rocks, V concentrations can range up to 130 mg/kg in shales and argillaceous sediments, and up to 45 mg/kg in limestones. Depending on the host minerals, V may remain within the residual rock-forming minerals or be mobilized and become incorporated in the secondary mineral structures (e.g., clays and Fe oxides). Kabata-Pendias (2001) report strong correlation between V and Mn as well as V and K. Adhesion of vanadate ions (VO₄³) to clay minerals, particularly Fe oxyhydroxides, may result in soil enrichment of V. However, concentrations of V in most soils are primarily related to the parent rock composition (Kabata-Pendias 2001). Soils developed from mafic rocks have the highest V concentration range: up to 460 mg/kg.

Nakamura and Sherman (1961) found a V concentration range in Hawaiian soils of 190–1,520 mg/kg, with highest concentrations limited to the Humic Ferruginous Latosols soil group, a group of soils that has been highly weathered and are rich in iron and titanium oxides. The EBA dataset include some of the data included in the Nakamura and Sherman (1961) study.

4.2.16.2 COMBINED PLOTS ANALYSIS

The combined plots for V are presented in Figure 38. The log-scale probability plot shows a relatively continuous and straight segment indicative of a log-normal distribution for V concentrations in the



dataset with no observed delimiting inflection point. There is a data discontinuity and a slight inflection point observed at 770 mg/kg. The two data points represent samples collected from Kaua'i and Maui. Both samples were collected as part of the study conducted by Nakamura & Sherman (1951, 1961). The study identified all of the higher concentrations of vanadium as being limited to a specific type of soil known as the Humic Ferruginous Latosols, which are highly weathered iron and titanium-oxide rich soils. Therefore, the maximum concentration of 1,090 mg/kg represents natural enrichment due to soil formation and thus represents the BTV for V. The UBC for V is estimated at 770 mg/kg where the discontinuity can be discerned from the figure.

4.2.17 Zinc (Zn)

The Zn dataset contains 125 data points, with no non-detect values. The concentration range is 3.57–1,200 mg/kg, with a mean of 132.47 mg/kg. No data point has reported concentration above the risk-based EAL for Zn (23,000 mg/kg). Spatial distribution of Zn concentrations in the dataset is illustrated in Figure 39.

4.2.17.1 SOURCES AND GEOCHEMISTRY

The distribution of Zn concentrations among the major magmatic rock types is relatively uniform; however, mafic rocks tend to have the highest levels, i.e., approximately 80-120 mg/kg (Kabata-Pendias 2001). In sedimentary rocks, the Zn concentration range is approximately 80-120 mg/kg in argillaceous rocks, and 19-25 mg/kg in limestones. Data representing O'ahu volcanic rocks indicate concentrations up to 340 mg/kg for the Waianae Volcanic series and up to 209 mg/kg for the Honolulu Volcanic series (Bishop Museum 2003). A continuous concentration range of up to 480 mg/kg has been reported for streambed sediments on O'ahu (USGS 1998). Zn minerals have high solubility; therefore Zn is mobile during weathering. Zn also has relatively strong affinity for mineral and organic particles, leading to accumulation in surface soils. Kabata-Pendias (2001) note that Zn in soils is associated with hydrous Fe and Al oxides and clay minerals, and that Zn concentrations show a strong inverse correlation with grain size due to sorption to fine-grained particles (e.g., clays). Zn concentrations in natural U.S. soils are as high as 220 mg/kg for loamy and clay soils and 600 mg/kg for iron-rich soils (Kabata-Pendias 2001). Soils in Hawai'i are typically fine-grained and derived from basalts, and are therefore likely to accumulate relatively high concentrations of Zn. Anthropogenic sources of Zn potentially include sewage sludge, ash from incinerators, and industrial facilities. De Carlo et al. (2004) report elevated Zn concentrations in suspended stream sediment samples collected during storm events in both urban areas and upstream of urban areas, suggesting that both natural and anthropogenic Zn sources are likely to affect background conditions for Hawaiian soils.

4.2.17.2 COMBINED PLOTS ANALYSIS

Combined plots for Zn are presented in Figure 40. Based on the data distribution shown by the cumulative probability plot, the two data points with the highest concentrations (990 and 1,200 mg/kg) are potential outliers as they clearly do not fit the population distribution indicated by the remaining data. The two outliers were removed and the combined plots were reconstructed to better display the distribution of the main population, as presented in Figure 40c. The two outliers were collected from the same site in Maui, representing silty loam soil presumably high in organic content. Therefore, the two high concentrations may represent localized enrichment of Zn due to the soil formation process that developed organic-rich soils. The BTV for Zn, therefore is estimated to be at the maximum value reported of 1,200 mg/kg.

The cumulative probability plots show a relatively continuous data distribution with a discontinuity at approximately 254.9 mg/kg. However, the two data points above the discontinuity fall roughly along the same slope as the rest of the data and are likely to be part of the background population. Therefore, based on the combined plots analysis, the UBC of background concentration estimated for Zn in Hawai'i soils is approximately 349 mg/kg.



4.3 RESULTS: ELEMENTS WITH NO ESTABLISHED EALS

This section presents the results of background evaluations for the group of target elements with no established EALs (HDOH 2011).

4.3.1 Aluminum (Al)

The AI dataset represents 92 samples with a concentration range of 2,500–166,138 mg/kg, and a mean concentration of 48,974 mg/kg. No non-detect values were reported for AI. The maximum AI concentration represents a sample collected on the island of Kaho'olawe, as shown on concentration distribution map in Figure 41.

4.3.1.1 SOURCES AND GEOCHEMISTRY

The Al concentration range in mafic rocks is 78,000–88,000 mg/kg, varying very little with the different magmatic rock types. In sedimentary rocks, Al concentrations can reach up to 100,000 mg/kg in argillaceous sediments, while in limestones Al concentrations typically range up to about 13,000 mg/kg (Kabata-Pendias 2001). O'ahu rock sample data indicate concentrations of up to 99,000 mg/kg for Ko'olau Volcanics (Bishop Museum 2003). Concentrations of Al in streambed sediment samples collected on O'ahu range up to 130,000 mg/kg (USGS 1998). Al derived from primary rock-forming minerals is incorporated into secondary minerals (primarily clay minerals) during weathering. Secondary Al minerals are generally low in solubility and therefore tend to accumulate and remain immobile in weathered soils (Kabata-Pendias 2001). Previous evaluation of background conditions for O'ahu soils indicates that background Al concentrations can exceed 150,000 mg/kg (Earth Tech 2006).

4.3.1.2 COMBINED PLOTS ANALYSIS

Figure 42 presents the combined plots constructed for AI. The cumulative probability plot forms a relatively continuous log-normal distribution with a data discontinuity at 137,528 mg/kg separating the maximum detected concentration (166,138 mg/kg) from the rest of the dataset. The maximum concentration represents a sample collected on the island of Kaho'olawe. The range of AI concentrations for Kaho'olawe is higher compared to the other islands; however, as shown in the sampling location univariate plot, the maximum AI concentration is likely to be part of the background population because it is not distinctly elevated compared to the rest of the Kaho'olawe dataset; therefore, the estimated BTV and UBC of the background AI concentration range for Hawai'i soils are 166,138 mg/kg.

4.3.2 Calcium (Ca)

The Ca dataset contains 92 data points with a concentration range of 31–77,208 mg/kg and a mean of 7,307.6 mg/kg. The dataset does not contain any non-detect concentrations. Figure 43 presents the concentration distribution of Ca in Hawai'i soils based on the dataset.

4.3.2.1 Sources and Geochemistry

Ca is a primary component of both magmatic and sedimentary rock-forming minerals (e.g., feldspar, calcite) as well as secondary minerals (e.g., clays) in rock and soil formations. Soils in Hawai'i are derived from both magmatic rocks and calcium carbonates (limestones); therefore, relatively high Ca concentrations are present in Hawai'i soils.

4.3.2.2 COMBINED PLOTS ANALYSIS

The cumulative probability plots for Ca presented in Figure 44 show a relatively straight segment in the log-scale plot, indicating a log-normal population distribution. There appears to be a data discontinuity separating the top two Ca concentrations from the rest of the dataset; however, the two highest concentrations fall along the same trend as the rest of the dataset and therefore are likely part of the same population. Based on the combined plots analysis, the estimated BTV and UBC of the background Ca concentration range for Hawai'i soils are 77,208 mg/kg.



4.3.3 Iron (Fe)

The Fe dataset contains 104 data points with no non-detect concentrations present. The Fe concentration range in the dataset is 1,713–260,082 mg/kg, with a mean of 95,550 mg/kg. The maximum concentration was reported for a sample collected on the island of Kaua'i (Figure 45). All data points represent detected concentrations and/or detected estimated concentrations (J-flagged).

4.3.3.1 SOURCES AND GEOCHEMISTRY

Fe concentrations are strongly correlated with rock type. Basalt and other mafic rocks have an intermediate Fe concentration range of 56,000–87,000 mg/kg (Kabata-Pendias 2001). Basaltic rocks from the Honolulu Volcanics have Fe concentrations up to 99,000 mg/kg (Bishop Museum 2003). Natural Fe concentrations in soil developed from basalts on O'ahu have reported Fe concentrations exceeding 200,000 mg/kg in weathered soil horizons due to redox and pH conditions favoring Fe precipitation (Earth Tech 2006).

4.3.3.2 COMBINED PLOTS ANALYSIS

Figure 46 presents cumulative probability and univariate plots for Fe. The cumulative probability plot shows data that closely fit a log-normal distribution with no distinct discontinuity. Sampling location univariate plot indicate that concentration ranges are relatively similar for most of the islands, extending all the way to the maximum concentration detected in the dataset. Therefore, the maximum concentration included in the database of 260,082 mg/kg represents the estimated BTV and UBC of the background concentration range for Fe in Hawai'i soils.

4.3.4 Manganese (Mn)

The Mn dataset contains 92 data points, with all values representing detected or detected estimated concentrations. The concentration range of Mn in the soil dataset is 13–4,880 mg/kg, with a mean concentration of 1,058 mg/kg. Figure 47 illustrates the spatial distribution of Mn concentrations throughout the Hawaiian islands based on the dataset.

4.3.4.1 SOURCES AND GEOCHEMISTRY

Mn is one of the most abundant of the trace elements, and is commonly found in basalts and other mafic rocks at a concentration range of 1,200–2,000 mg/kg (Kabata-Pendias 2001). Mn concentrations reported for Ko'olau Volcanics range up to 2,014 mg/kg, and up to 3,872 mg/kg for Honolulu Volcanics (Bishop Museum 2003). Mn is relatively mobile with a pronounced tendency to adsorb to clay particles, thereby accumulating in loamy or clay soils. Kabata-Pendias (2001) report Mn concentrations for loam and clay soils derived from basalts and andesites ranging from 670 mg/kg to 9,200 mg/kg. Mn tends to have uneven distribution in the soil substrate and may be highly concentrated in nodules and concretions with high levels of other trace elements.

4.3.4.2 COMBINED PLOTS ANALYSIS

The combined plots presented in Figure 48 indicate a single relatively continuous log-normal distribution for Mn in the dataset. There is a slight discontinuity separating the top two concentrations with the rest of the data; however, the two segments fall along the same trend, and therefore are likely part of the same background population range. The maximum reported concentration of 4,880 mg/kg is considered to represent both the BTV and the UBC for background Mn in Hawai'i soils.

4.3.5 Strontium (Sr)

The Sr dataset contains 77 data points, 12 of which are non-detect concentrations. The Sr concentration range in the dataset is 2U (non-detect concentration)–1,094 mg/kg, with a mean of 93.93 mg/kg. Figure 49 presents a map of spatial distribution of concentrations included in the Sr dataset for all Hawaiian islands.



4.3.5.1 SOURCES AND GEOCHEMISTRY

The Sr concentration range in mafic rocks is approximately 140–460 mg/kg. For sedimentary rocks, the range is 300–450 for argillaceous sediments, and 450–600 mg/kg for limestones. The geochemical characteristics of Sr are similar those of Ca, and Sr is therefore typically associated with Ca in soils and rocks. Sr is easily mobilized, particularly in oxidizing acidic environments, becoming incorporated in clay minerals and bound by organic matter. Soil concentrations of Sr are primarily controlled by the parent rock material, with a Sr concentration range in U.S. topsoils of approximately 110–445 mg/kg (Kabata-Pendias 2001).

4.3.5.2 COMBINED PLOTS ANALYSIS

Figure 50 presents the combined plots constructed for strontium. After removing the non-detect concentrations from the dataset, the cumulative probability plot (Figure 50b) shows a relatively linear segment in the log-scale plot indicating a log-normal distribution. Although several discontinuities appear along the segment, all of the data points fall relatively along the same slope with respect to the log-scale, and are therefore likely to be part of the background population. Most of the high Sr concentrations correspond to samples collected on O'ahu. However, the O'ahu data cover the entire range up to the maximum detected concentration, suggesting that the O'ahu data fit the background population. Therefore, the estimated BTV and UBC of the background concentration range for Sr correspond to the maximum concentration in the dataset: 1,094 mg/kg.

4.3.6 Tin (Sn)

The Sn dataset contains 107 data points, with a concentration range of 0.6–150 mg/kg and a mean of 12.43 mg/kg. The dataset contains 34 non-detect values. The maximum Sn concentration represents a sample collected on the southern coast of the island of Kaua'i (Figure 51).

4.3.6.1 SOURCES AND GEOCHEMISTRY

The Sn concentration range in mafic rocks is approximately 0.9–1.5 mg/kg. Argillaceous sedimentary rocks have the highest concentrations of Sn of all the common rock types at 6–10 mg/kg. Sn concentrations in limestone are generally lower i.e., up to only about 0.5 mg/kg. Kabata-Pendias (2001) noted that the range of Sn in soils in the United States is 1.7–4.0 ppm.

4.3.6.2 COMBINED PLOTS ANALYSIS

Figure 52 presents the combined plots for Sn. After removal of the non-detect concentrations, the two highest concentrations present in the dataset lie well outside of the distribution range for the rest of the data (Figure 52b), indicating that these two points are outliers that are most likely not associated with background conditions. Figure 52b also shows a continuous log-normal data distribution up to an inflection point at 10 mg/kg. The four data points above the inflection point (including the two outliers) fall along the same trend, indicating that they are likely not part of the background population. In addition, these four data points have concentrations that are well above the range of Sn in U.S. soils as noted by Kabata-Pendias (2001), therefore they are likely attributed to anthropogenic sources.

The two outliers were removed from the dataset and the combined plots were reconstructed as presented in Figure 52c. The resulting log-scale cumulative probability plot shows a continuous log-normal distribution represented by a straight line segment extending up to 10 mg/kg. Data points with concentrations above 10 mg/kg represent samples collected on Kaua'i, O'ahu, and Maui. The elevated data points do not fit the continuous ranges corresponding to the remaining data, and are well above the reported range of Sn concentrations in soils in the United States as discussed in the previous section. Therefore, the BTV and the UBC for Sn are estimated at 10 mg/kg.



4.3.7 Titanium (Ti)

The Ti dataset contains 92 data points with no non-detect values. The Ti concentration range in the dataset is 3,809–53,032 mg/kg, with a mean of 21,112 mg/kg. Figure 53 presents the spatial distribution of Ti concentrations included in the dataset.

4.3.7.1 SOURCES AND GEOCHEMISTRY

The Ti concentration in mafic rocks is 900–13,800 mg/kg. The typical concentration range of Ti is 3,800–4,600 mg/kg in argillaceous sedimentary rocks, and 300–400 mg/kg in limestones. Ti minerals are highly resistant to weathering, and therefore tend to exist in soils as unweathered mineral particles. The solubility of Ti in the soil environment is very limited, resulting in accumulation in the surface soil horizon. The Ti concentration range generally reported for soils is approximately 1,000–9,000 mg/kg (Kabata-Pendias 2001).

4.3.7.2 COMBINED PLOTS ANALYSIS

The combined plots constructed for Ti are presented in Figure 54. The log-scale cumulative probability plot shows a relatively straight segment with no distinct inflection point, indicating a log-normally distributed population. Therefore, based on the combined plots analysis, the BTV and the UBC for background Ti in Hawai'i soils correspond to the maximum value detected in the dataset of 53,032 mg/kg.

4.3.8 Tungsten (W)

The W dataset contains 50 data points, 21 of which are non-detect values. The W concentration range is 0.002–5.43 mg/kg, with a mean of 1.18 mg/kg. Figure 55 presents spatial distribution of W concentrations included in the dataset.

4.3.8.1 SOURCES AND GEOCHEMISTRY

W concentrations are strongly correlated with rock type, with a concentration range in mafic rocks of 0.36–1.1 mg/kg, and increasing in more acidic magmatic rocks (e.g., granites, dacites). The W concentration range is approximately 1.8–2.0 mg/kg in argillaceous sedimentary rocks, and up to about 0.6 mg/kg in limestones (Kabata-Pendias 2001). W minerals are only slightly soluble and therefore have limited mobility during weathering. The W concentration range in U.S. soils is 0.5–5 mg/kg.

4.3.8.2 COMBINED PLOTS ANALYSIS

Combined plots for W are presented in Figure 56. Due to the limited number of detected concentrations, the combined plots analysis is inconclusive. However, there is no evidence to suggest that the maximum W concentration (5.43 mg/kg) is not part of the background population. Therefore, based on available data the BTV and the UBC for W is estimated at 5.43 mg/kg.

4.4 ADDITIONAL TARGET ELEMENTS

Magnesium, sodium, potassium, and phosphorus were considered for the EBA in order to evaluate potential correlation with the other target elements and provide a comprehensive assessment of background conditions for the major chemical elements that occur in Hawaiian soils.

4.4.1 Magnesium (Mg)

The Mg dataset contains 92 data points with 12 non-detects included. The Mg concentration range in the dataset is 25U (non-detect concentration)–68,611 mg/kg, with a mean of 9,364 mg/kg. Higher concentrations of magnesium are observed for O'ahu and the island of Hawai'i compared to the rest of the main Hawaiian islands (Figure 57).



4.4.1.1 COMBINED PLOTS ANALYSIS

Combined plots for Mg were constructed for the full dataset and for data representing only detected concentrations, as shown in Figure 58a and Figure 58b. The log-scale cumulative probability plot shows a relatively continuous data distribution with no distinct discontinuities. Although the univariate plots indicate that relatively high Mn concentrations occur in soils on O'ahu and the island of Hawai'i, the data appear to fit the log-normal population distribution indicated by the remaining data. Therefore, the maximum detected concentration of 68,611 mg/kg represents the BTV and UBC for background in Hawai'i soils.

4.4.2 Phosphorus (P)

The dataset for non-metallic element P contains 92 data points with no non-detect values reported. The P concentration range in the dataset is 170–10,178 mg/kg, with a mean of 1,993 mg/kg. Figure 59 shows the spatial distribution of concentrations reported in the P dataset.

4.4.2.1 COMBINED PLOTS ANALYSIS

Figure 60 shows the combined plots constructed for P. Cumulative probability plot confirmed a single background population with the BTV and UBC corresponding to the maximum concentration detected of 10,178 mg/kg.

4.4.3 Potassium (K)

The K dataset contains 92 data points, with a concentration range of 37–10,850 mg/kg and a mean of 2,525 mg/kg. The dataset contains no non-detect values. Spatial distribution of K concentrations included in the dataset is presented in Figure 61.

4.4.3.1 COMBINED PLOTS ANALYSIS

Figure 62 presents the combined cumulative probability and univariate plots for K. The log-scale cumulative probability plot shows a continuous data distribution. Therefore, the entire dataset most likely represents a single population of background concentrations extending up to the maximum detected concentration of 10,850 mg/kg. The BTV and UBC therefore are defined as the maximum detected concentration of 10,850 mg/kg.

4.4.4 Sodium (Na)

The Na dataset contains 92 data points, including four non-detect values. The Na concentration range is 63U (non-detect concentration)–18,078 mg/kg, with a mean of 1,992 mg/kg. Figure 63 shows the spatial distribution of Na included in the dataset.

4.4.4.1 COMBINED PLOTS ANALYSIS

The combined plots for Na are presented in Figure 64. The cumulative probability plot shows a single continuous population with no distinct inflection point or data discontinuity. The estimated BTV and UBC for background Na therefore correspond to the maximum detected concentration of 18,078 mg/kg.

5.0 GEOCHEMICAL ASSOCIATION

Correlation coefficient and geochemical regression studies can be used to estimate background concentration ranges for metals and other elements that tend to be associated with each other in natural soils. The distribution of naturally occurring elements in non-impacted soils is controlled by geochemical and biological processes; therefore, these natural processes are important in controlling elemental distributions and groupings. In contrast, a chemical release may disrupt the natural elemental associations in the soil. Therefore, potential contaminants and background concentration ranges can be identified by examining the concentration relationships between metals and other elements.



The correlation coefficient measures the strength of the linear association between two quantitative variables. It does not distinguish between the explanatory or response variables and is not affected by changes in the unit of measurement of either or both variables. For example, if there are n observations on two variables x and y, denoted by:

$$(x_1, y_1), (x_2, y_2), \dots, (x_n, y_n)$$

Then the correlation coefficient *r*, for variables *x* and *y* computed is:

$$r = \left[\sum (x_i - \mu_x) \left(\sum y_i - \mu_y \right] / (n - 1) s_x s_y \right]$$

Where μ_x and s_x are the mean and standard deviation of the *x* observation, and μ_y and s_y refer to the *y* observation. The basic properties of *r* follow:

The value of r always falls between -1 and 1. Positive r indicates positive association between the variables, and negative r indicates negative association.

- 1. The extreme values r = -1 and r = 1 occur only in the case of perfect linear association.
- The value of *r* is not changed when the unit of measurement of *x*, *y*, or both changes. The correlation coefficient *r* has no unit of measurement; it is a dimensionless number between 1 and 1.

The unfiltered concentration data were used to calculate a correlation coefficient for each pair of target elements to identify statistically significant correlation relationships that might be useful for evaluating background. The resulting correlation coefficient matrix is presented in Table 4. If the correlation coefficient for a pair of elements exceeded 0.5, then the concentration relationship for that element pair was examined further to determine whether it was appropriate for evaluating background. A particular concentration relationship was used to evaluate background only if it could be explained by natural processes, such as geochemical association in the parent rock from which the soil was derived, or by adsorption to clay minerals and/or organic matter that occurs during weathering and soil formation.

The association relationship between element-pairs that that may be correlated as a result of natural processes was modeled using the least-square regression line (r^2) , which is a straight line that describes how a response variable changes in response to an explanatory variable. Regression, unlike correlation, requires an explanatory variable and a response variable. Aluminum and iron generally are explanatory variables, and other metals are response variables. It should be noted that correlation and regression are mathematically related to *r*. In the geochemical regression model, the upper and lower limits of the 95% prediction interval are used to predict a current sample population and a future observation.

5.1 IRON (FE) VS. VANADIUM (V)

As shown in Table 4, the correlation coefficient (*r*) value for Fe vs. V is 0.55, indicating statistically significant correlation between these two metals. Basalts generally have relatively high V concentrations (200–250 mg/kg) compared to other rock types. The mobility of V during weathering and soil formation is dependent on the host minerals: V may remain within the residual rock-forming minerals, or may be incorporated in the mineral structures of secondary minerals (primarily clays and Fe oxides). However, the V concentrations of most soils are closely related to concentrations in the parent rocks, and V is usually distributed relatively uniformly across the soil horizons. Soils developed over mafic rocks typically have the highest V concentrations (150–460 mg/kg); V concentrations in some loamy and silty soils, as well as some Ferralsols, exceed those of their parent rocks. V concentrations range up to 150 mg/kg for loamy and clay soils in the United States, and up to 330 mg/kg for loamy and clay soils derived from basalts and andesites in New Zealand. V concentrations reported for Ferralsols range up to 530 mg/kg (Kabata-Pendias 2001).



Nakamura & Sherman (1961) identified high concentrations of vanadium (up to 1,500 mg/kg) limited to a group of highly weathered soils known as the Humic Ferruginous Latosols, which are rich in iron and titanium oxides. The correlation between vanadium and iron observed for Hawaiian soils can therefore be explained by geochemical association relationships reported for Fe and V in mafic volcanic rocks and the soils derived from these rocks. The combined plot analysis for Fe indicates that all detected iron concentrations represent background conditions for Hawaiian soils. Figure 65 illustrates the relatively strong positive correlation between Fe and V concentrations, and shows that that the maximum V concentration only slightly above the upper bound of the 95% prediction interval. Therefore, the Fe vs. V correlation evaluation supports the conclusion that the maximum V concentrations are within the natural background concentration range for Hawaiian soils.

5.2 ALUMINUM (AL) VS. IRON (FE)

As shown in Table 4, the r value for Fe vs. Al is 0.72. Figure 66 illustrates this strong positive correlation, particularly in the higher aluminum and iron concentration ranges. According to the literature, basalts and other mafic rocks generally have a Fe concentration range of 56,000-87,000 mg/kg (Kabata-Pendias 2001). The UTL reported for Fe concentrations in the Ko'olau Volcanics of O'ahu is 99,000 mg/kg (Bishop Museum 2003). Previous Navy background evaluation experience indicates that natural Fe concentrations in soils developed from O'ahu basalts can exceed 200,000 mg/kg, particularly in weathered soil horizons where reduction/oxidation (redox) and pH conditions promote Fe precipitation. The UTL reported for Al concentrations in Ko'olau basalt samples is 99,000 mg/kg (Bishop Museum 2003), and the UTL reported for Al concentrations in O'ahu streambed sediment samples is 130,000 mg/kg (USGS 1998). The rock and stream sediment data indicate that the Hawaijan volcanic rocks represent a substantial natural source of both AI and Fe. Maximum AI and Fe concentrations are typically higher in soil than in the parent rocks due to natural enrichment that occurs during weathering and soil formation, when AI and Fe are released from the primary rock-forming minerals and incorporated into secondary minerals, primarily clay minerals. Therefore, the highest concentrations of AI and Fe tend to occur in the clay-rich weathered soil horizons, particularly the B horizon (i.e., the zone of accumulation beneath the surface soil horizon). As shown on Figure 66, the maximum Fe concentrations are below the upper bound of the 95% prediction interval. Therefore, the Al vs. Fe correlation evaluation supports the conclusion that the maximum Fe concentrations are within the natural background concentration range for Hawaiian soils.

5.3 ALUMINUM (AL) VS. MANGANESE (MN)

As shown in Table 4, the *r* value for Al vs. Mn is 0.66. The typical Mn concentration range in basalts and other mafic rocks is approximately 1,200–2,000 mg/kg (Kabata-Pendias 2001). Mn is one of the most abundant of the trace elements. The UTL reported for Mn concentrations in the Ko'olau Volcanics is 2,014 mg/kg (Bishop Museum 2003). Mn is relatively mobile and tends to be distributed unevenly in soil substrata; in addition to various nodules, Mn may be concentrated at certain locations with high levels of other trace elements. Mn released from parent rocks is readily adsorbed to clay particles and forms numerous oxide and hydroxide secondary minerals during weathering and soil formation. Kabata-Pendias (2001) reported a Mn concentration range of 670–9,200 mg/kg for loamy and clay soils derived from basalts and andesites in New Zealand. The correlation between Al and Mn illustrated in Figure 67 can be attributed to adsorption of manganese to clay (aluminosilicate) minerals in the soil and formation of other secondary minerals containing aluminum. As shown on Figure 67, the maximum manganese concentrations are below the upper bound of the 95% prediction interval. Therefore, the correlation evaluation supports the conclusion that the maximum manganese concentrations are within the natural background concentration range for Hawaiian soils.

5.4 BARIUM (BA) VS. BERYLLIUM (BE)

As shown in Table 4, the *r* value for Ba vs. Be is 0.70. According to the literature, the typical Ba concentration range in basalts and other mafic rocks is 250–400 mg/kg. Ba shows a strong affinity for clays; therefore, increased concentrations in soil relative to the parent rock can be attributed to the natural enrichment that occurs during weathering and soil formation. According to Kabata-



Pendias (2001), Ba concentration ranges are typically 20–1,500 mg/kg for podzols and sandy soils, 200-1,500 mg/kg for loess and silty soils, and 150-1,500 mg/kg for natural loamy and clay topsoils. Govindaraju (1994) reported a Ba concentration range of 290-2,240 mg/kg for U.S. reference soils. Potential anthropogenic background Ba sources include atmospheric fallout from industrial facilities and application of phosphate fertilizers. According to the literature, Be concentration ranges are generally 0.3-1.0 mg/kg for basalts and other mafic rocks. The geochemical characteristics of Be are similar to those of AI; therefore, Be tends to accumulate in clay-rich weathered soil horizons due to leaching and substitution for AI in clay minerals (Kabata-Pendias 2001). Be concentrations ranging between 0.27 mg/kg and 1.95 mg/kg were reported for 27 unpolluted surface soils in Japan (Kabata-Pendias 2001). Asami and Fukazawa (1985) report background Be concentrations of 0.59-1.57 mg/kg for Andisols (i.e., soils formed from recent volcanic ash deposits) and 0.67-2.47 mg/kg for calcareous soils (i.e., soils derived from limestones). Activities involving combustion of coal and other fossil fuels are the most significant anthropogenic background Be sources (Kabata-Pendias 2001). The correlation between Ba and Be illustrated in Figure 68 can be attributed to Ba-rich clay minerals containing Be. Be concentrations above the upper bound of the 95% prediction interval shown on Figure 68 represents data collected from soil samples that are high in organic content that may concentrate Be due to its affinity for organic carbon; therefore, these data points represent natural outliers and were retained as part of the background population for Be in Hawai'i soils.

5.5 BARIUM (BA) VS. PHOSPHORUS (P)

As shown in Table 4, the *r* value for Ba vs. P is 0.66. As discussed above, Ba shows a strong affinity for clays, and therefore tends to accumulate in clay-rich weathered soil horizons along with Fe and Al. Phosphates in natural Hawaiian soils are derived from weathering of the basaltic volcanic and coralline limestone rocks that dominate the island chain. The mean P content reported for tholeitic basalts is 0.1% and for alkali olivine basalts 0.17% (Nockolds 1954). Phosphate released from rocks during weathering and soil formation tends to be associated with clay and organic matter particles. Organic phosphate compounds occur in surface soil due to uptake of phosphate by plants, and are mineralized to inorganic phosphate as organic material is decomposed in the soil. The geochemical characteristics of Ba and P indicate that Ba tends to be correlated with P in Hawaiian soils due to the tendency of both elements to accumulate in clays and other fine-grained soil particles rich in Al and Fe. As shown on Figure 69, the maximum Ba concentrations are below the upper bound of the 95% prediction interval; therefore, the Ba vs. P correlation evaluation supports the conclusion that the maximum Ba concentrations are below the upper bound of the 95% therefore, as discussed above, phosphate fertilizers contain relatively high Ba concentrations; therefore, elevated Ba and P concentrations could be attributable to fertilizer application.

5.6 CALCIUM (CA) VS. STRONTIUM (SR)

As shown in Table 4, the *r* value for Sr vs. Ca is 0.87. Sr is a relatively common trace element, and tends to be concentrated in rocks including intermediate magmatics and carbonate sediments (Kabata-Pendias 2001). Ca is a major component of the primary minerals that form coralline limestones (e.g., calcite) and basaltic volcanic rocks (e.g., feldspars), and the secondary minerals formed by weathering (e.g., clays). Ca and Sr are both elements of Group IIA, the alkaline earth metals, and the cations of both elements have very similar radii; therefore, Sr readily substitutes for Ca in rock and soil minerals and is frequently associated with Ca in soil (Kabata-Pendias 2001). The strong correlation between Ca and Sr as illustrated in Figure 70 can therefore be attributed to the geochemical characteristics of these metals. The Ca vs. Sr correlation evaluation supports the conclusion that the maximum Sr concentrations are within the natural background concentration range for Hawaiian soils.

5.7 IRON (FE) VS. CHROMIUM (CR)

As shown in Table 4, the *r* value for Fe vs. Cr is 0.69. Cr concentrations in the upper range of the natural background population occur in soils derived from the Fe-rich volcanic rocks that dominate the Hawaiian island chain. Hawaiian volcanic rocks contain relatively high Cr concentrations: The UTLs reported for Cr concentrations in O'ahu basalts are 1,061 mg/kg for the Ko'olau Volcanics, 870



mg/kg for the Waianae Volcanics, and 600 mg/kg for the Honolulu Volcanics (Bishop Museum 2003). Hawaiian volcanic rocks therefore represent substantial natural Cr sources. Although Cr concentrations in natural soils tend to increase with increasing clay fractions, suggesting adsorption to clay minerals (which are rich in iron and aluminum), Cr concentrations in O'ahu soils have been found to be highest in the coarse-grained fractions because they contain more primary igneous minerals (e.g., olivine and pyroxene) (De Carlo and Anthony 2002, De Carlo et al. 2004). Kabata-Pendias (2001) reports Cr concentrations ranging up to 1,100 mg/kg for loamy and clay soils derived from basalts and andesites in New Zealand. The information and data therefore indicate that parent rock type is the most important factor controlling natural background conditions for Cr. Therefore, soils developed on mafic rocks (i.e., Mg- and Fe-rich rocks such as Hawaiian basalts) are likely to have relatively high Cr concentrations. Figure 71 illustrates the relatively strong positive correlation between Fe and Cr concentrations, and shows that that none of the Cr concentrations exceed the upper bound of the 95% prediction interval. Therefore, the correlation evaluation supports the conclusion that the maximum Cr concentrations are within the natural background concentration range for Hawaiian soils.

5.8 COBALT (CO) VS. MANGANESE (MN)

As shown in Table 4, the *r* value for Co vs. Mn is 0.60. As discussed above, Mn occurs in Hawaiian basalts at relatively high concentrations (greater than 2,000 mg/kg), and tends to be enriched in soil due to its mobility and affinity for clays and other fine-grained particles and the formation of oxide and hydroxide secondary minerals. The UTL reported for Co concentrations in the Ko'olau Volcanics is 118 mg/kg (Bishop Museum 2003), and the UTL reported for Co concentrations in O'ahu streambed sediment samples is 70 mg/kg (USGS 1998). During weathering Co is mobile in oxidizing environments; however, because it adsorbs strongly to clay and Fe/Mn oxides, Co is relatively immobile once deposited in most soils. The correlation between Co and Mn illustrated in Figure 72 is therefore explained by the tendency of both metals to adsorb to clay particles and form secondary oxide and hydroxide minerals in the soil. As shown on Figure 72, one manganese concentration value exceeds the upper bound of the 95% prediction interval; however, the associated concentration (4,880 mg/kg) may represent background conditions due to the uneven distribution of Mn and its ability to form nodules and concretions in soil. In addition, the maximum Mn concentration is within concentration ranges reported for other uncontaminated soils throughout the world (Kabata-Pendias 2001).

5.9 COBALT (CO) VS. NICKEL (NI)

As shown in Table 4, the r value for Co vs. Ni is 0.54. According to literature sources, basalts typically have Ni concentrations ranging from 45-410 mg/kg (Alloway 1990). However, the UTL reported for Ni concentrations in Ko'olau basalt samples is 1,524 mg/kg (Bishop Museum 2003). Ni concentrations detected in O'ahu streambed sediment samples show a relatively continuous range extending up to a maximum of 430 mg/kg (USGS 1998). The rock and stream sediment data indicate that Hawaiian basalts represent a substantial natural Ni source. Ni is easily mobilized during weathering, and then co-precipitates with Fe and Mn oxides; therefore, strong association with Fe and Mn oxides is often observed in soils. During weathering, Ni is released from the primary rockforming minerals and incorporated into secondary minerals, primarily clay minerals. However, De Carlo and Anthony (2002) suggest that (like Co) the Ni content of O'ahu soils and sediments is usually controlled by Ni within primary mineral particles derived from the basaltic source rocks; therefore, relatively high concentrations of naturally occurring Ni tend to occur in coarse-grained soils. The correlation between Co and Ni illustrated in Figure 73 can therefore explained by the occurrence of both metals in the primary minerals of the parent rocks, as well as the tendency of both metals to adsorb to clay particles and form secondary oxide and hydroxide minerals during weathering and soil formation.

6.0 SUMMARY AND DISCUSSIONS

An EBA was performed to evaluate concentrations of 29 elements in Hawai'i soil to develop estimates for background concentration ranges. Hawai'i surface soils database was compiled from literature review of previous research projects, soil data requested from the NRCS database, and soil



data collected by the HDOH. A total of 180 samples representing surface soil concentrations of 29 chemicals throughout the seven main Hawaiian islands (Kaua'i, O'ahu, Moloka'i, Lana'i, Maui, Kaho'olawe, and Hawai'i island) were included for the EBA.

6.1 BACKGROUND CONCENTRATION DISTRIBUTION

The background concentration ranges for all 29 elements are presented in Table 6 and compared to the current Tier 1 EALs (HDOH 2011). Estimated background ranges were primarily generated from evaluation of the cumulative probability plots and spatial and soil type distribution univariate plots (i.e., the combined plots analysis). For metals that show strong correlation with reference metals (e.g., Al, Fe), geochemical association analysis was performed to validate the estimates made using the combined plots analysis.

| Element (mg/kg) | HDOH EAL ^ª | EBA Dataset Range ^b | Background | | | | | |
|--------------------|--------------------------|-----------------------------------|---------------------------------|------------------|---------|-------------------|-------------------------|-------------------------|
| | | | Range (min–max) ^c | BTV ^d | UBC ° | Mode ^f | 95% UCL ^g | 95th Per- centile |
| Target Elemen | ts with Esta | blished EALs | | | | | | |
| Antimony | 8.2 | 0.004–31.5U | 0.004-2.4 | 2.4 | 2.4 | 0.27 | 0.7 | 1.43 |
| Arsenic | 23 | 0.3–283.8 | 0.3–50 | 50 | 24 | 2.20 | 11 | 23.6 |
| Barium | 15,000 | 4.5–926 | 4.5–926 | 926 | 694 | 120 | 242 | 607 |
| Beryllium | 160 | 0.05-3.82 | 0.05-3.82 | 3.82 | 3.0 | 0.36 | 1.3 | 2.83 |
| Cadmium | 70 | 0.02–17 | 0.02–17 | 17 | 2.3 | 1.10 | 2.6 | 4.6 |
| Chromium | N/A ^h | 8.52–3,180 | 8.52–3,180 | 3,180 | 1,145 | 120 | 365 | 1,010 |
| Cobalt | 23 | 0.69–113.5 | 0.69–113.5 | 113.5 | 80 | 28.0 | 36.4 | 71.2 |
| Copper | 3,100 | 2.38–450 | 2.38-450 | 450 | 252 | 43 | 98.5 | 204 |
| Lead | 200 | 0.76–380 | 0.76–72.8 | 72.8 | 73 | 12.0 | 21.3 | 54.2 |
| Mercury | 23 | 0.017U-1.4 | 0.017U-1.4 | 1.4 | 0.72 | 0.12 | 0.25 | 0.65 |
| Molybdenum | 390 | 0.06–4 | 0.06–4.0 | 4.0 | 4.0 | 0.06 | 0.94 | 2.20 |
| Nickel | 3,800 | 2.1–767.2 | 2.1–767 | 767 | 410 | 110 | 179 | 340 |
| Selenium | 390 | 0.24–12.2 | 0.4–12.2 | 12.2 | 7.1 | 1.5 | 2.4 | 5.27 |
| Silver | 390 | 0.02–5 | 0.02–2.9 | 2.9 | 1.5 | 0.06 | 0.57 | 1.17 |
| Thallium | 0.78 | 0.25U–15.05J | 0.25U-15 | 15 | 0.25 | N/A | N/A | N/A |
| Vanadium | 390 | 0.25-1,090 | 0.25-1,090 | 1,090 | 770 | 110 | 301 | 720 |
| Zinc | 23,000 | 3.57-1,200 | 3.57-1,200 | 1,200 | 349 | 120 | 127 | 232 |
| Target Elemen | ts with No I | Established EALs | ł | 1 | 1 | | 1 | I |
| Aluminum | N/A | 2,500–166,138 | 2,500–166,138 | 166,138 | 166,138 | 4,400 | 68,627 | 122,454 |
| Calcium | N/A | 31–77,208 | 31–77,208 | 77,208 | 77,208 | 6,200 | 10,611 | 29,680 |
| Iron | N/A | 1,713–260,082 | 1,713–260,082 | 260,082 | 260,082 | 44,000 | 108,013 | 225,097 |
| Manganese | N/A | 13–4,880 | 13–3,522 | 4,880 | 4,880 | 95 | 1,167 | 2,434 |
| Strontium | N/A | 2U-1,094 | 2U-1,094 | 1,094 | 1,094 | 22 | 219.7 | 435 |
| Tin | N/A | 0.6–10 | 0.6–10 | 10 | 10 | 7.2 | 5.1 | 8.8 |
| Titanium | N/A | 3,809–53,032 | 3,809–53,032 | 53,032 | 53,032 | 14,000 | 22,907 | 41,385 |
| Tungsten | N/A | 0.002-5.43 | 0.002-5.43 | 5.43 | 5.43 | 0.01 | 4.96 | 5.1 |
| Additional Tar | get Element | s | 1 | I | I | | | |
| Magnesium | N/A | 25U-68,611 | 25U-68,611 | 68,611 | 68,611 | 1,800 | 18,201 | 50,368 |
| Potassium | N/A | 170–10,178 | 170–10,850 | 10,178 | 10,178 | 1,400 | 2,958 | 4,338 |
| Sodium | N/A | 37–10,850 | 37–10,850 | 10,850 | 10,850 | 1,200 | 3,454 | 6,564 |
| Phosphorus | N/A | 63U-18,078 | 63U–18,078 | 18,078 | 18,078 | 1,500 | 2,276 | 7,430 |

Table 6: Estimated Background Range for 29 Target Elements in Hawai'i Soils



J detect, estimated concentration

N/A not enough detection data to calculate background concentration ranges for thallium

U non-detect concentration, reporting limit value presented.

^a HDOH (2011) EAL: Table I-1, Unrestricted Direct Exposure Soil Action Levels (non carcinogens, HQ = 1)

^b Minimum and maximum concentrations in the full dataset, including non-detects and outliers.

^c Range of background concentration defined as the minimum to background threshold value.

^d Background threshold value: the maximum concentration that can be attributed to background conditions, which may or may not include natural outliers.

^e Upper bound concentration: upper limit of the range of background concentrations that fit a relatively continuous distribution and do not include any of the natural outliers.

^f Mode: 50th percentile (single concentration that occurs most often in the dataset)

⁹ 95th percentile upper confidence limit (UCL) estimated using EPA ProUCL software, v. 4.1.00. Value reported is ProUCL recommended 95% UCL that is most appropriate for the data distribution. See appendix B, Attachment 1 for the complete ProUCL calculation.

^h Direct Exposure Soil Action Level is defined only for chromium III and VI, not total chromium.

Table 6 includes the following parameters to describe the concentration distribution related to background conditions for each target element: range of background concentration defined as the minimum value up to the BTV, the BTV, the UBC, the mode, and the 95% upper confidence limit (UCL), and the 95th percentile calculated to the BTV. These parameters are illustrated graphically on the generalized logarithmic distribution graph in Figure 74. Concentrations above the BTV are assumed to be associated with site contamination. Concentrations above the UBC are considered as potential outliers due to natural enrichment processes or anthropogenic contribution.

6.2 SOIL HETEROGENEITY AND BACKGROUND CONCENTRATIONS

The background concentration ranges estimated based on the results of this EBA exclude concentrations that are attributed to site contamination; therefore, the values presented in Table 6 represent the concentration ranges expected to be associated with background conditions and not site-related contamination. The variability in background concentrations of a target element is primarily a function of the heterogeneity of the soil samples included in the analysis, which can be attributed to different parent rock type, soil formation and weathering process, and contribution from anthropogenic sources.

The soil order classification presented in Section 2.0 summarizes in detail the soil characteristics based on parent rock type and soil development and extent of weathering and the typical enrichment or depletion of certain target elements associated with each soil order. Concentrations of target elements in a particular soil sample will vary depending on the type of rock from which the soil was derived. The parent rock for most of Hawai'i soils are mafic volcanic rocks (primarily basaltic) rich in metals such as AI, As, Cr, Fe, Pb, Mg, Mn, TI, V, and Zn (Earth Tech 2006); therefore, soils derived from volcanic rocks will generally be enriched in these elements. Soils derived from marine coral fragments are present along the coastal areas; these soils will have lower concentrations of those elements typically associated with mafic volcanic rocks and caprock sediment, and higher concentrations of elements such as Ca, Na and Sr typical of carbonate rocks (Kabata-Pendias 2001). Compositional heterogeneity is also present within mafic volcanic parent rock. The composition of basaltic magma changes from tholeiitic (higher silica content, lower Na content) to alkali basalts (lower silica content, higher Na content) in the latter stages of Hawaiian volcanism. These two types of magmas produced lavas with different mineralogy, and therefore the resulting soils derived from these lavas will have different range of concentrations of target elements. Smallerscale heterogeneity is also present within a single lava flow unit due to crystallization of phenocrysts, which depletes the remaining liquid of certain metals with lava flow cooling as it flows away from the vent. The percent crystallinity therefore decreases from the head to the toe of the lava flow. Soils derived from lava flows (e.g., oxisols) will have different ranges of certain target elements based on whether the soils were derived from the head or the toe of the lava flow.

Concentrations of target elements in background soils can also vary depending on soil formation process (i.e., how well developed the soil is) and the extent of weathering. Well-developed soils typically have higher content of clay and organic materials compared to young soils, therefore are



typically more enriched in target elements with affinity to clay and organic particles (e.g., Mg, Mn). Highly weathered soils typically also have higher clay-content with higher concentrations of target elements with affinity to clay particles (e.g., Ba) compared to similar soils that are less weathered. Other geomorphologic processes during soil formation process can also contribute to the heterogeneity of the soil. For example, fluvial transport, can deposit sediments comprised of materials derived from multiple parent rocks. Rainfall amount also have significant impact on the concentrations of highly mobile target elements in background soils. High rainfall amount will tend to increase soil acidity and leaching capability; therefore the soil will generally be depleted in mobile target elements such as Na and K.

Natural soils can also be enriched in certain target elements relative to their parent source material due to contribution from anthropogenic sources such as previous widespread use of pesticides in agricultural lands, atmospheric fallout from urban activities such as emissions from automobiles and large plants and factories. These anthropogenic sources can potentially contribute to low-level regional concentrations of certain target elements that are not initially expected based on evaluation of the parent rock type and soil formation and weathering characteristics of the soil. For example, the typical concentration range of Pb in natural soils in the United States is 10–70 mg/kg; however, De Carlo et al. (2004) reported concentrations of Pb of up to 900 mg/kg from urban sources in O'ahu. Fossil fuel combustion has also been recognized to cause atmospheric deposition and accumulation of Cd in natural soil. De Carlo and Anthony (2002) also noted anthropogenic enrichment of As in O'ahu soils as a result from previous agricultural activities from the use of arsenical pesticides.

7.0 FUTURE EVALUATION

This section presents the potential data gaps identified during the EBA and recommends future activities to address potential data gaps and improve on the results of the estimated background concentration ranges for target elements in Hawai'i soils.

7.1 POTENTIAL DATA GAPS

Three major data and information gaps were identified during the EBA:

- Number of non-detects
- Soil type and site conditions information
- Identification of major soil groups

7.1.1 Number of Non-detects

There are significant number of non-detect values included in the datasets for some of the target elements that impacted confidence of performing the EBA. Lack of sufficient detect concentrations hinders the ability to create a cumulative probability plot that represents the data distribution population, identify outliers and inflection point, and thereby lower the analytical power in the estimated background concentration ranges. The following metals were identified with significant numbers of non-detect values:

- Antimony: 81 non-detects in 121 total samples
- Molybdenum: 34 non-detects in 181 total samples
- Silver: 43 non-detects in 121 total samples
- Thallium: 57 non-detects in 61 total samples
- Tin: 34 non-detects in 107 total samples
- Tungsten: 29 non-detects in 21 total samples



Although the previous sampling was intended to specifically sample non-impacted areas, there are potentially other non-impacted areas that are currently not represented in the dataset. The required data include the interior areas of Kaua'i; the interior, northeast, and west side of O'ahu; the northern shores of Moloka'i; the entire island of Lana'i; the central valley area of Maui; and the South Kona District of the Big Island.

7.1.2 Soil Type Information

There is limited information on soil type (e.g., particle size, Unified Soil Classification System [USCS] soil designation code). Data collected by the HDOH has USCS soil type information designated in the field but the samples were not submitted for lab analysis for particle size distribution. The NRCS data, on the other hand, has some particle size distribution information but no field designated USCS soil type code. The EBA attempted to address the soil type issue by using the USDA soil order classification to evaluate soil type. Although the information is useful for evaluating different ranges of concentrations present in each soil order, the soil order classification system is very general and does not provide specific particle size information (i.e., some soil orders may include particle sizes from sands to clays). Therefore, the information relative to particle size remains limited.

Site condition from where the samples were collected is also an important parameter to consider for evaluating background concentrations, whether or not the site is truly "non-impacted," or was there previous site release in the nearby areas. Limited information can be gathered from the data itself as well as through the use of land use maps prepared by the State of Hawai'i; however, the accuracy of the descriptions from the field or the sampling location relative to the land use map may not be sufficient to provide reliable information on site conditions. It is recommended to conduct a soil survey to document soil condition and distribution where samples were collected.

7.1.3 Identification of Major Soil Groups

The EBA estimated background concentration ranges for island-wide soils; however, each island potentially has different soil groups with different parent rock and soil formation histories due to different weathering patterns and climate. These different soil groups may associate different background concentration ranges of target elements. For example, soils developed from corals versus soils developed from volcanic ash may have significantly different concentrations of certain target elements. EBA of metals in soil at Navy O'ahu facilities (Earth Tech 2006) identified four major soil groups, where soils derived from Ko'olau Volcanics soils have different ranges compared to soils derived from Waianae Volcanics, and subsequently both have different ranges compared to coralline limestone soils and caprock soils. While such detailed classifications are not recommended, it is important to note that the estimated background range may not be applicable to soils with naturally low metal concentrations such as carbonate coral formation. This concern can be noted if a soil survey is conducted as recommended in Section 7.1.2.

7.2 ADDITIONAL SCOPE

In order to improve the confidence and statistical power on the estimates of background concentrations presented in this report, the following additional scope is recommended:

- Conduct additional soil sampling. Design future sampling to address the spatial data gap as well as the use of analytical methods with lower detection limits, to improve on the number of detections for EBA.
- *Conduct a soil type survey.* Conduct a soil type survey along with additional soil sampling to evaluate soil type and site conditions for the existing sampling locations, to evaluate a consistent soil type and evaluate site conditions associated with the existing dataset.
- *Identify major soil groups.* Establish major soil groups on each island. Compare concentration and soil type data to generalized geologic and soil maps for each island, to determine representative concentration datasets suitable to evaluate background concentrations for that particular soil group.



• Create a background guidance document: Prepare a guidance document for the general public. Include information on how to use the estimated background ranges, identify appropriate major soil groups, compare data collected at future soil investigation sites, determine whether site-specific EBA is necessary, and conduct site-specific EBA.

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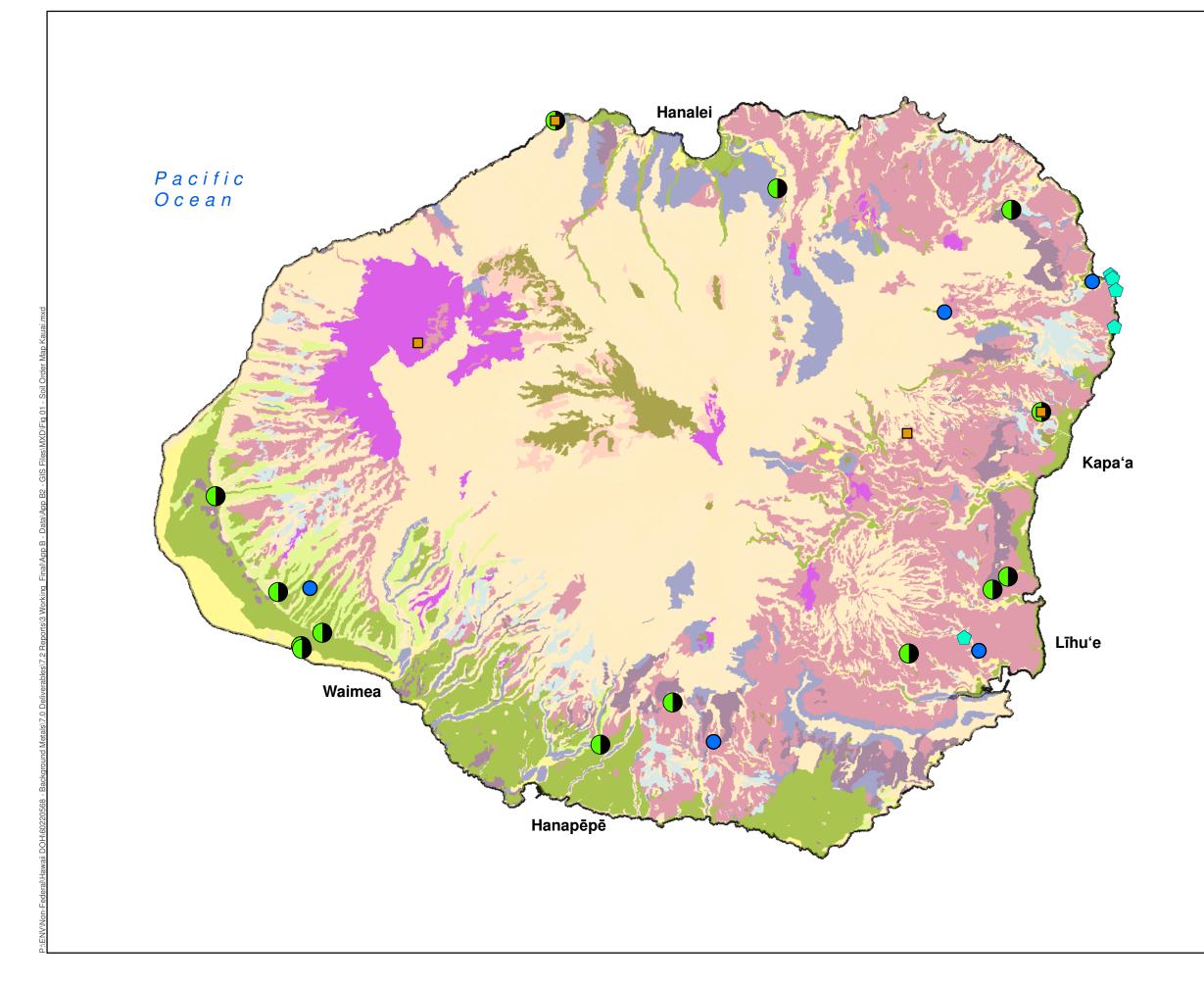
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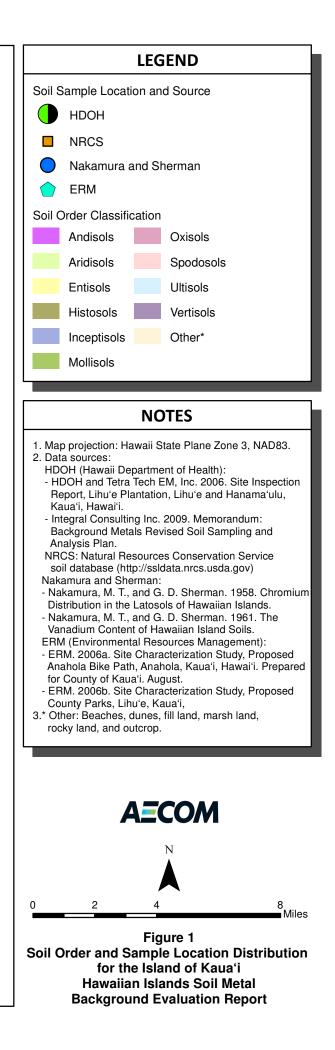
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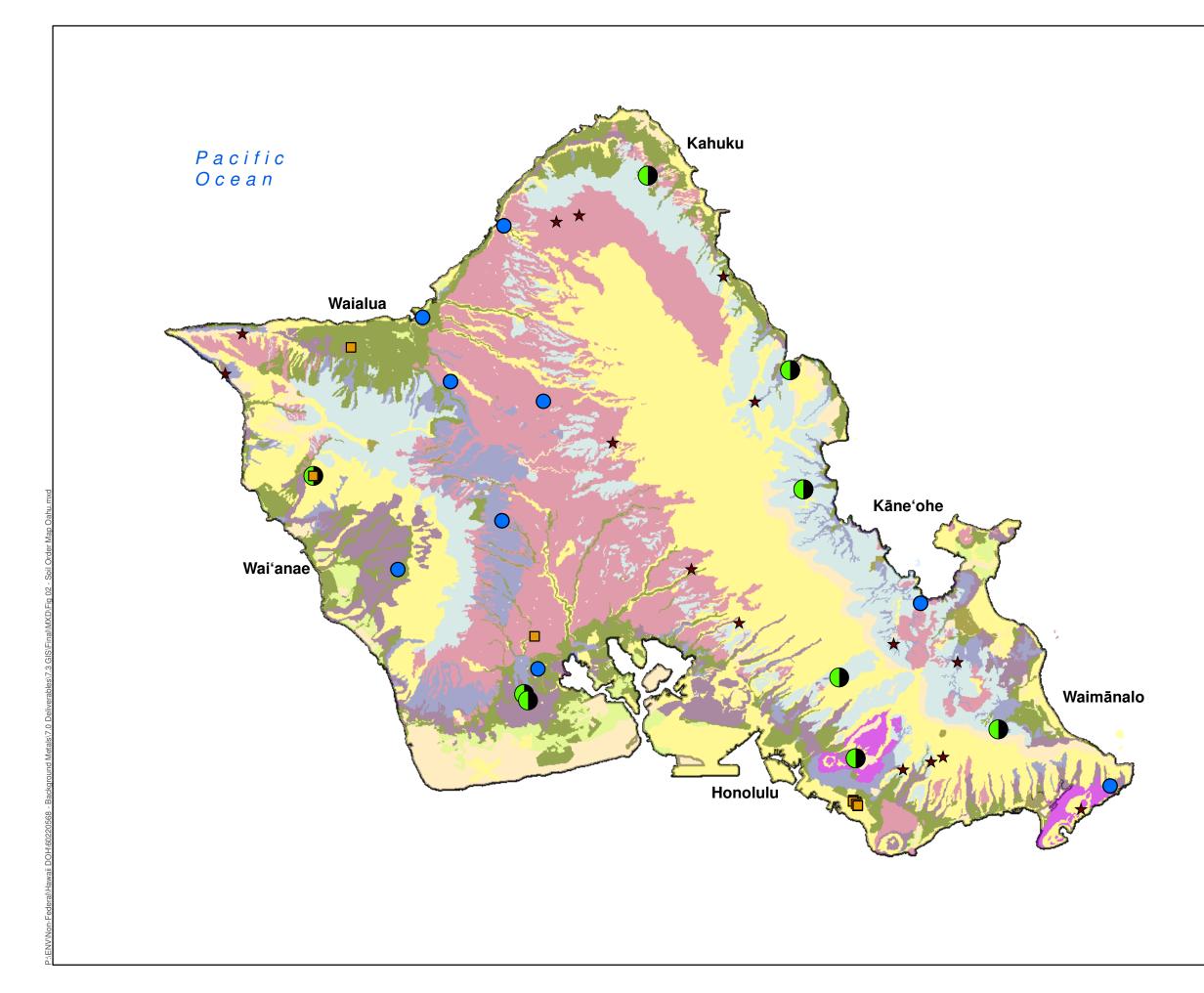
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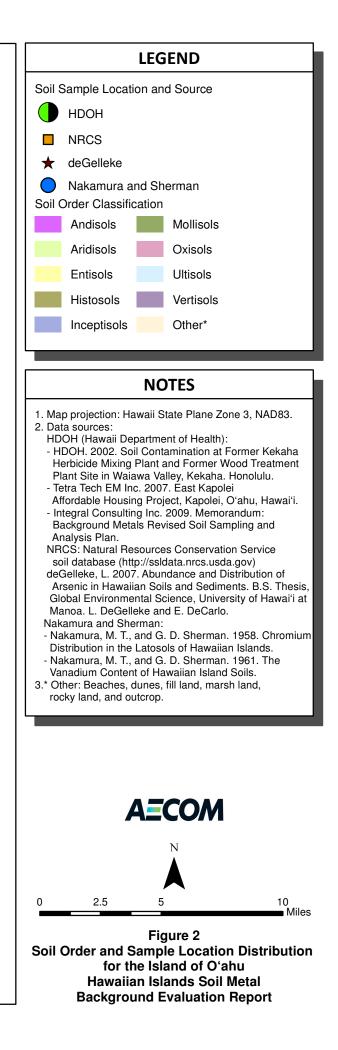


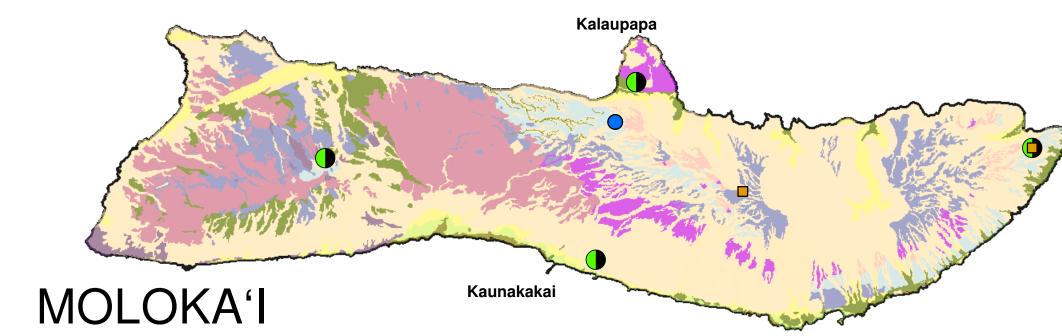
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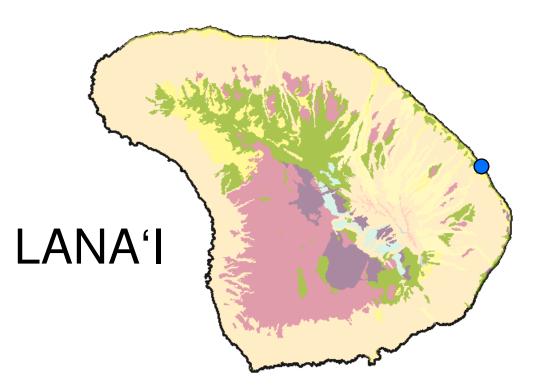


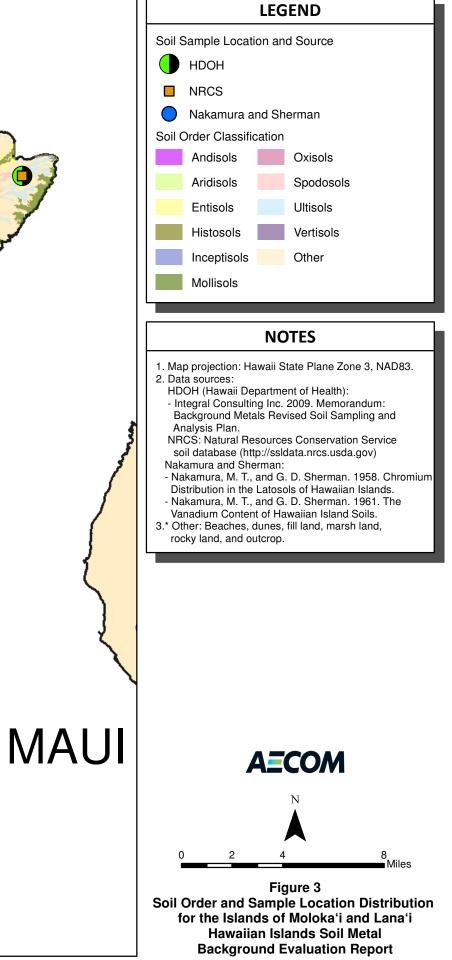


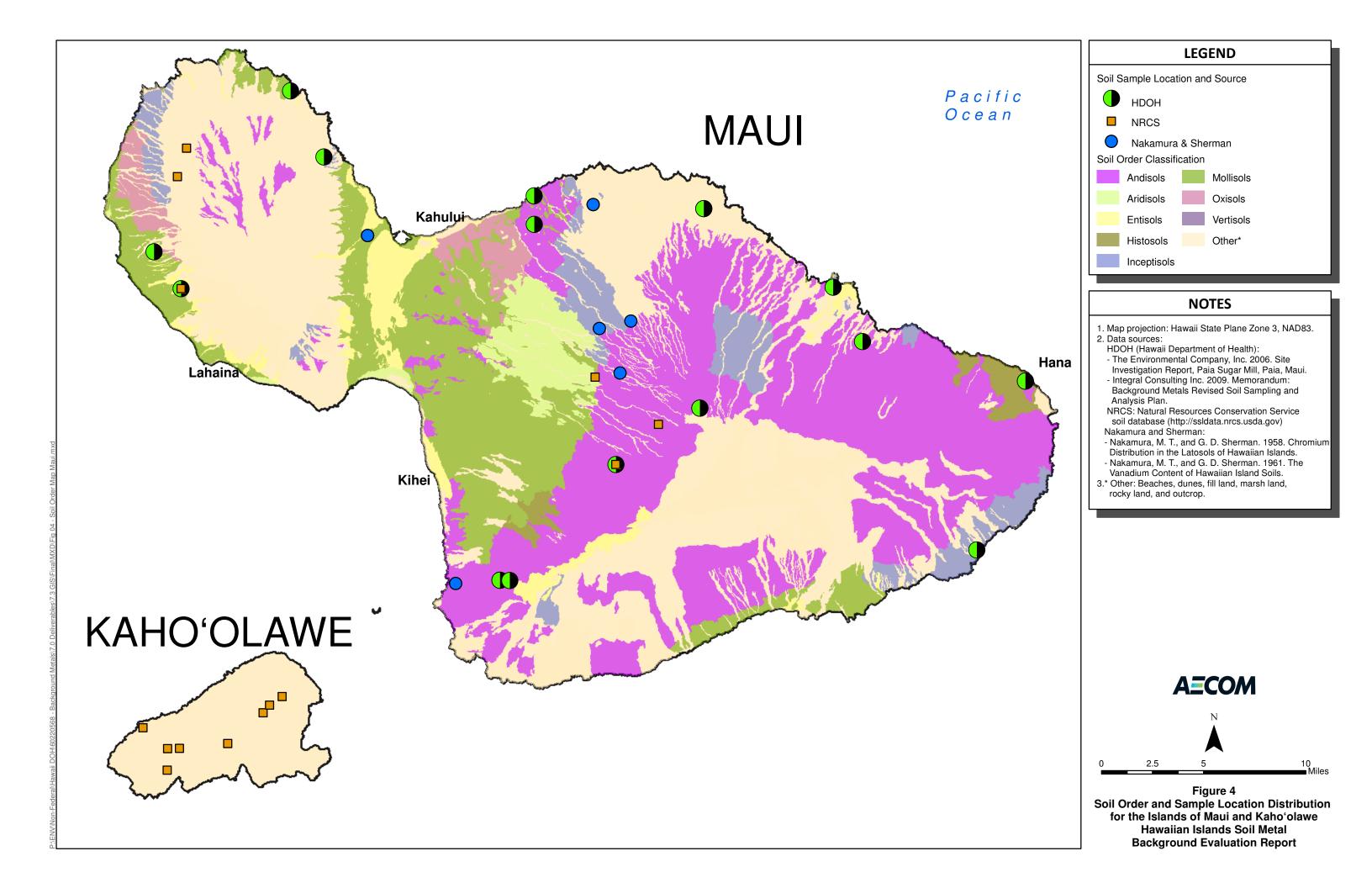


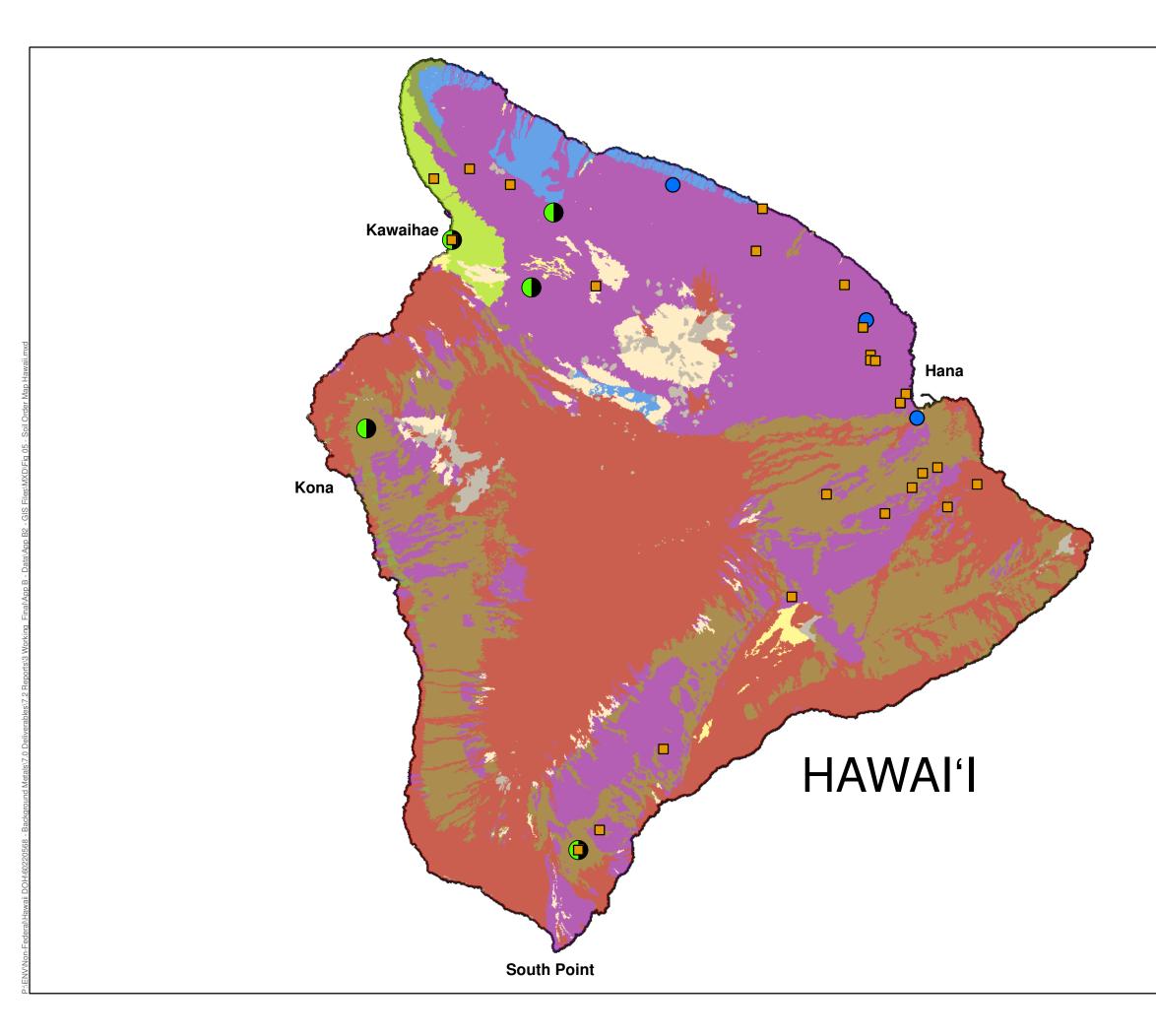


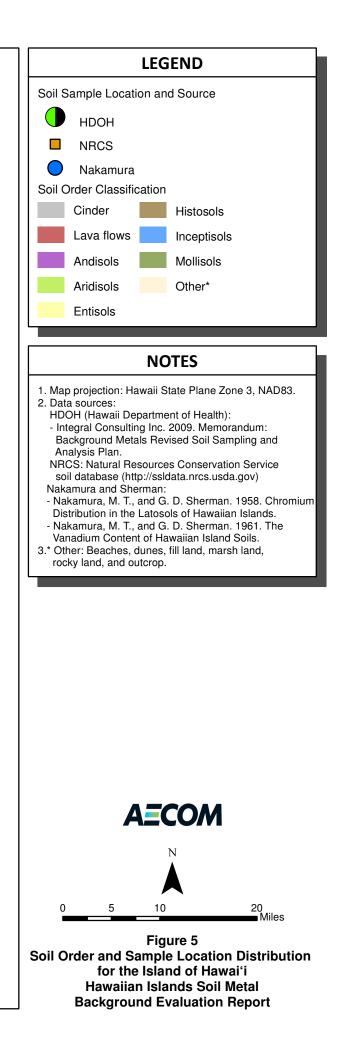


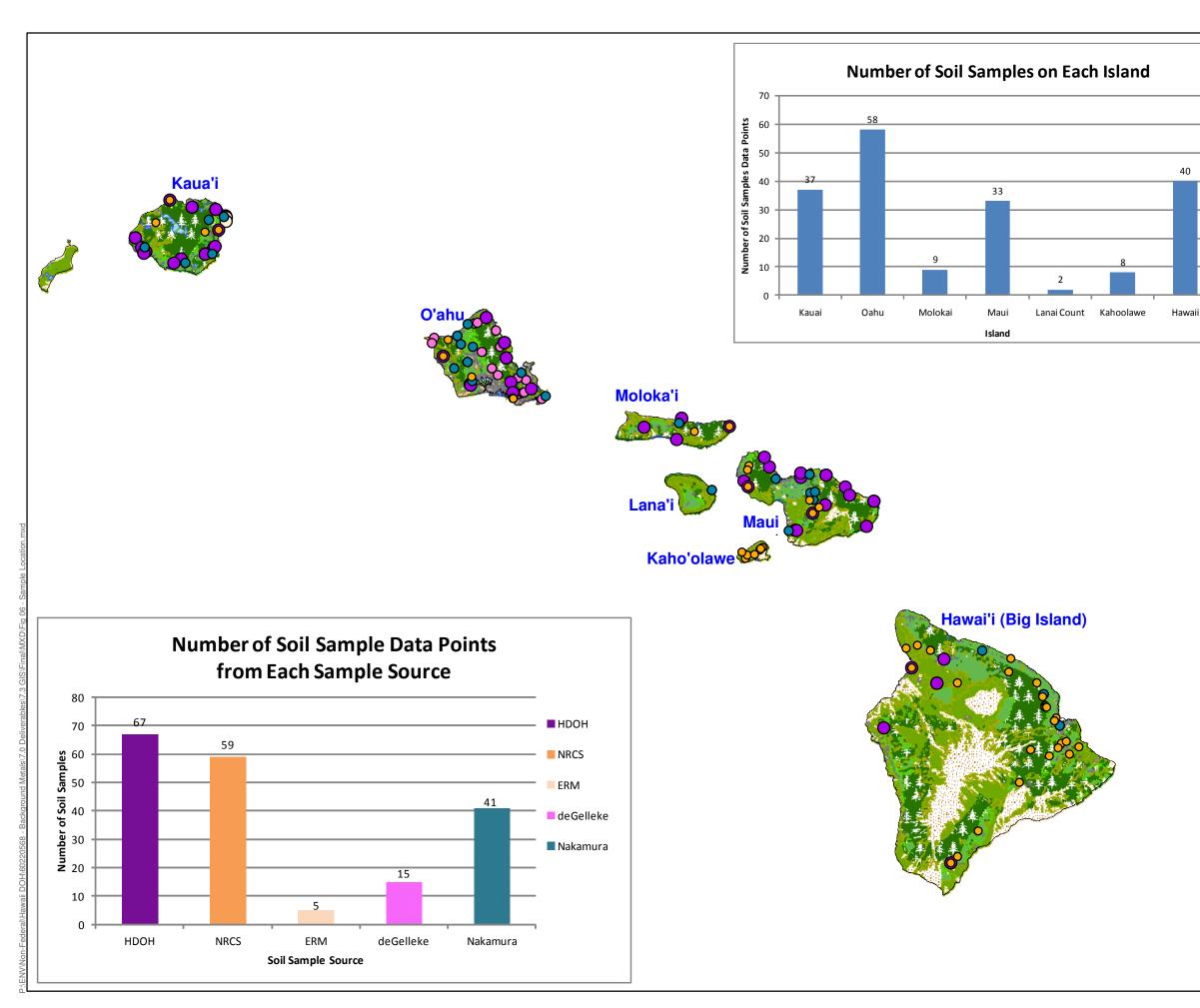


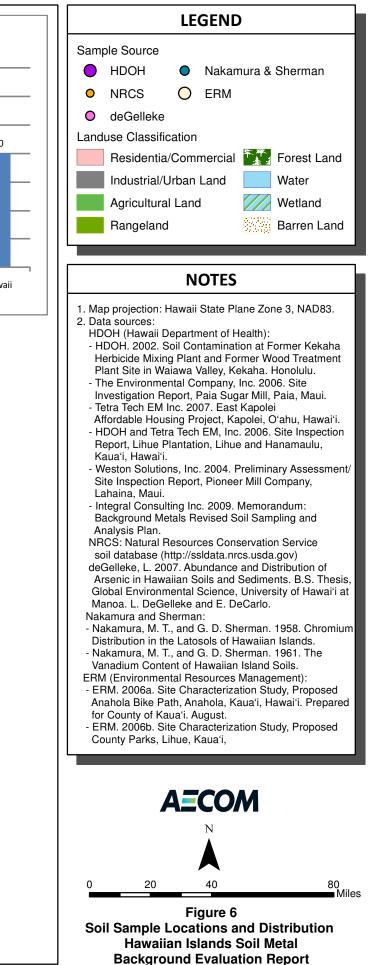


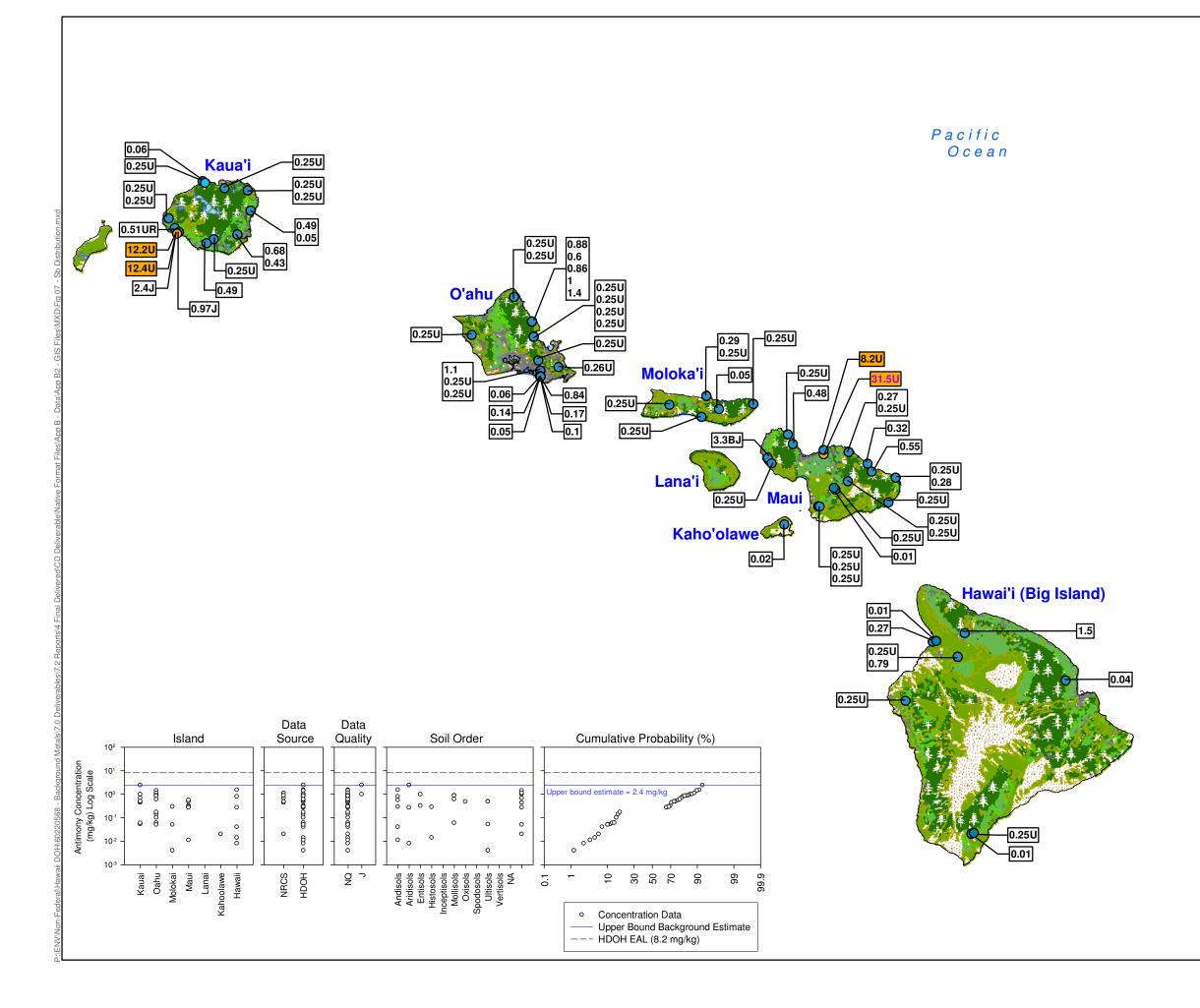


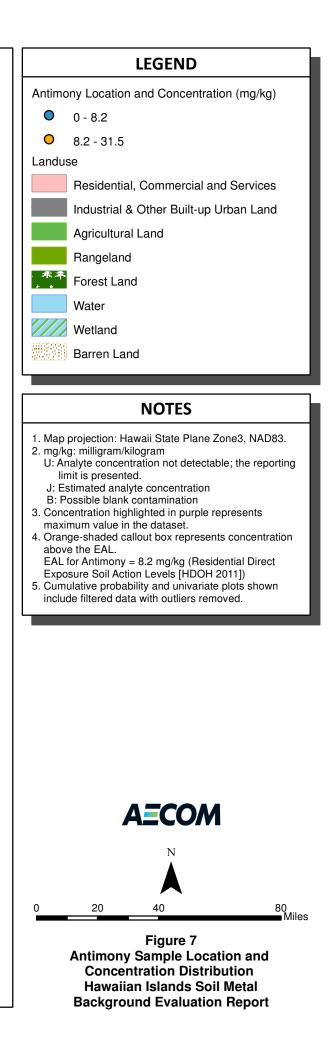


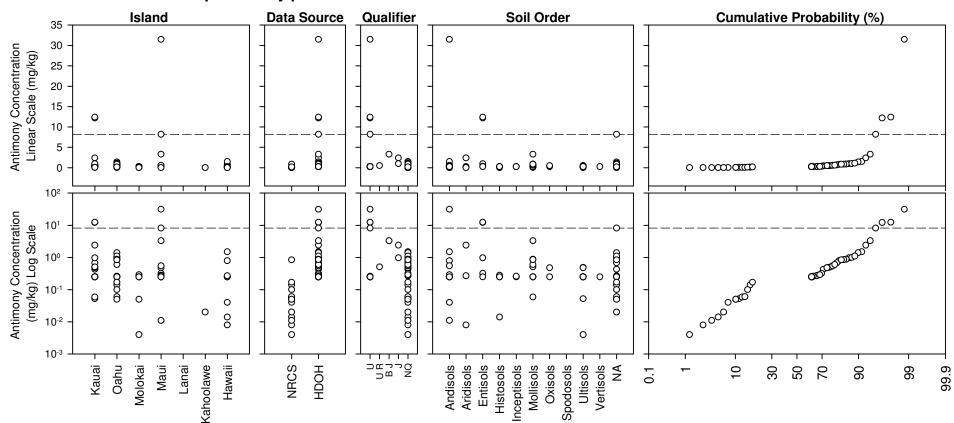




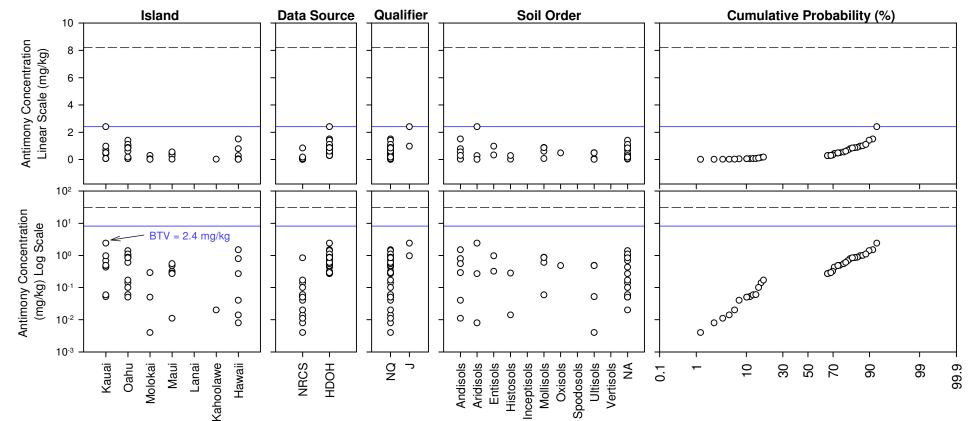


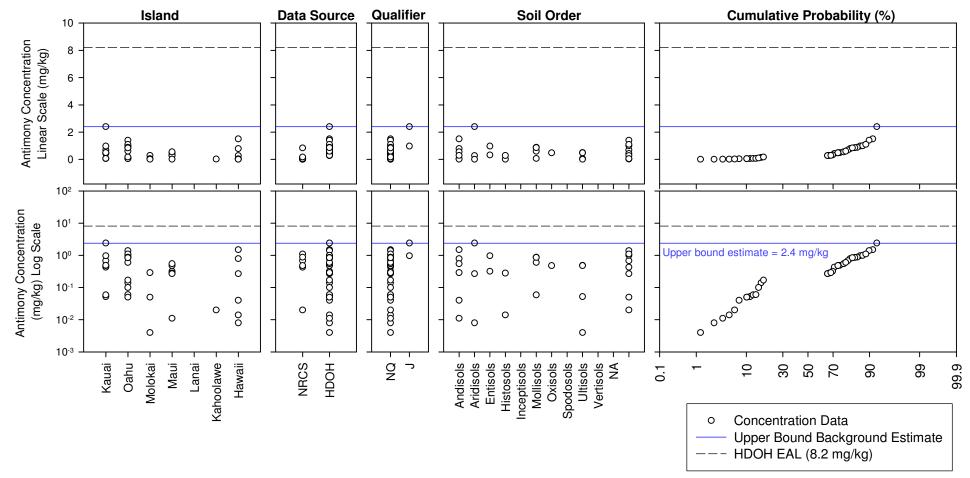


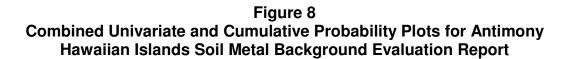


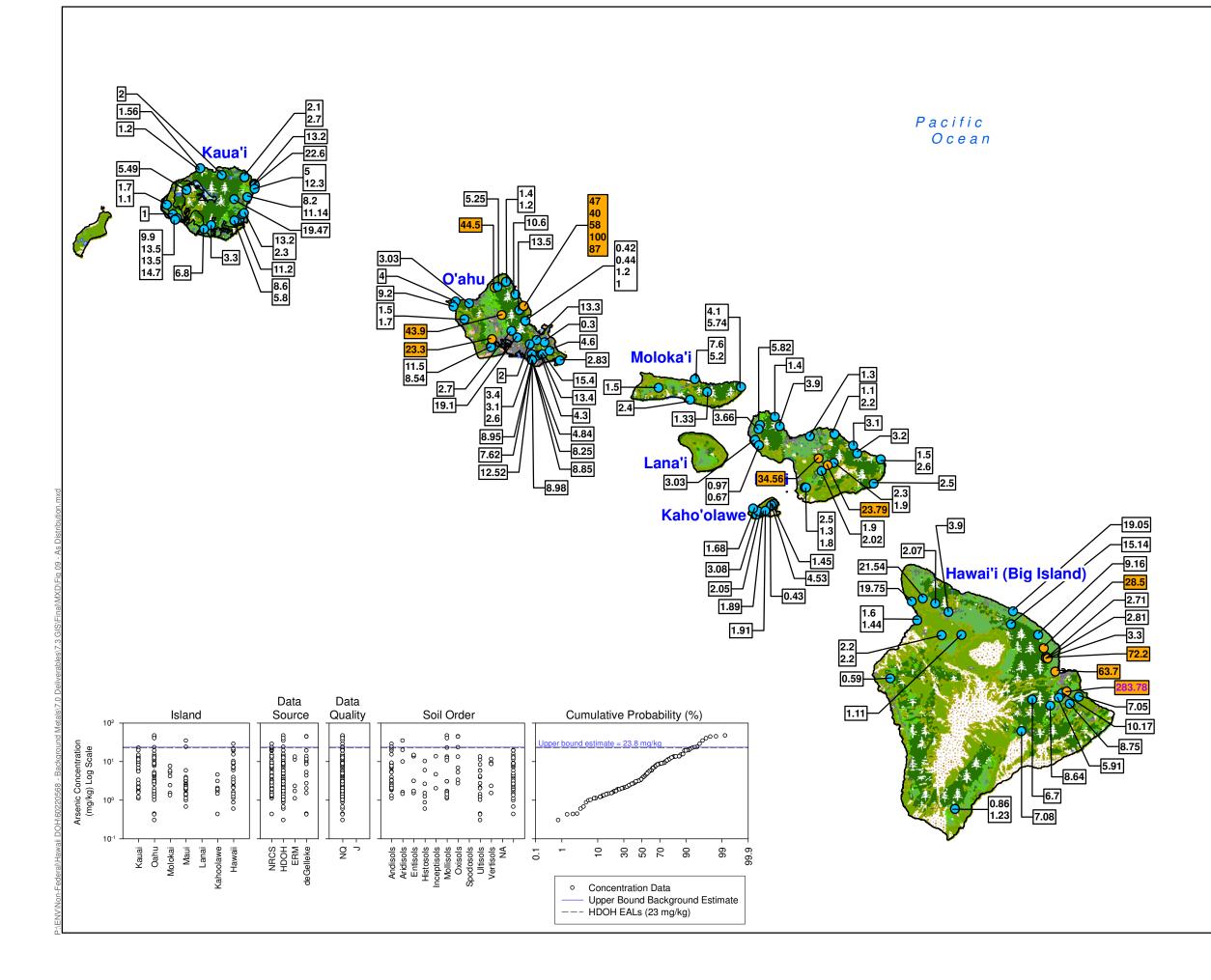


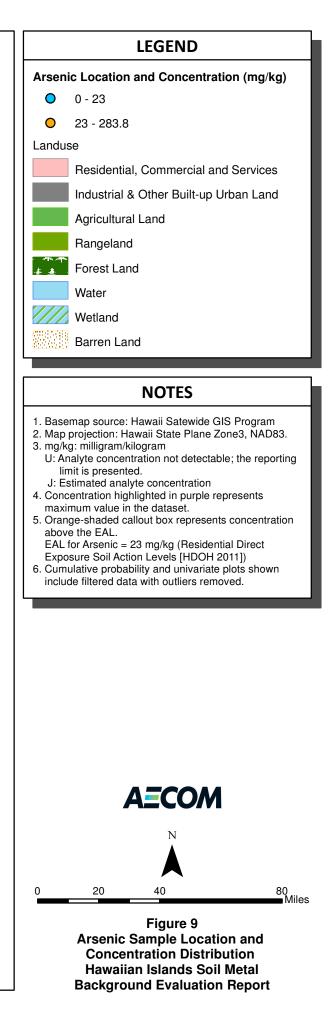
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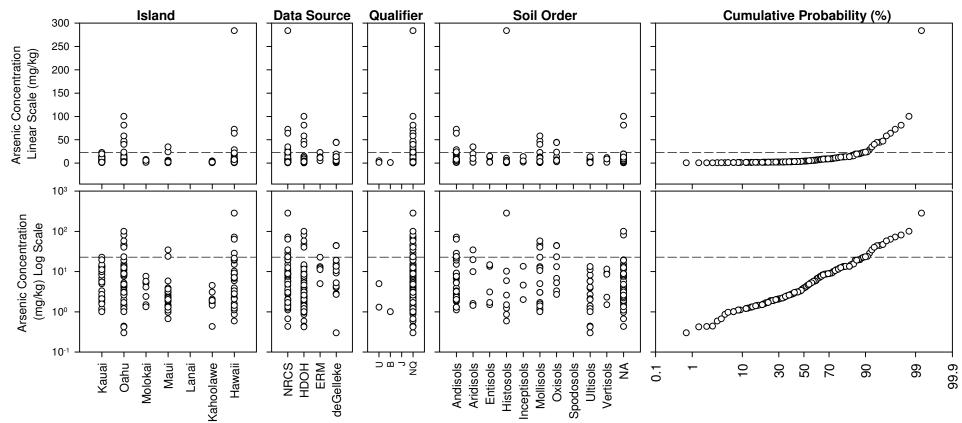




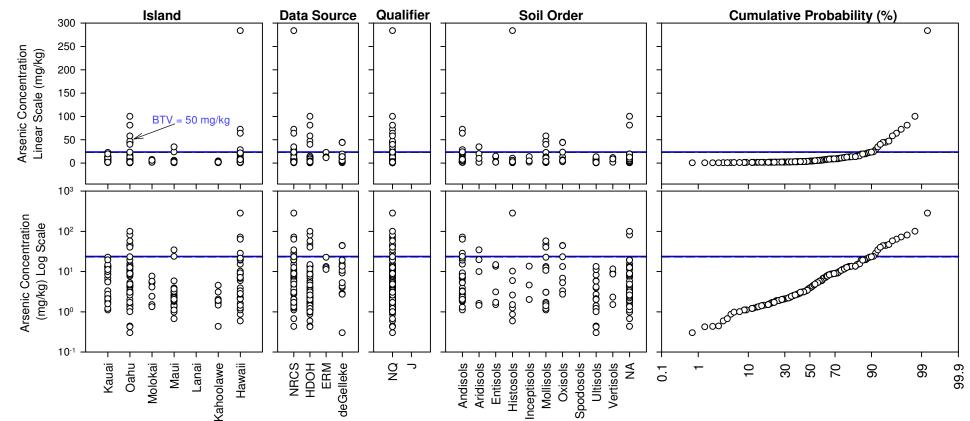


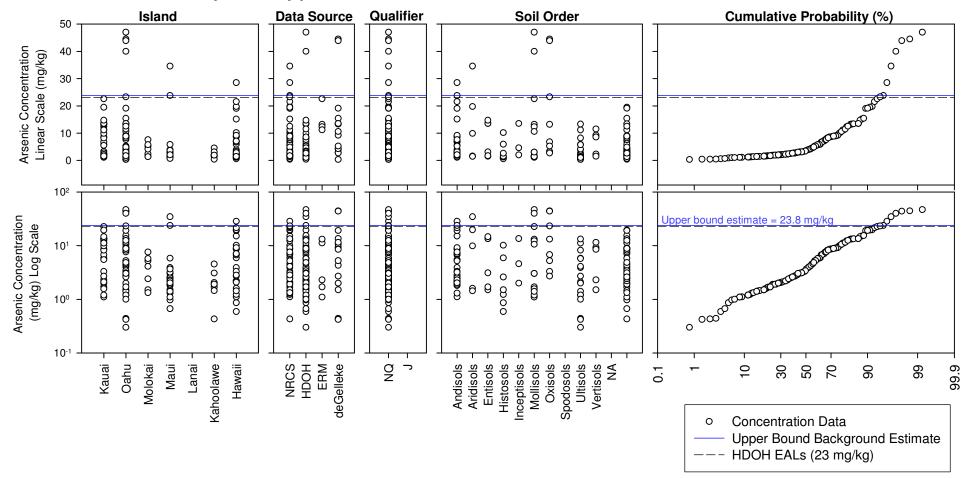


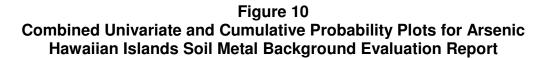


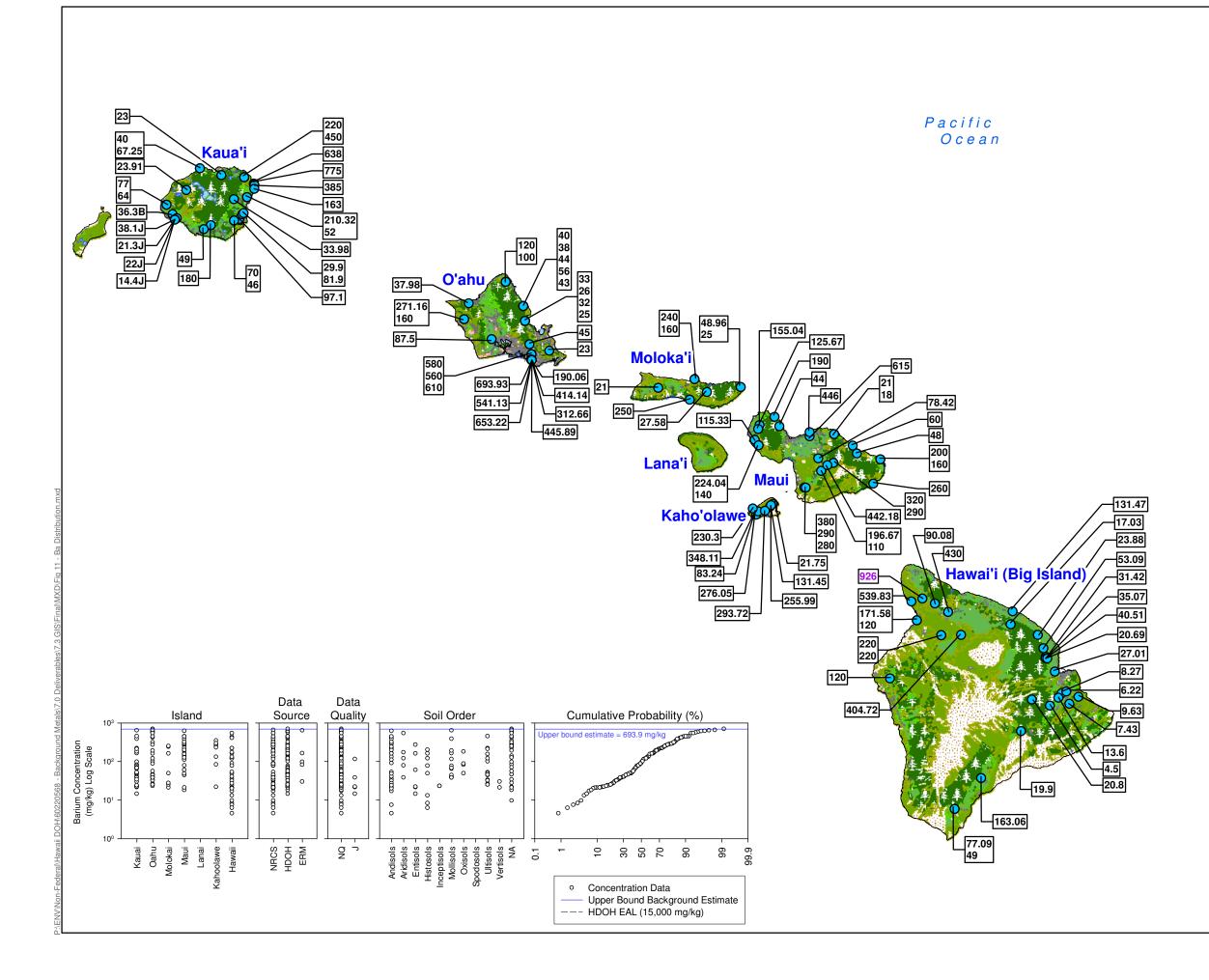


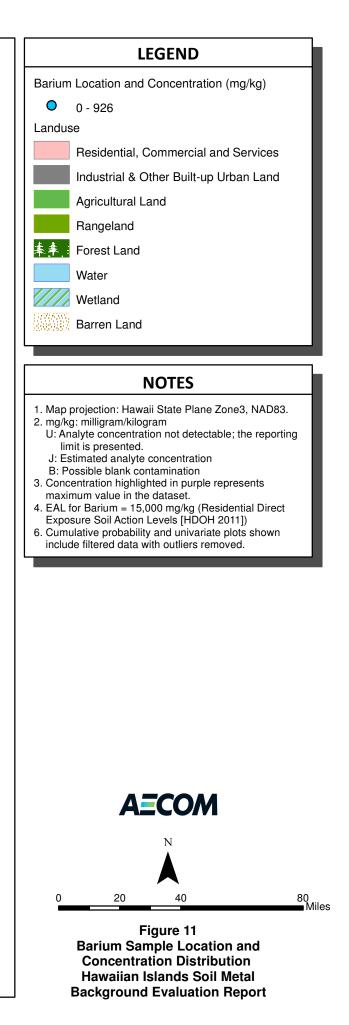
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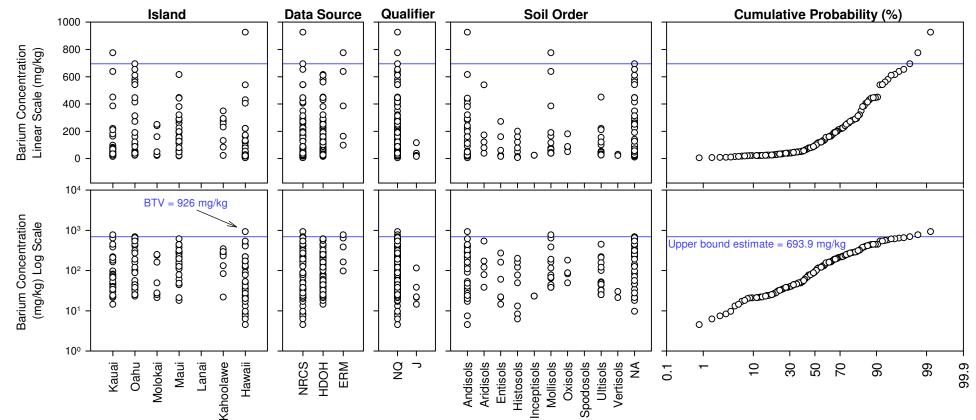
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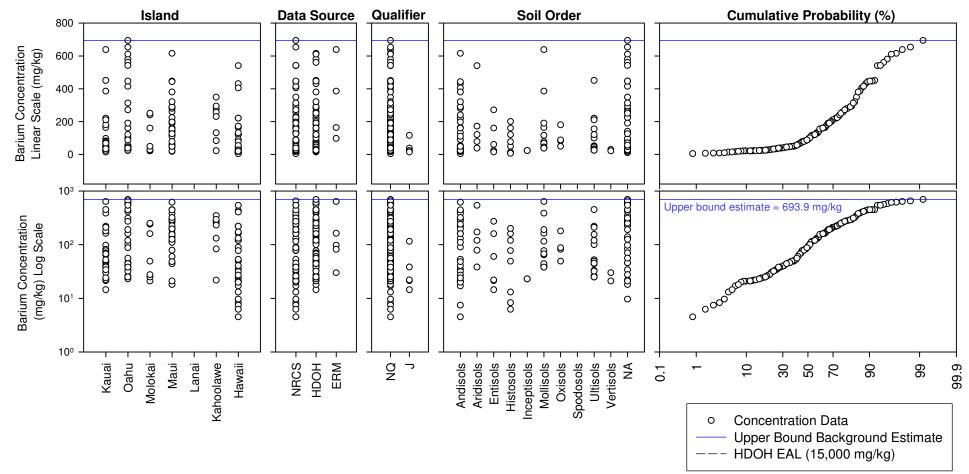
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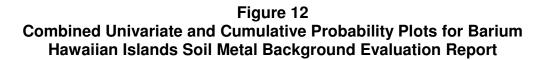
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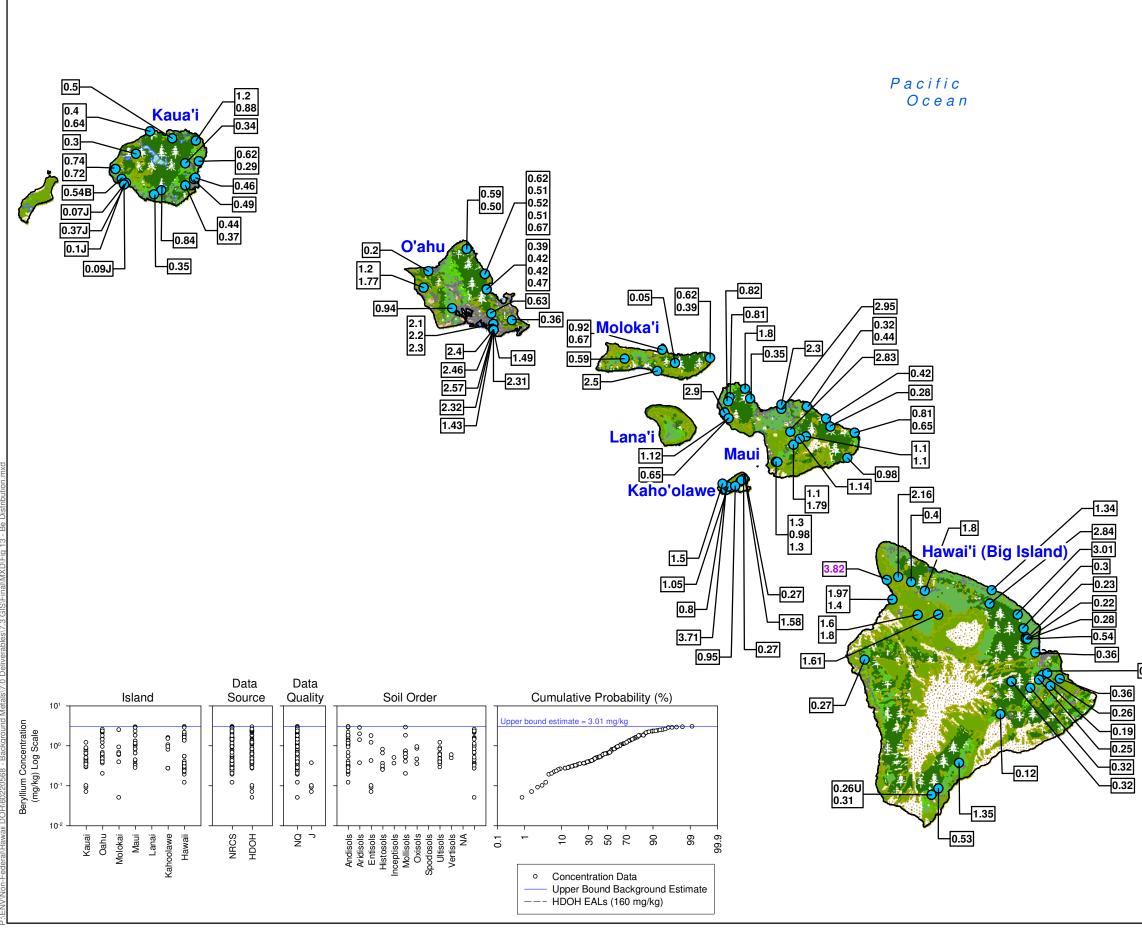
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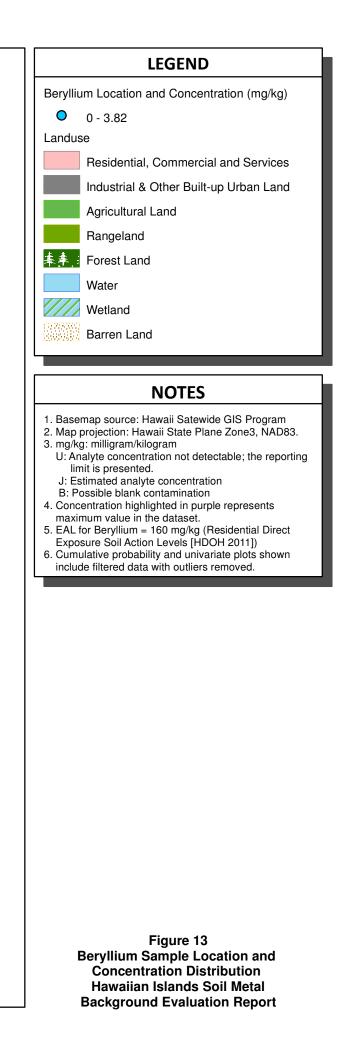
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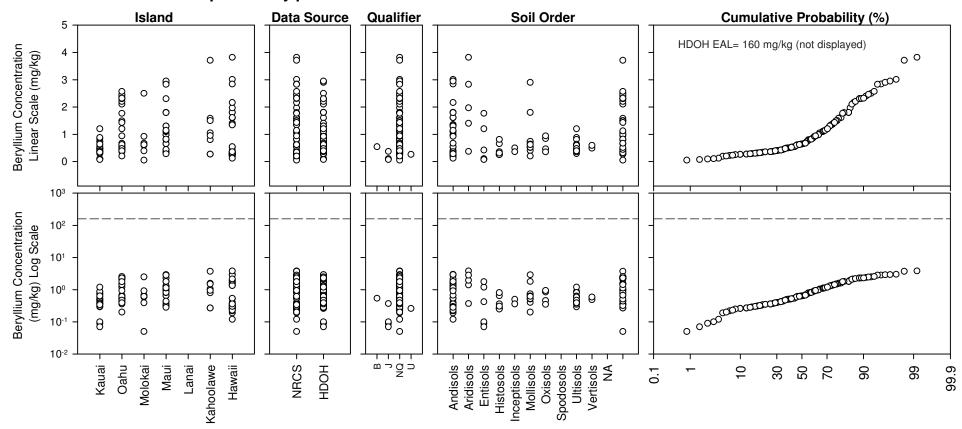




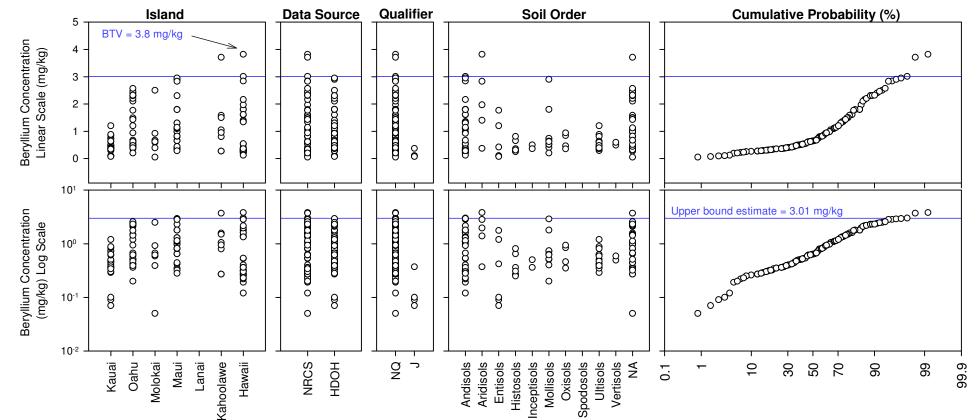


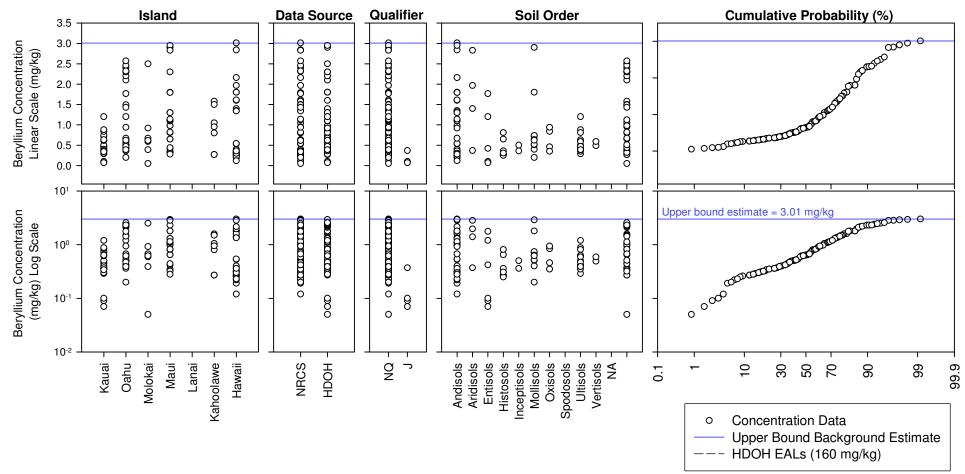


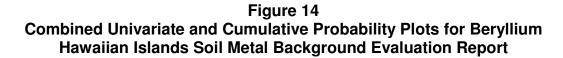
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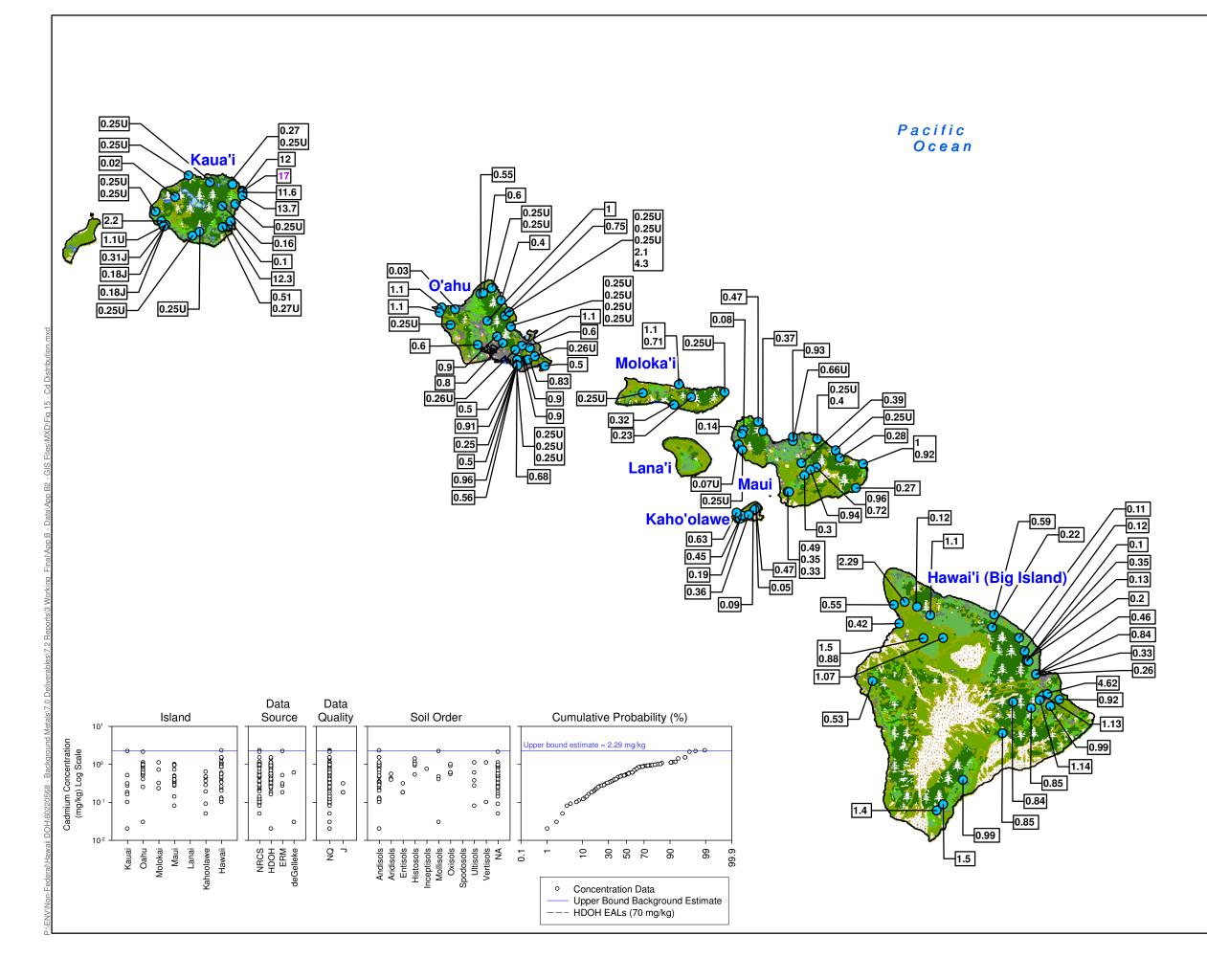


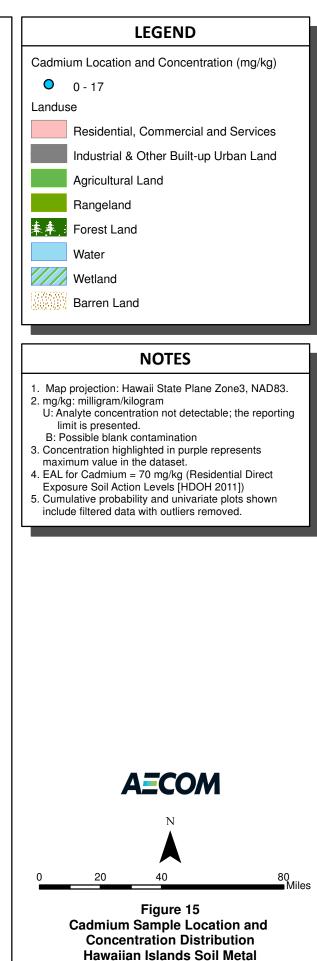
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



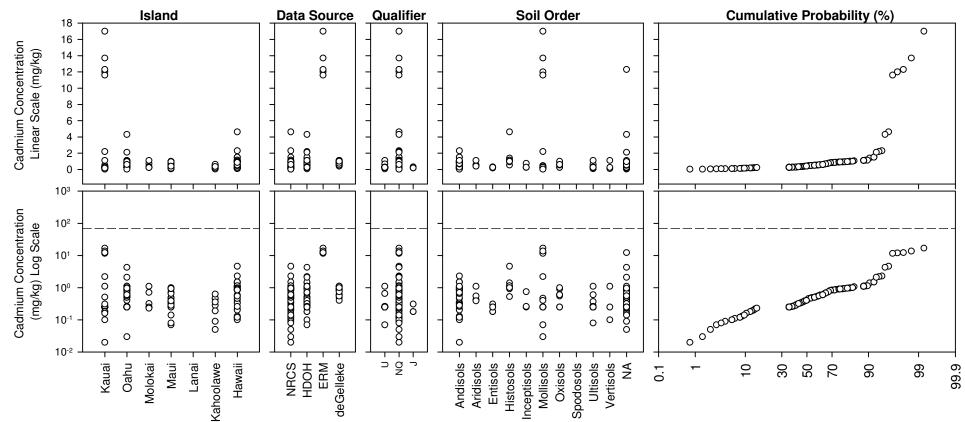




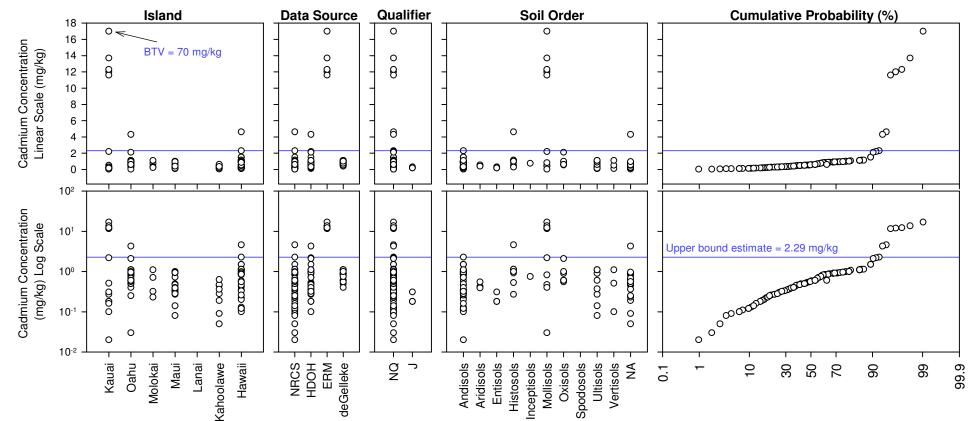


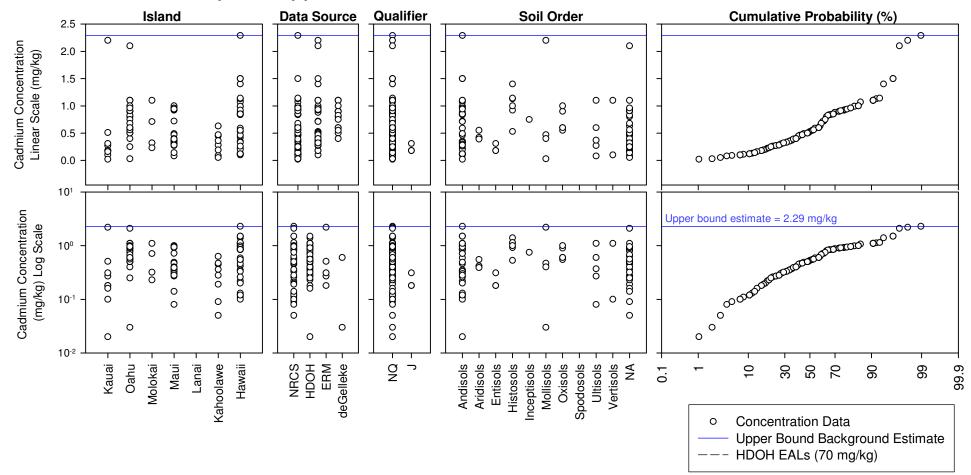


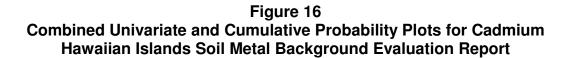
Background Evaluation Report

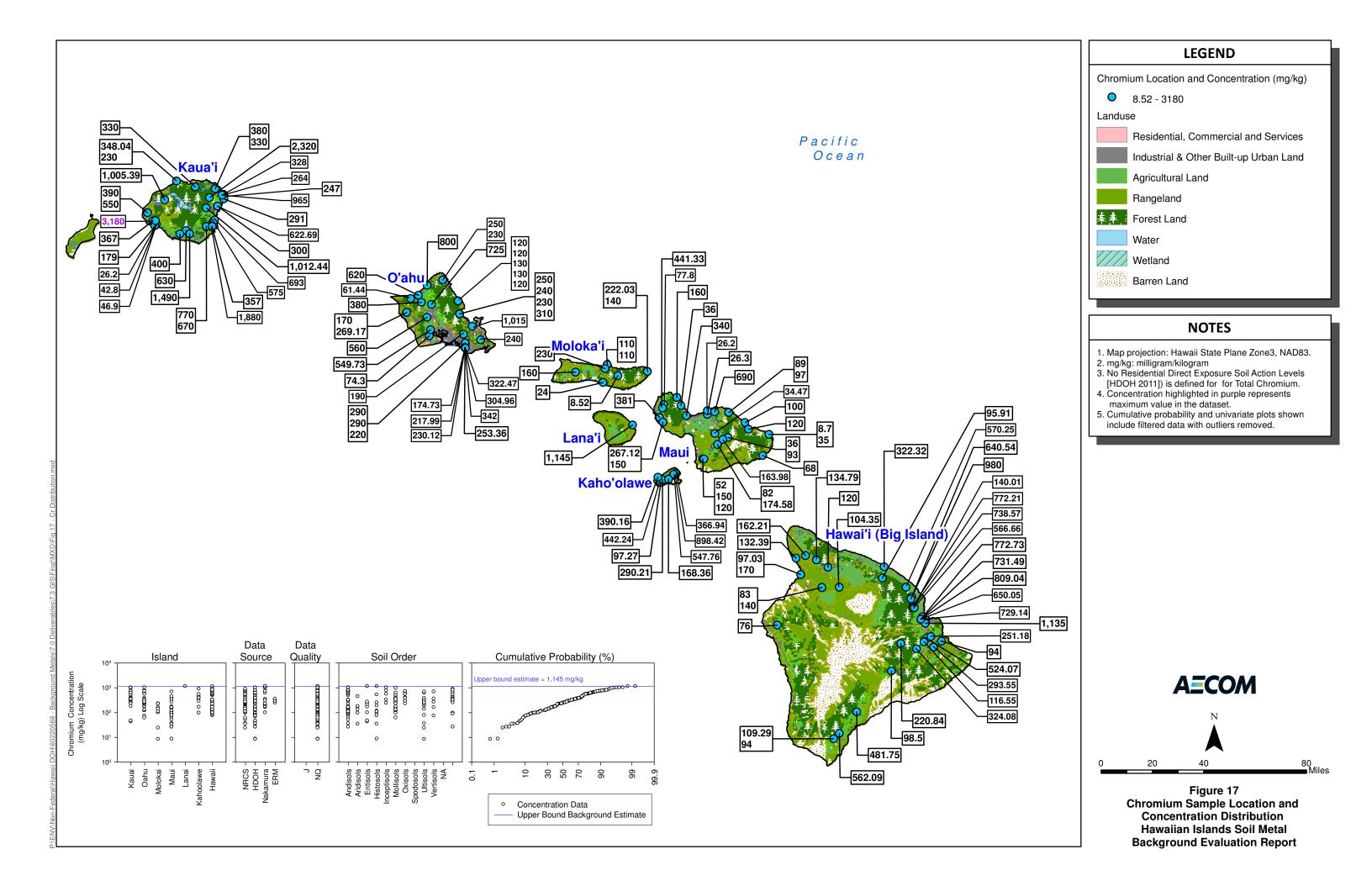


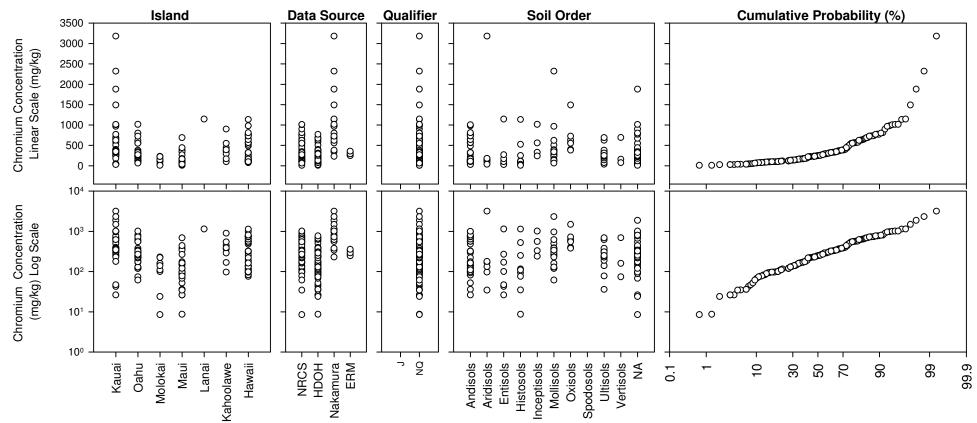
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



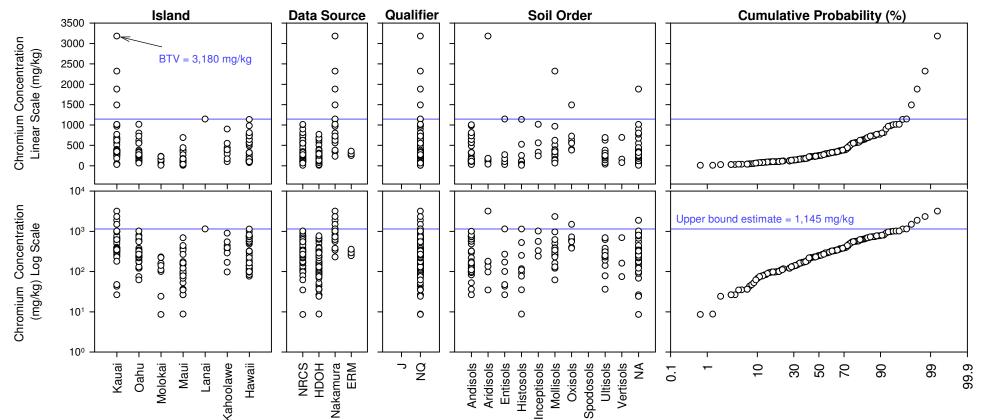


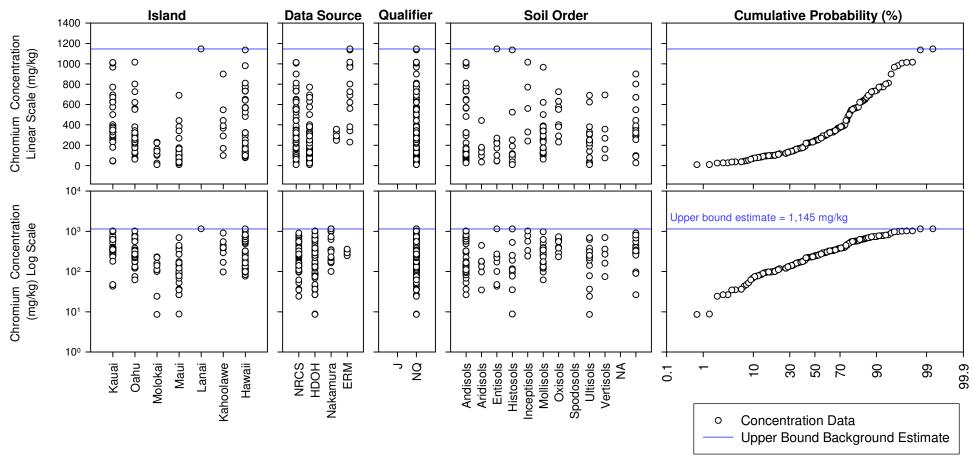


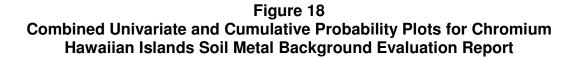


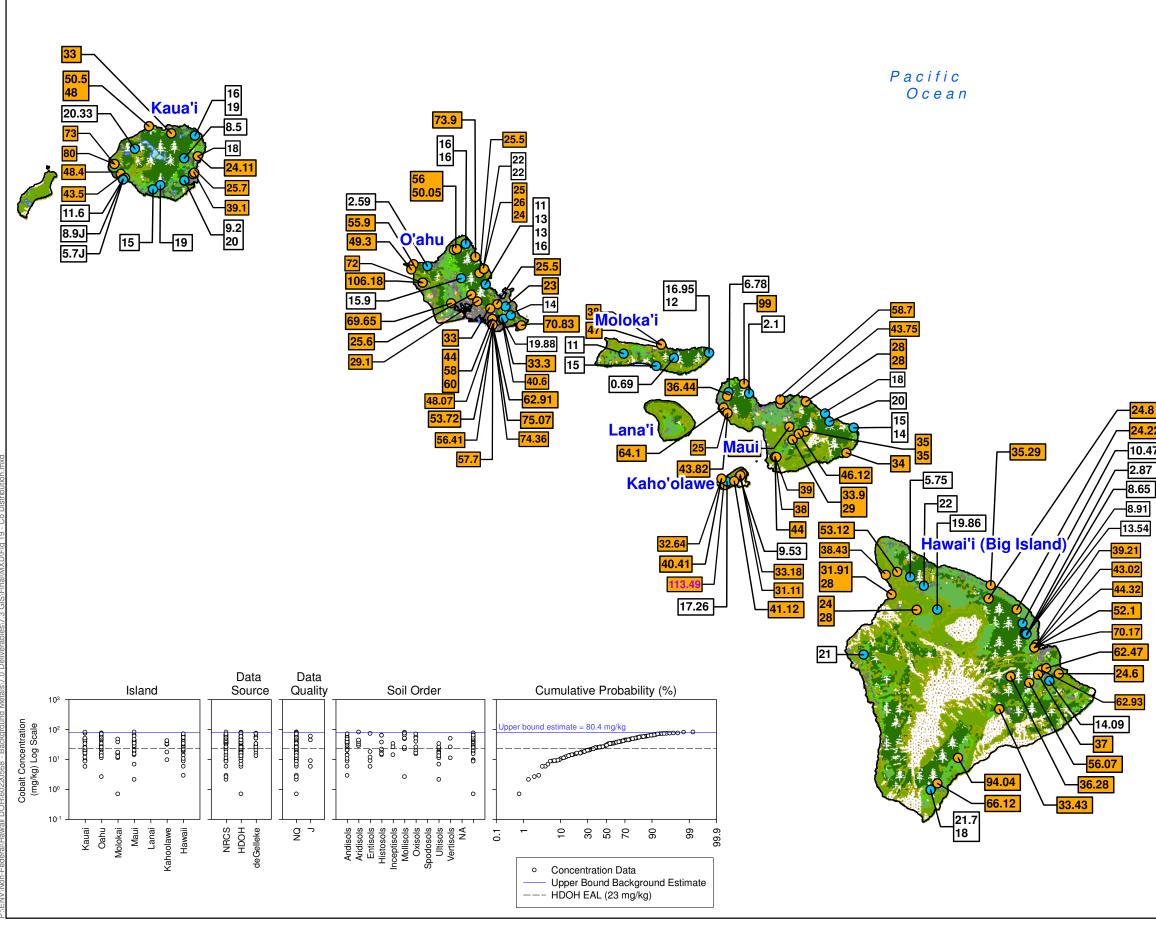


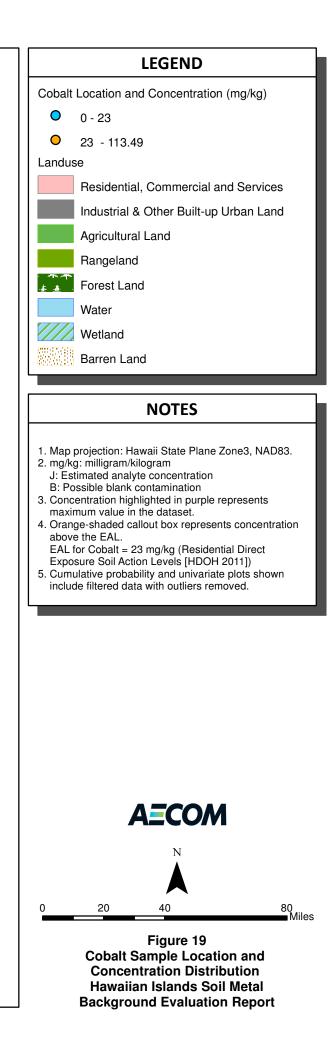
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



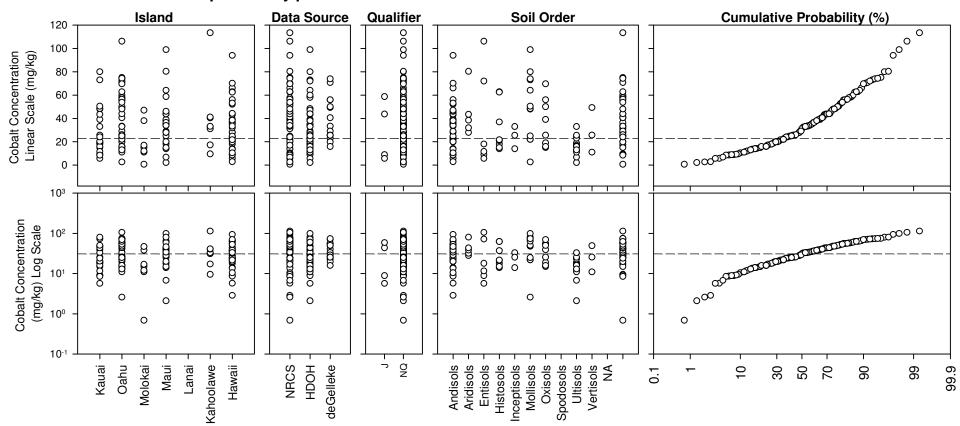




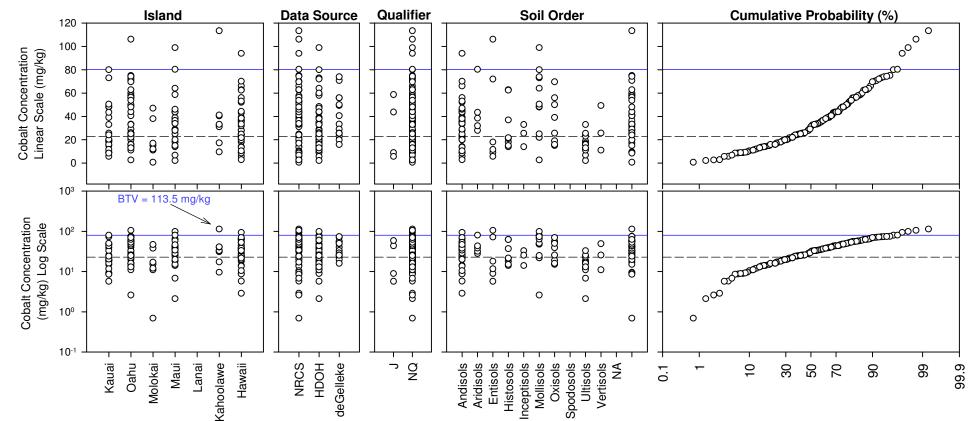




24.8 10.47



b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

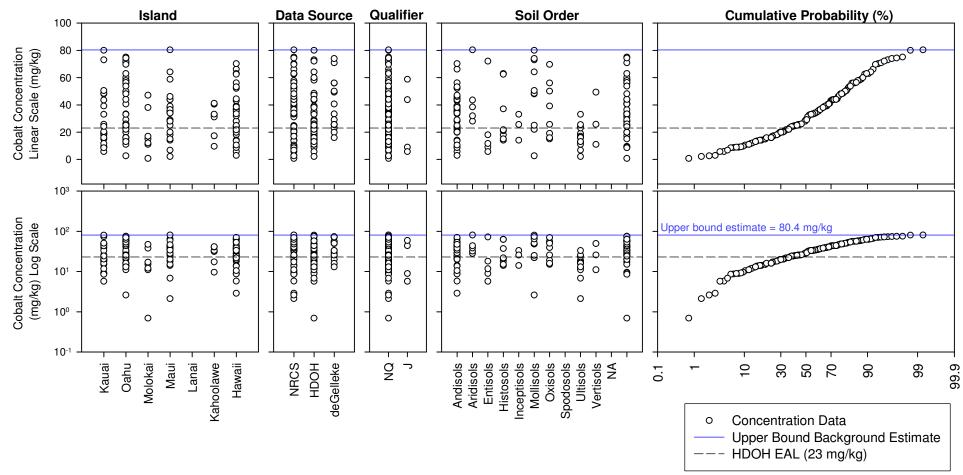
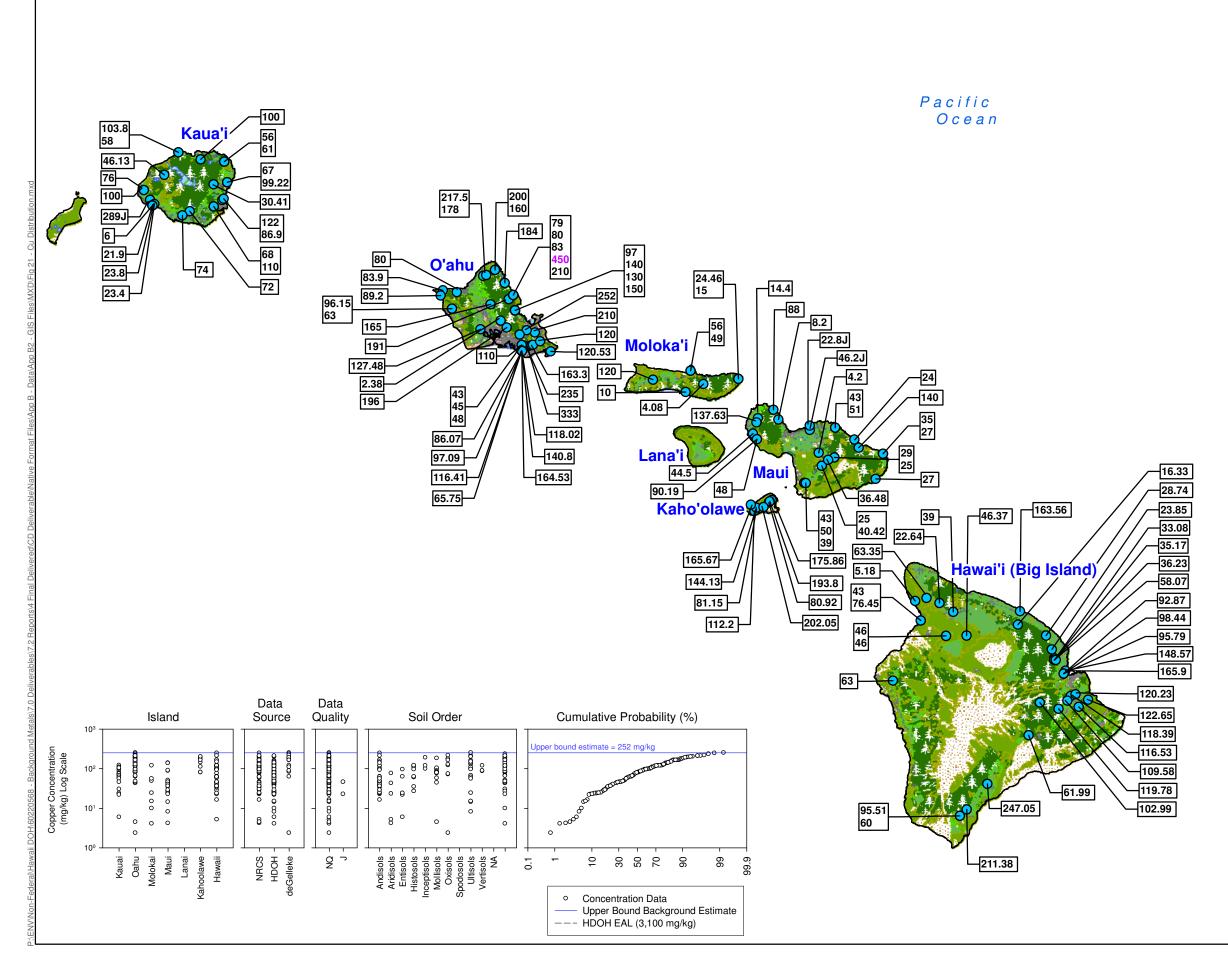


Figure 20 Combined Univariate and Cumulative Probability Plots for Cobalt Hawaiian Islands Soil Metal Background Evaluation Report



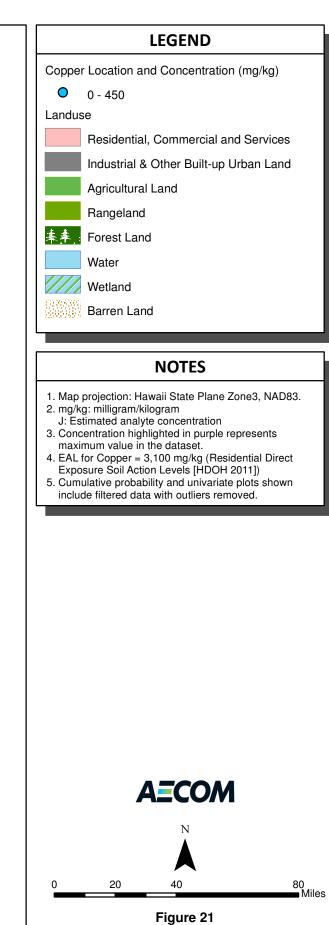
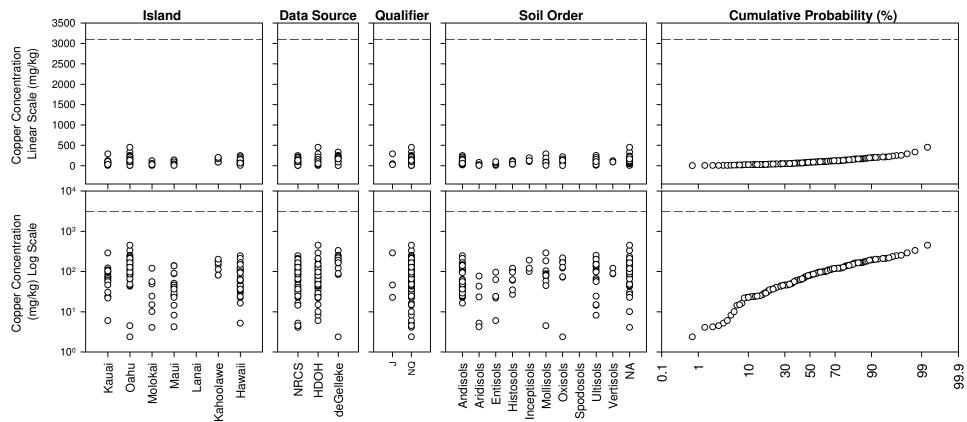
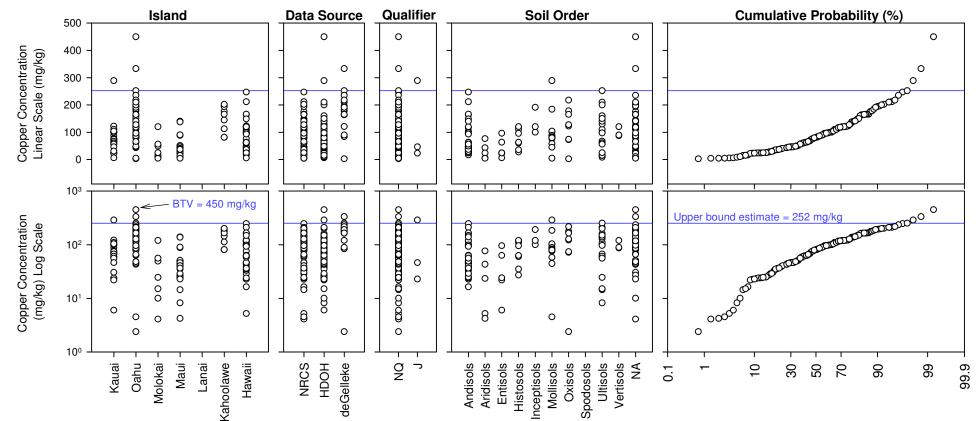


Figure 21 Copper Sample Location and Concentration Distribution Hawaiian Islands Soil Metal Background Evaluation Report



b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

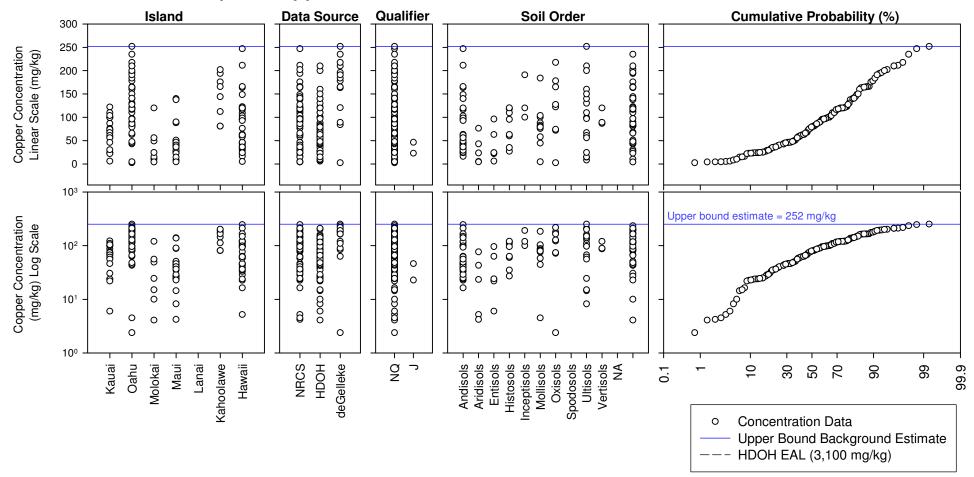
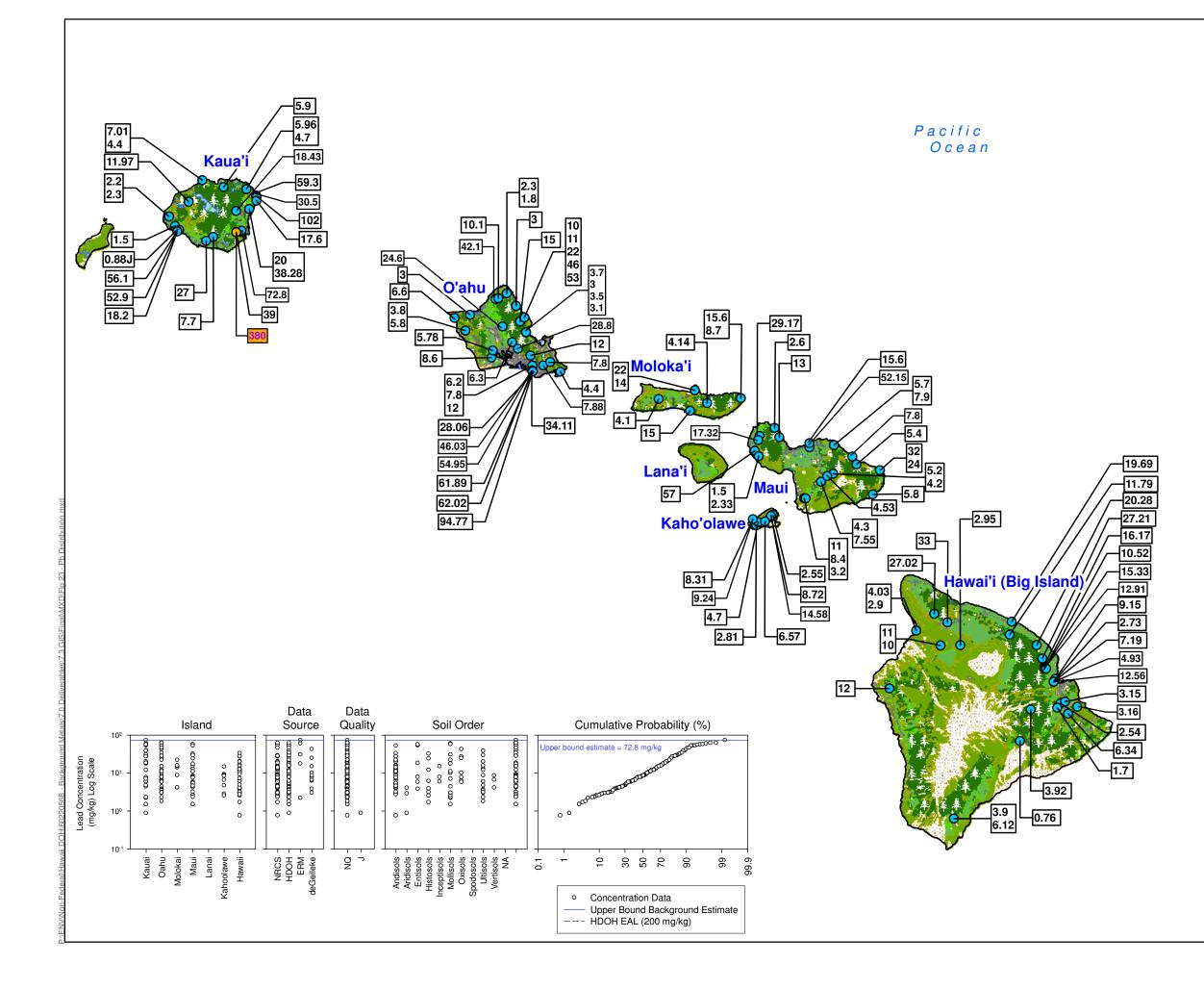
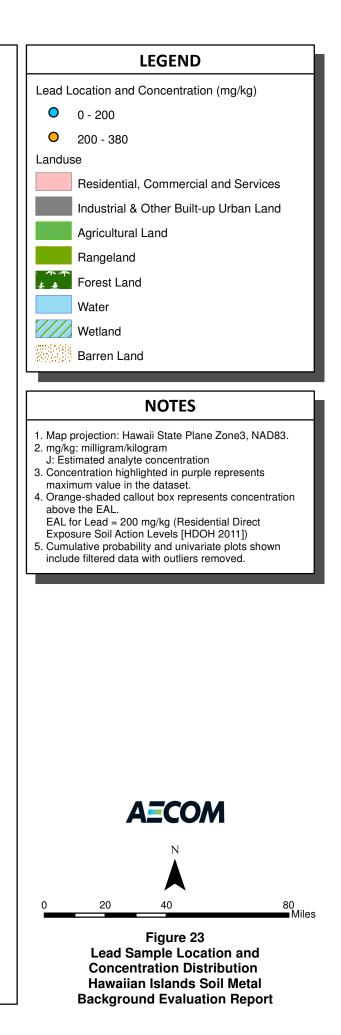
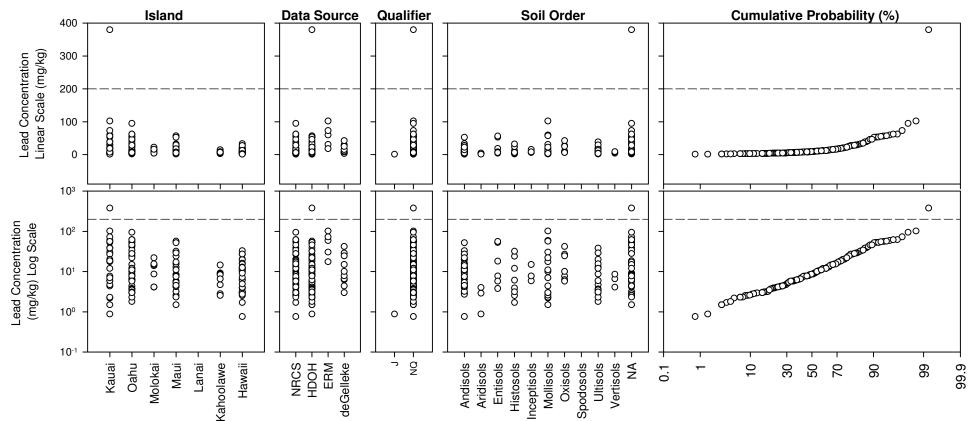


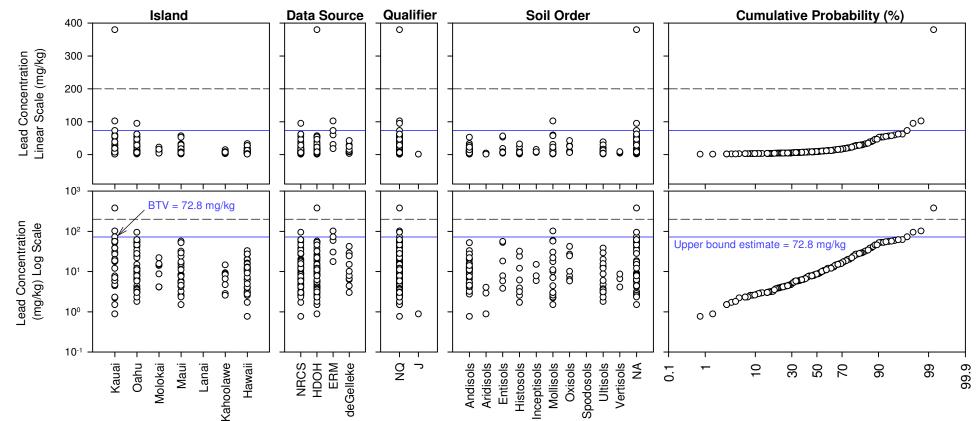
Figure 22 Combined Univariate and Cumulative Probability Plots for Copper Hawaiian Islands Soil Metal Background Evaluation Report







b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

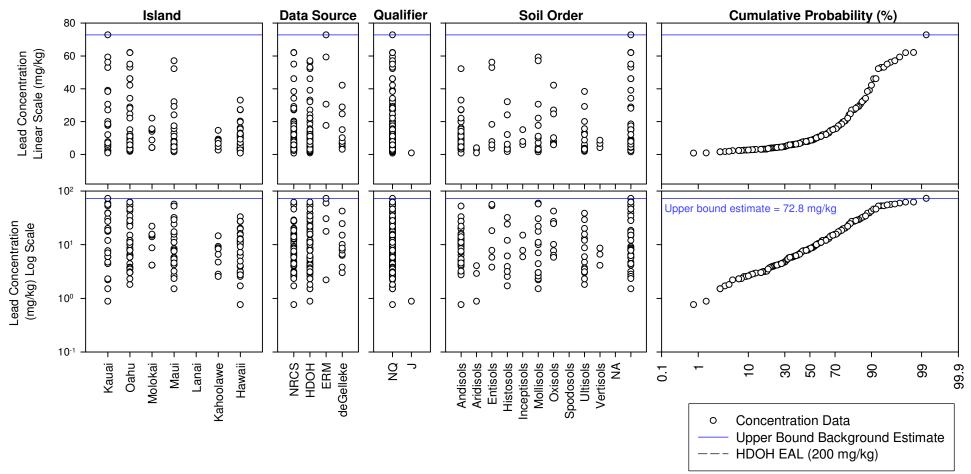
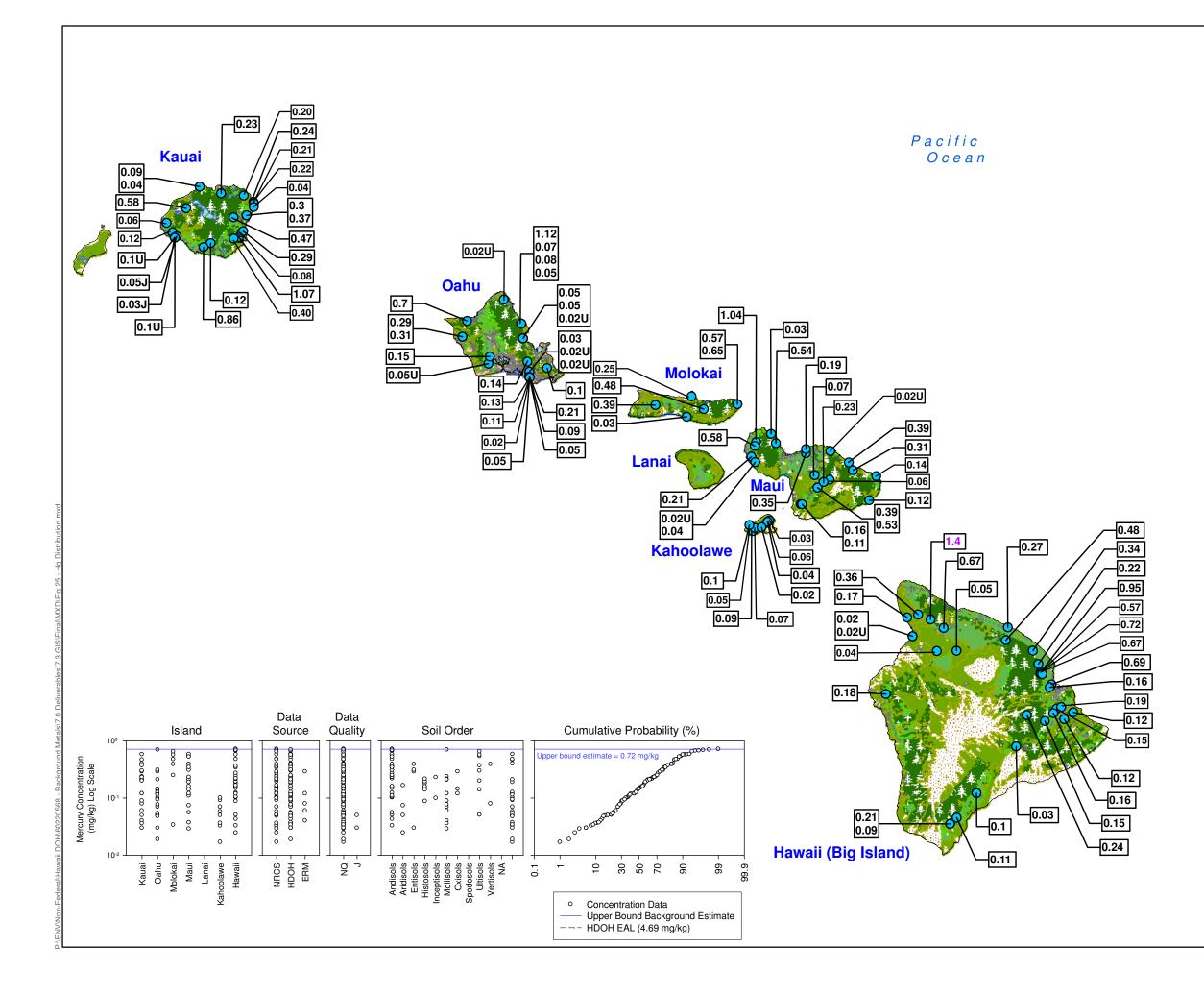
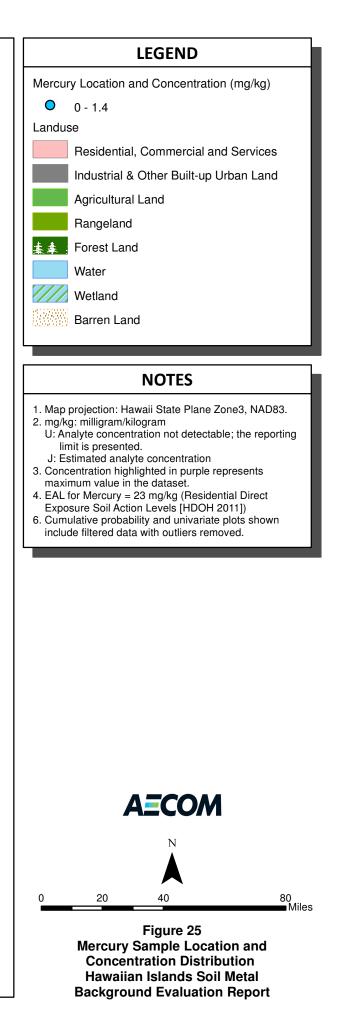
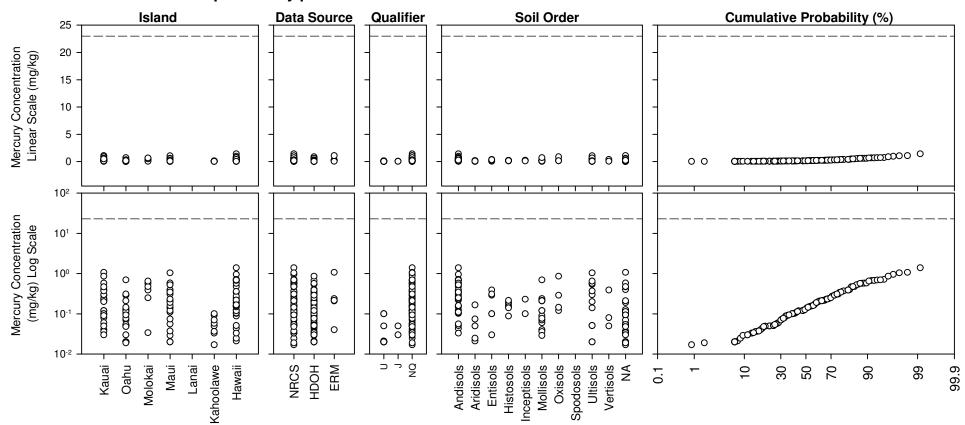


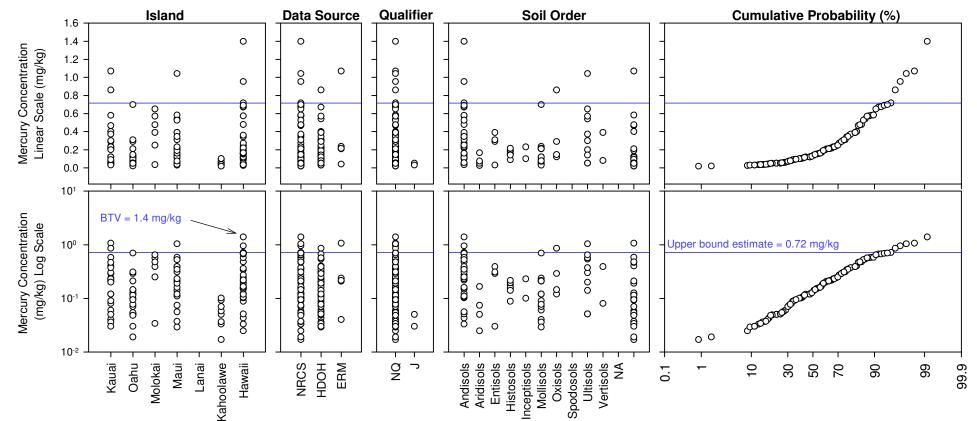
Figure 24 Combined Univariate and Cumulative Probability Plots for Lead Hawaiian Islands Soil Metal Background Evaluation Report

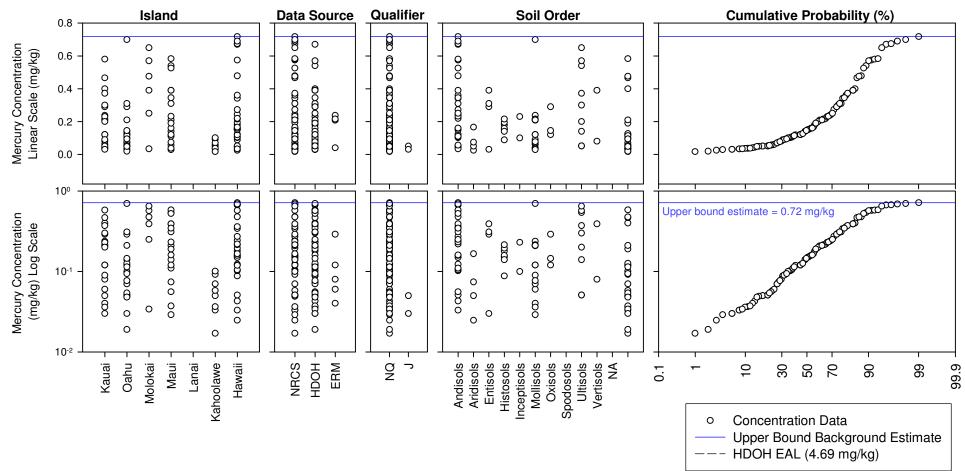


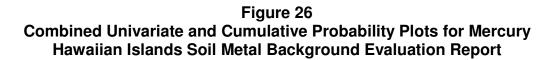


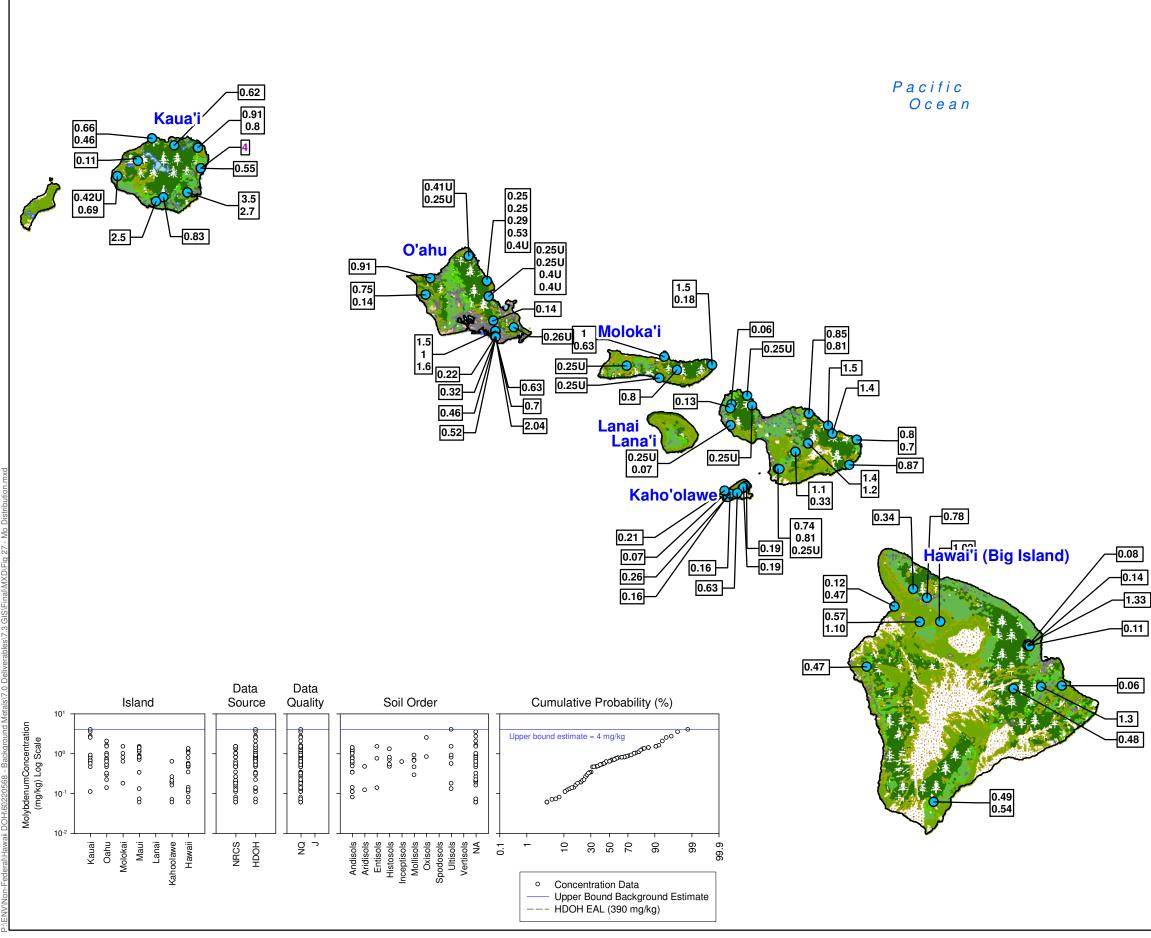


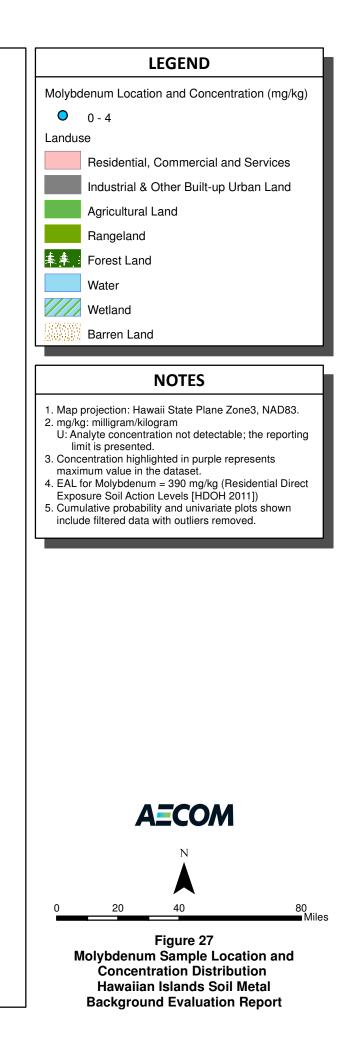
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

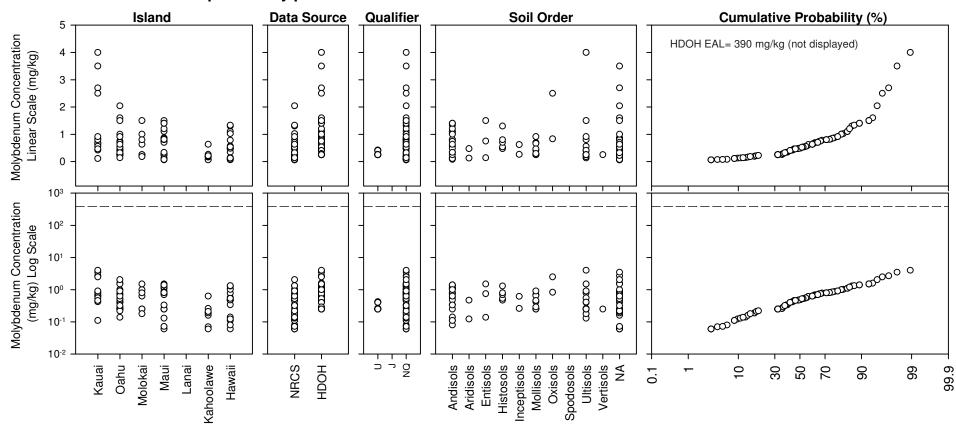




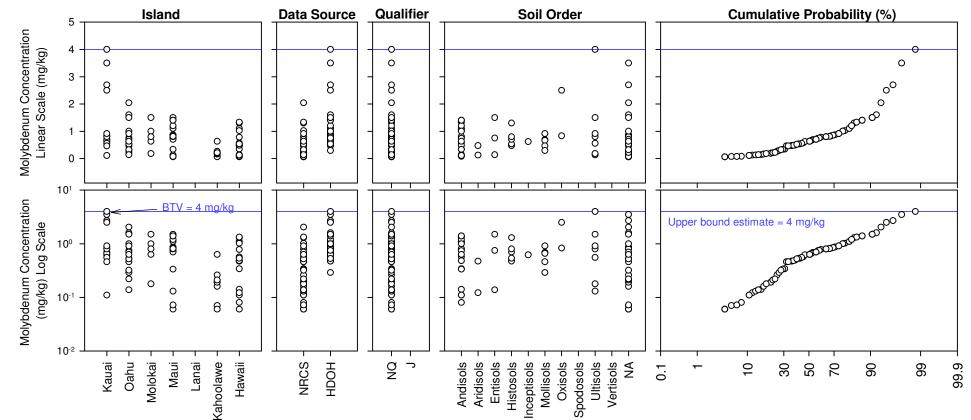








b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

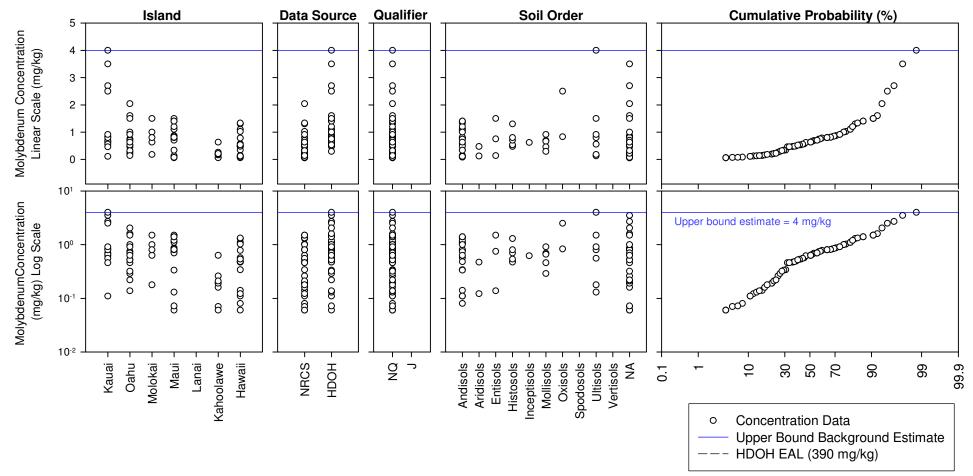
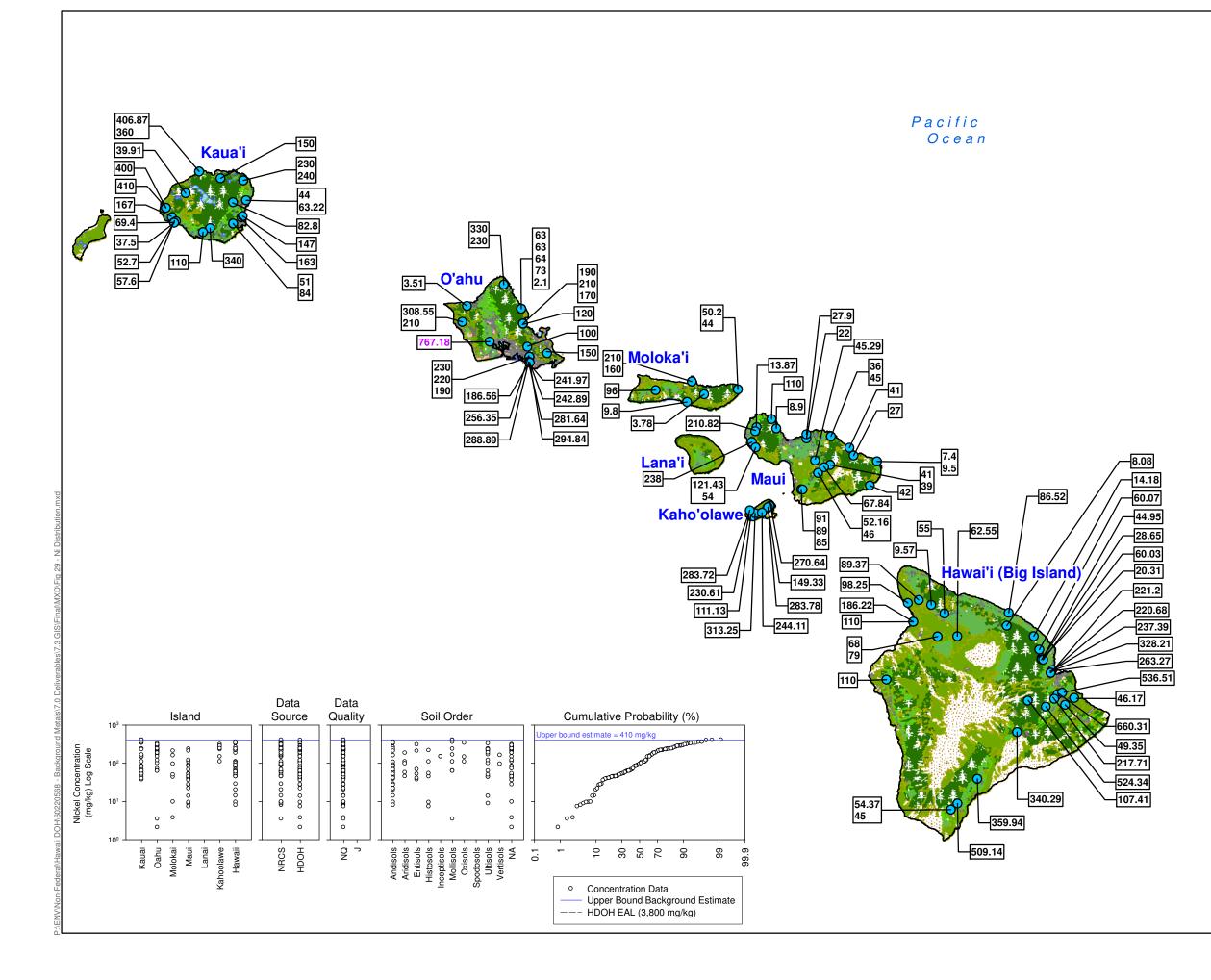
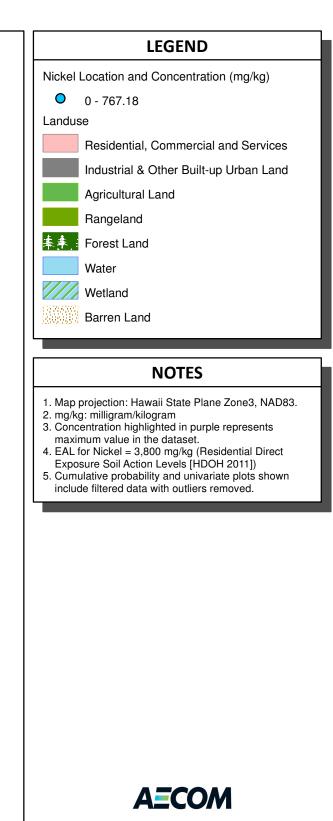
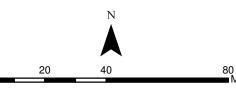


Figure 28 Combined Univariate and Cumulative Probability Plots for Molybdenum Hawaiian Islands Soil Metal Background Evaluation Report

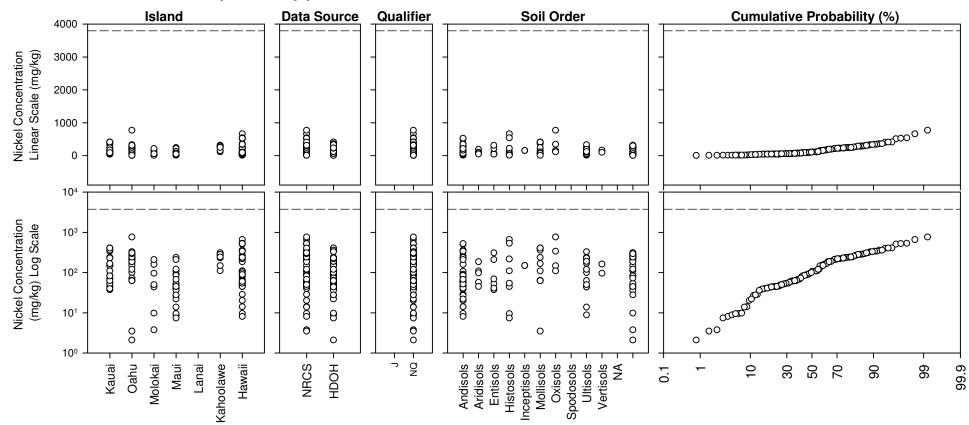




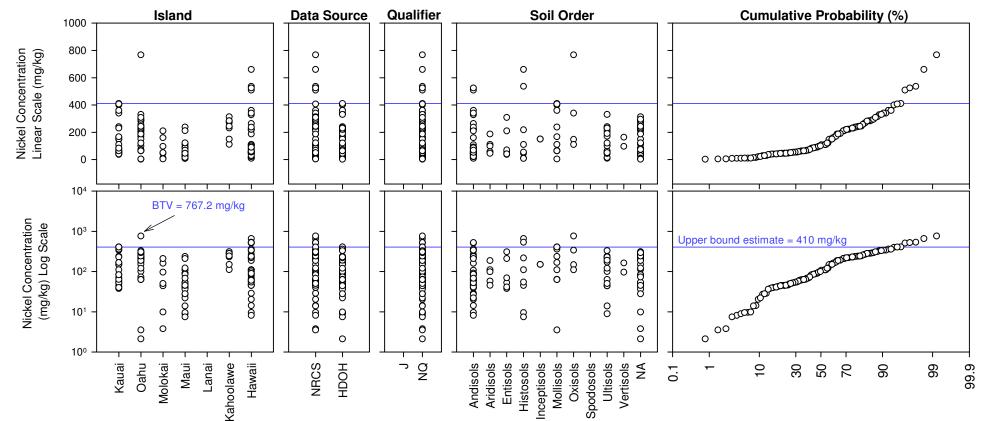


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Figure 29 Nickel Sample Location and Concentration Distribution Hawaiian Islands Soil Metal Background Evaluation Report



b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

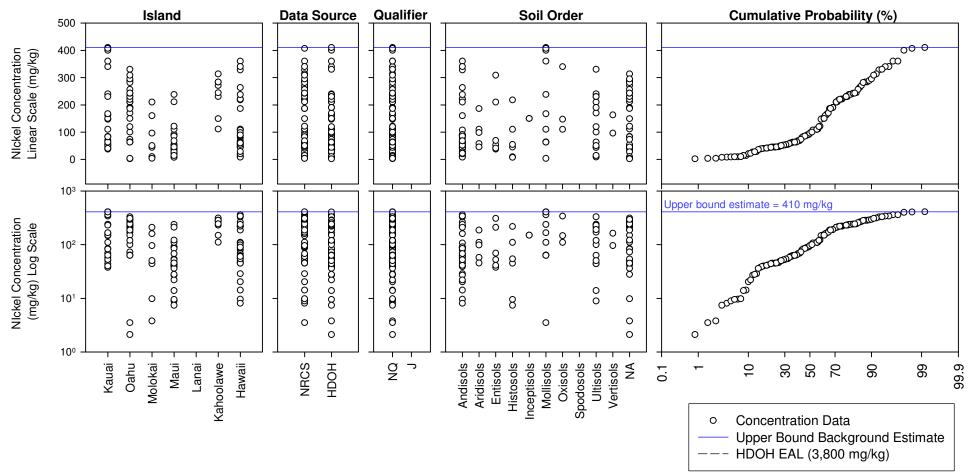
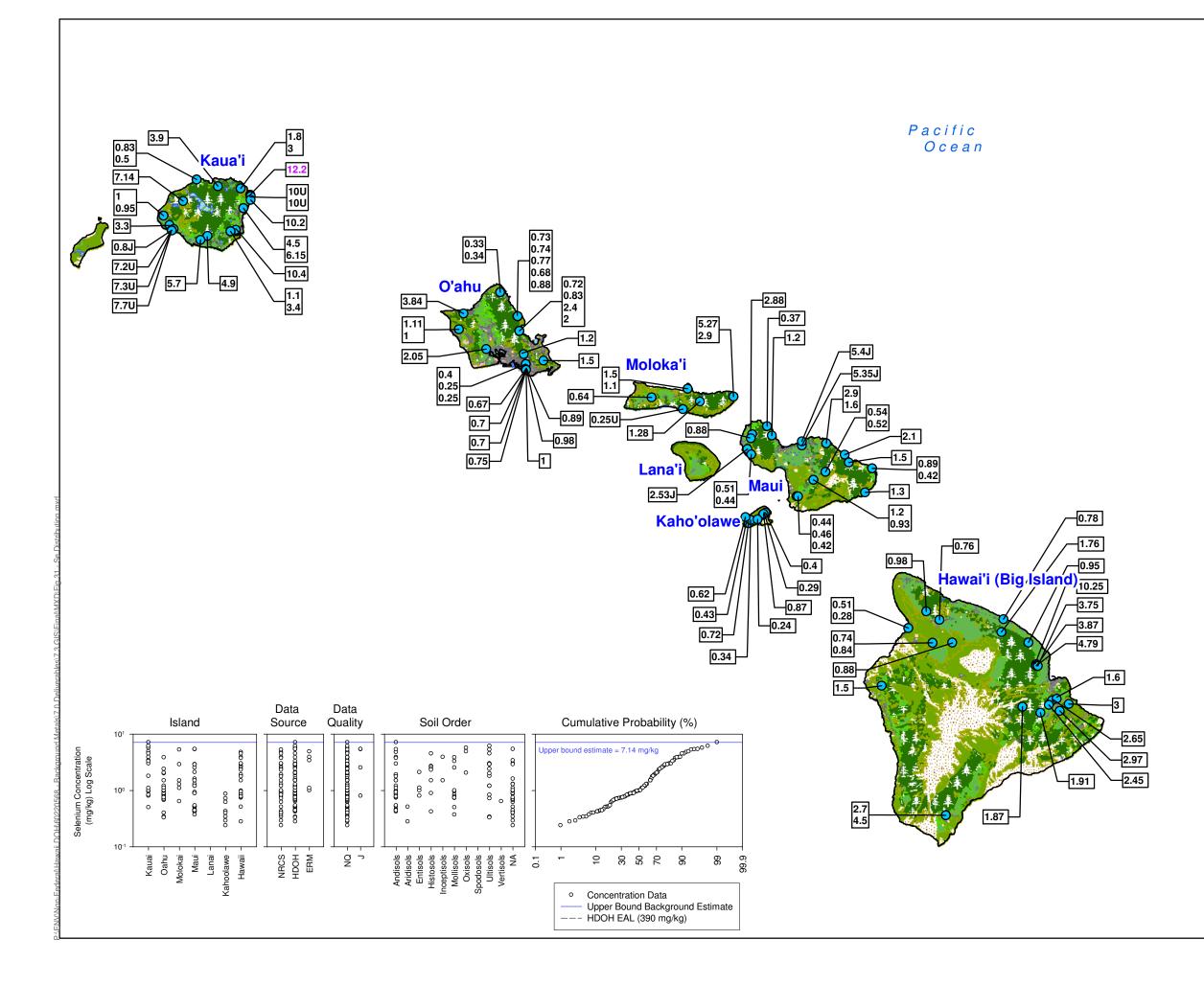
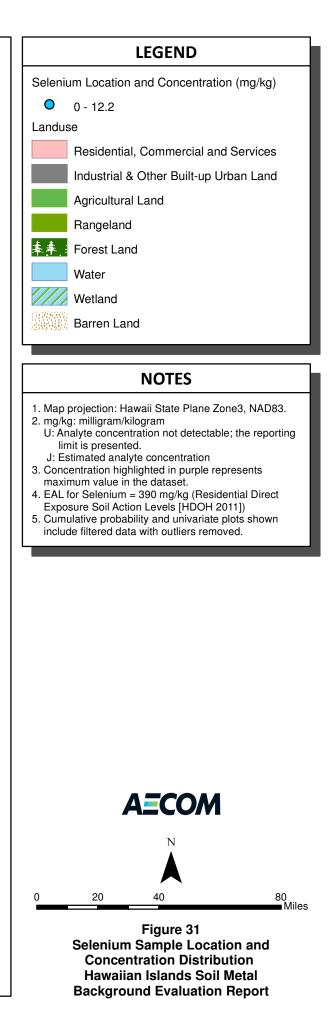
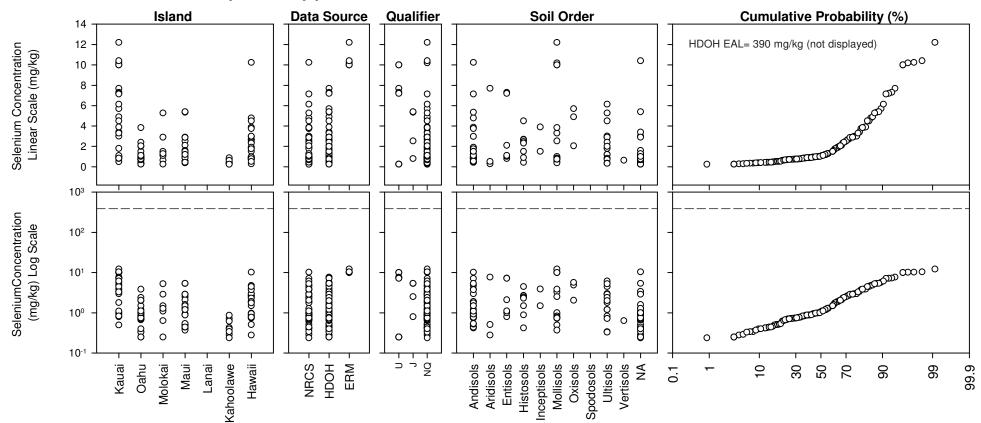


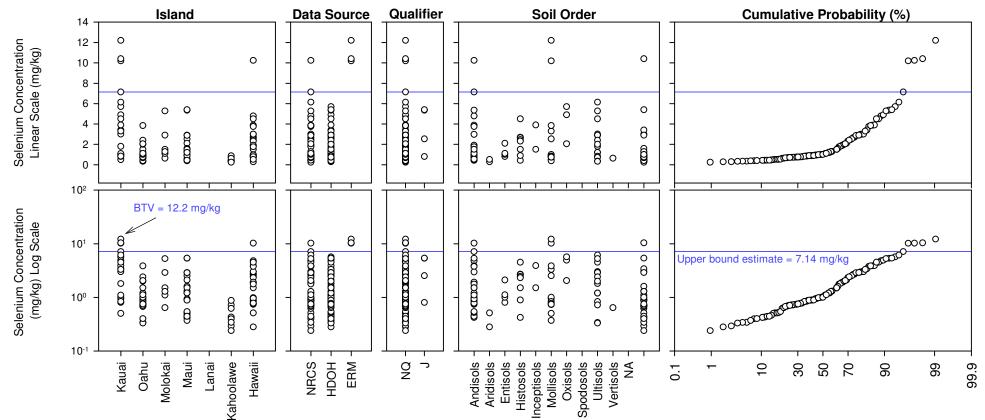
Figure 30 Combined Univariate and Cumulative Probability Plots for Nickel Hawaiian Islands Soil Metal Background Evaluation Report

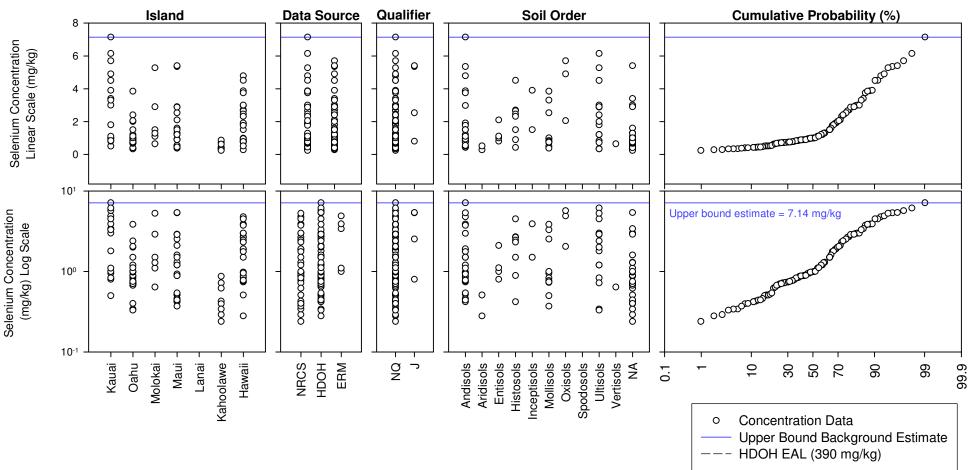


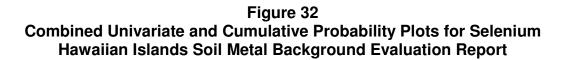


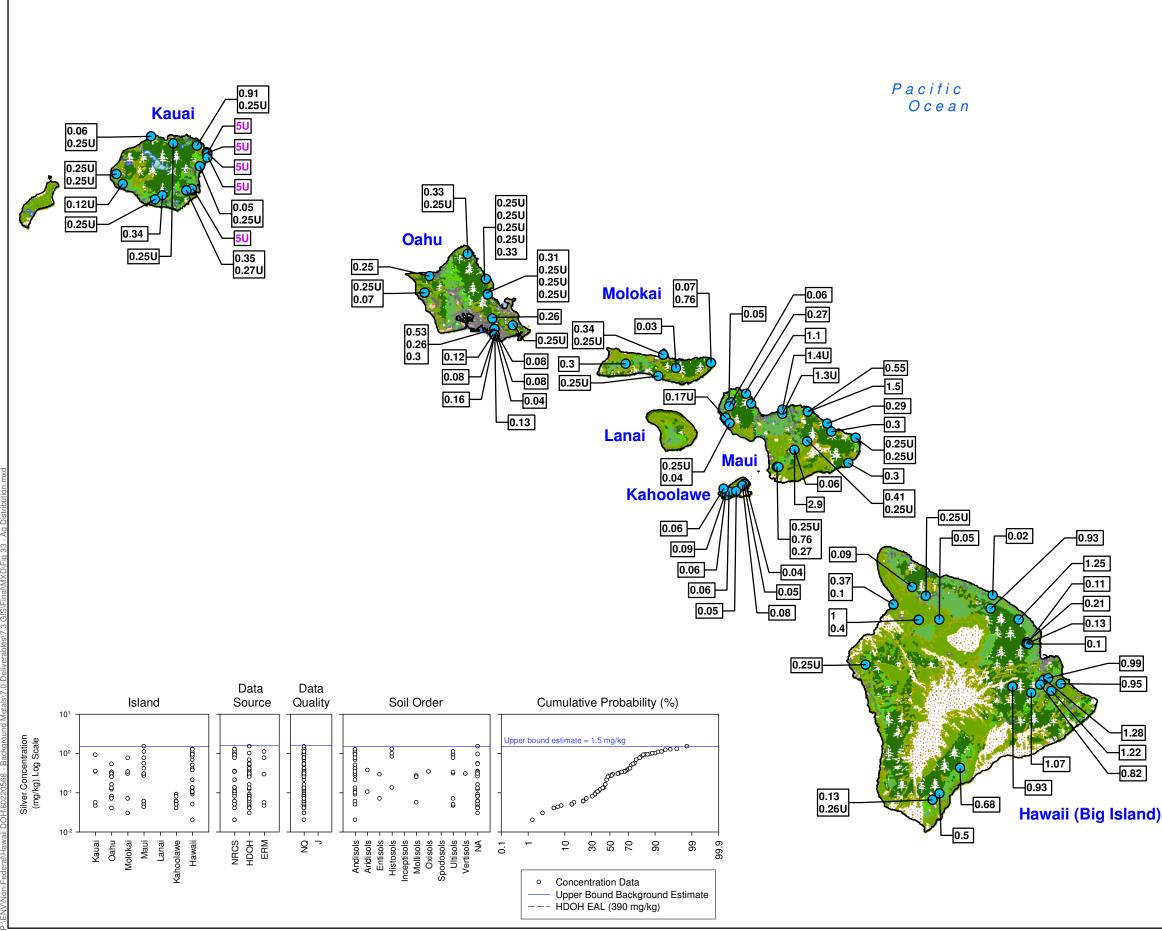


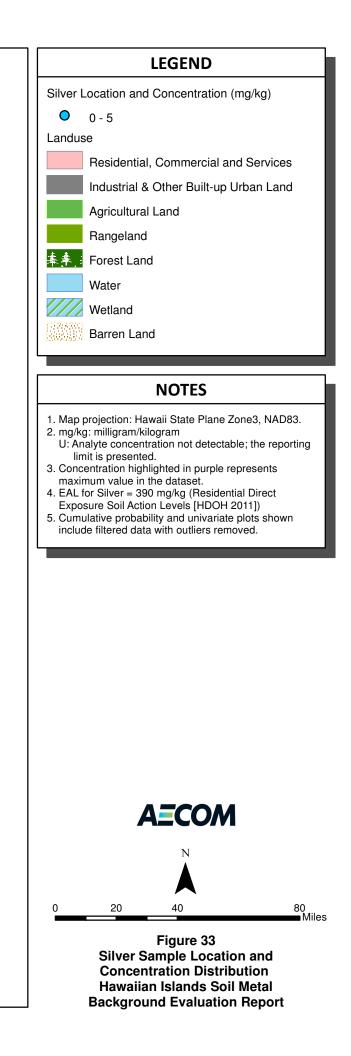
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

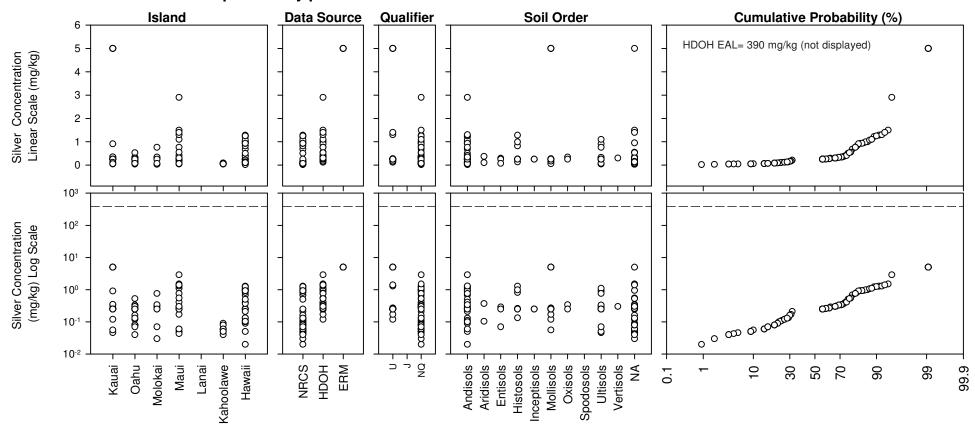




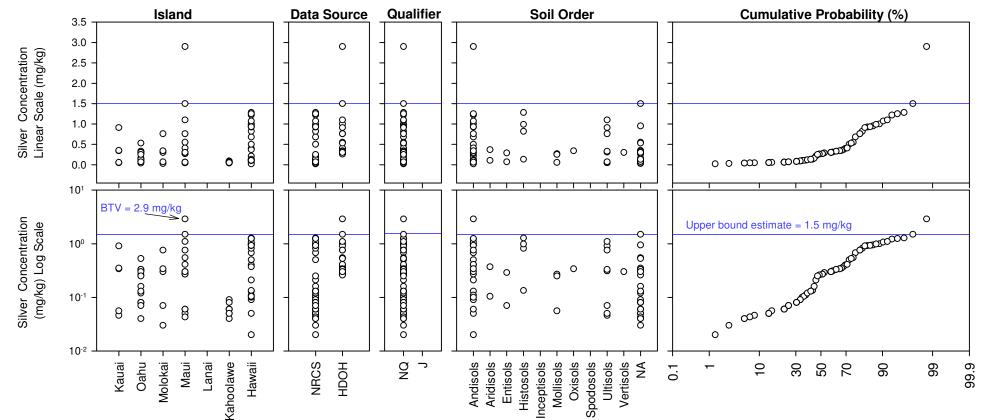








b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

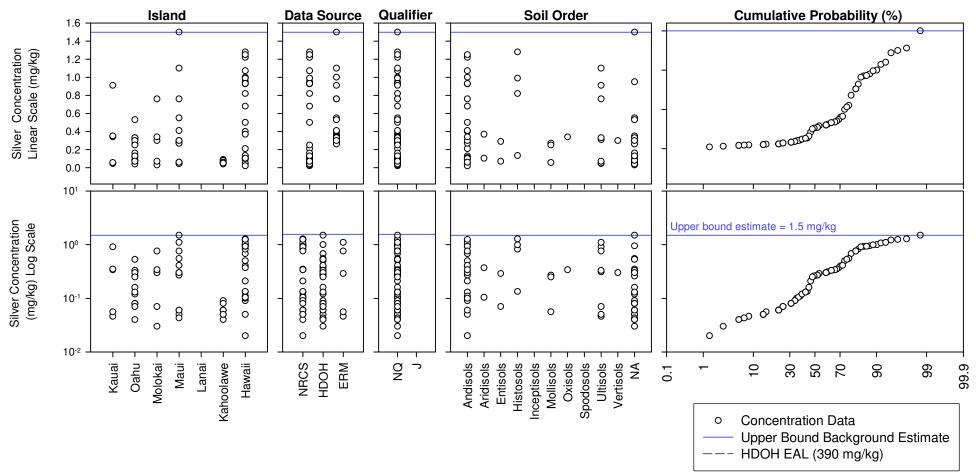
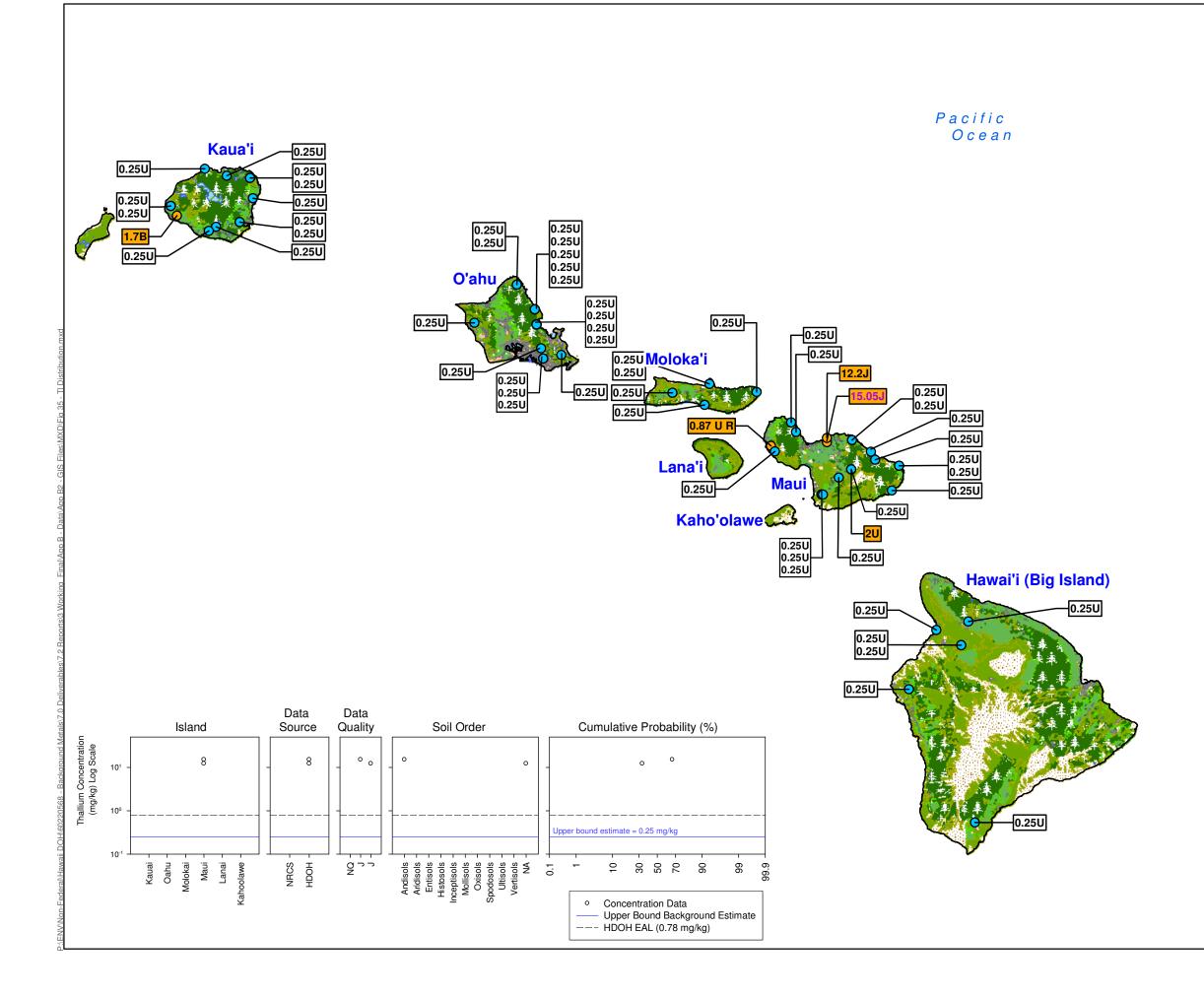
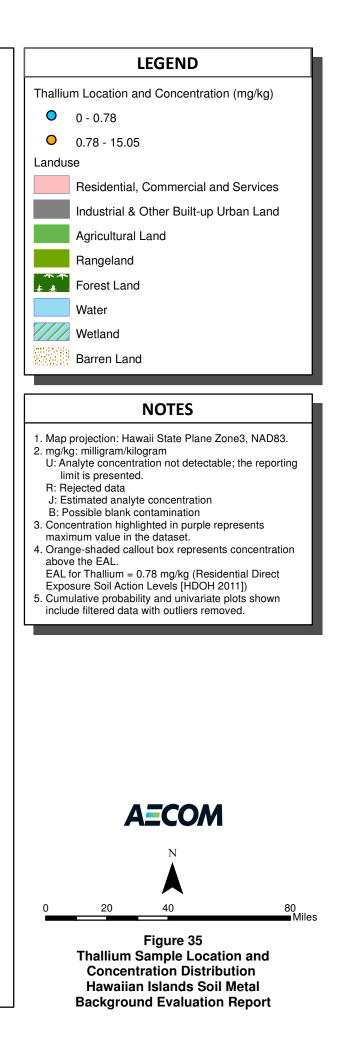
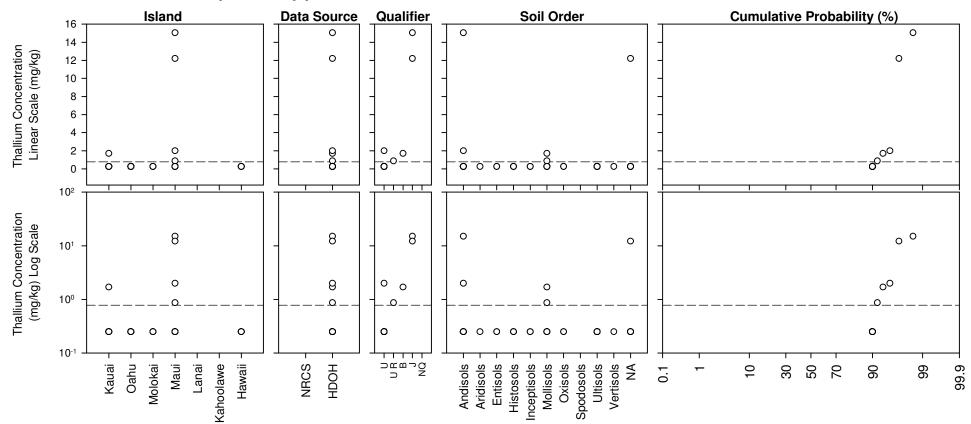


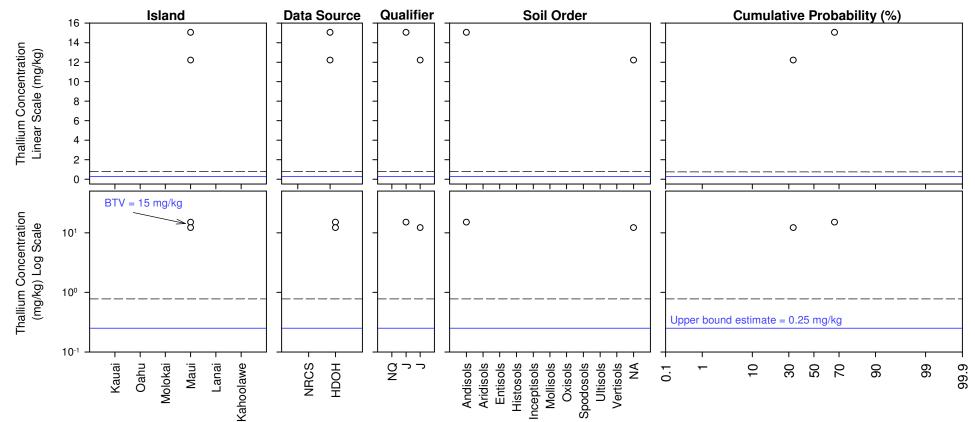
Figure 34 Combined Univariate and Cumulative Probability Plots for Silver Hawaiian Islands Soil Metal Background Evaluation Report

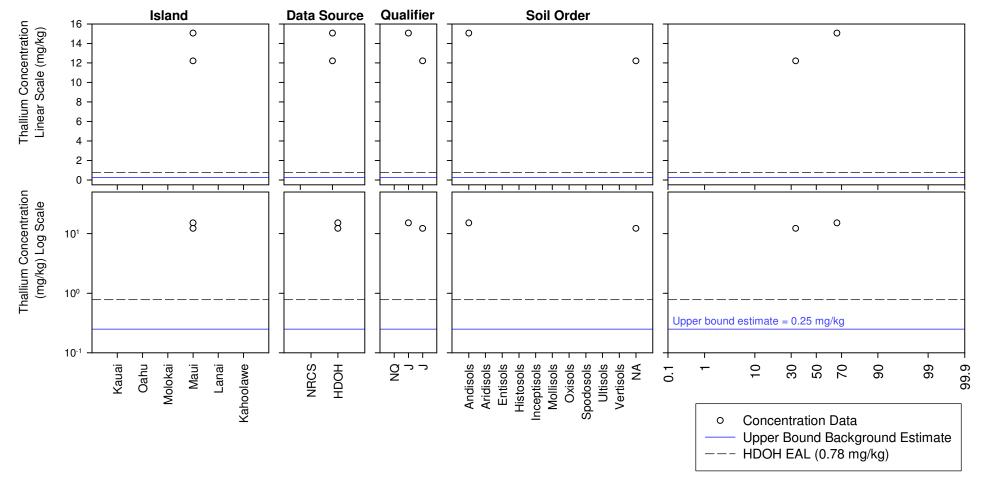


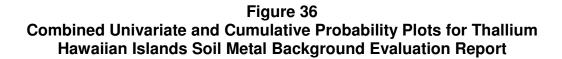


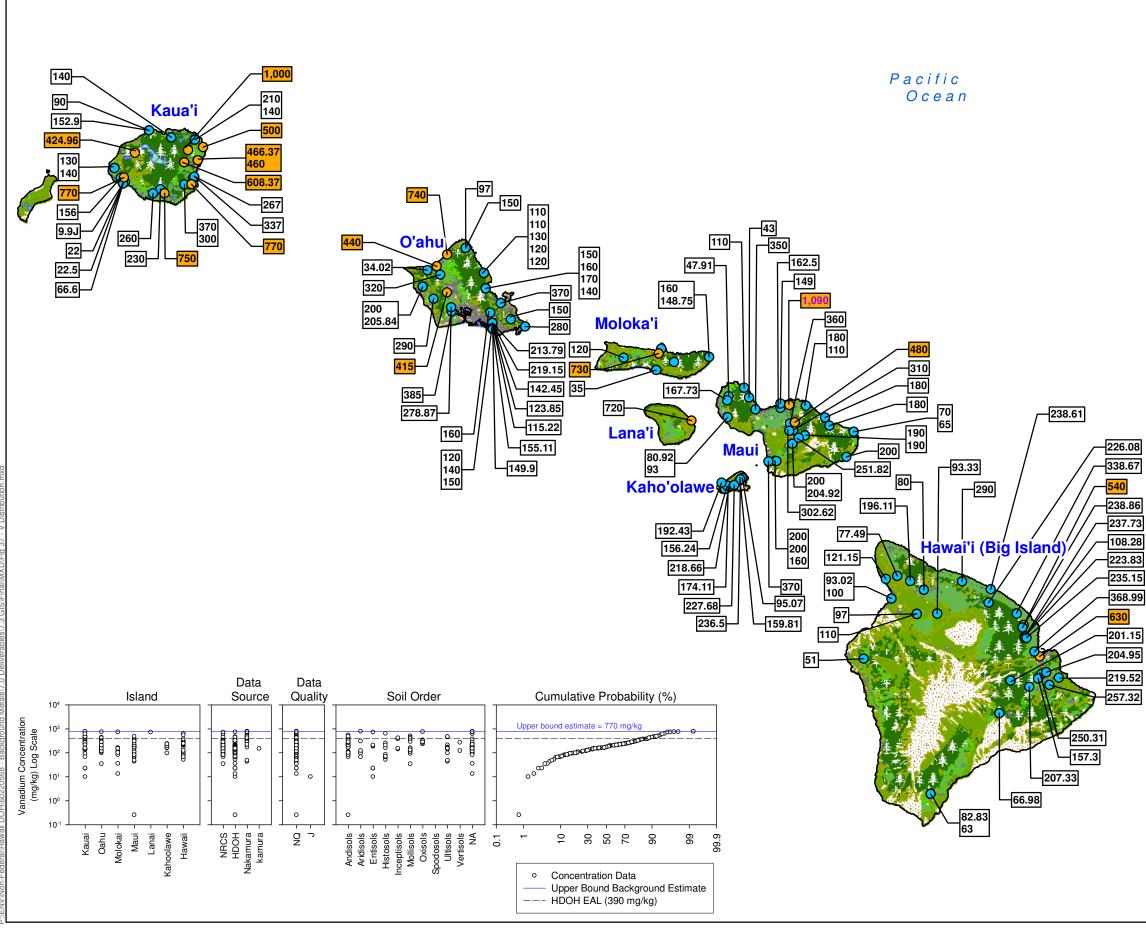


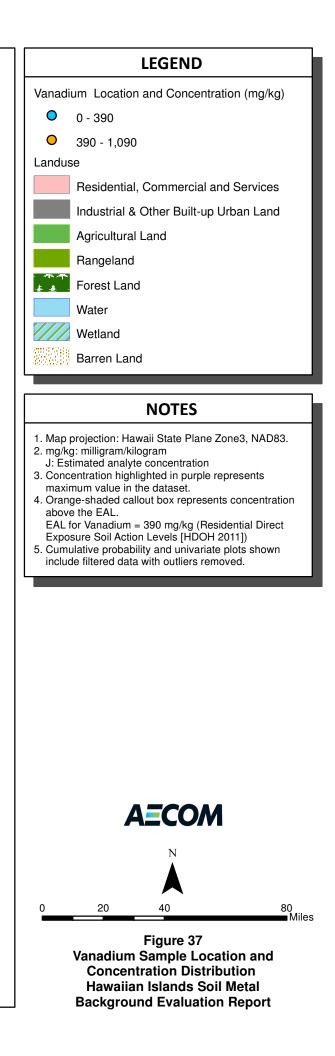
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



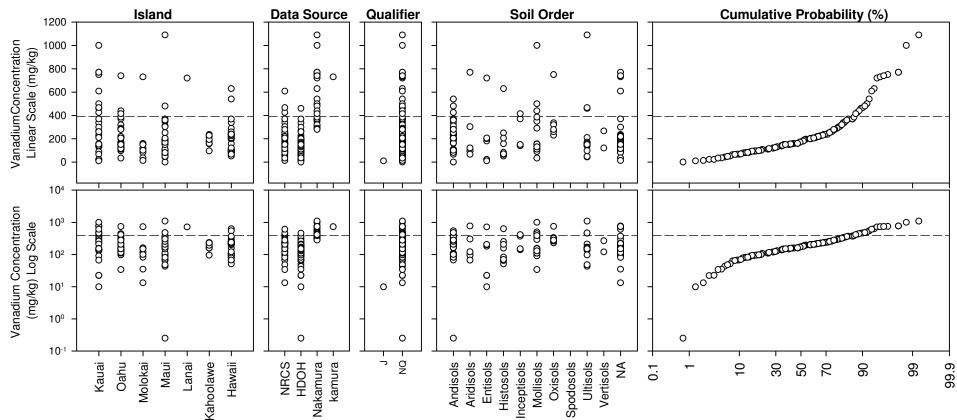




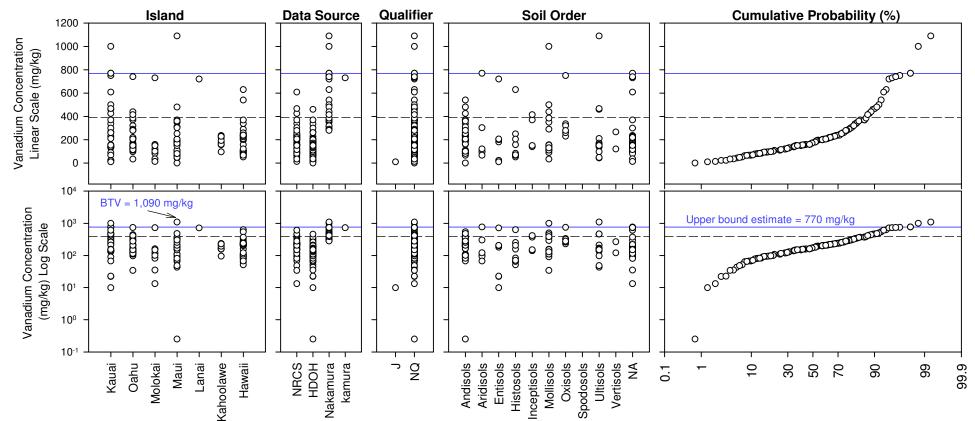


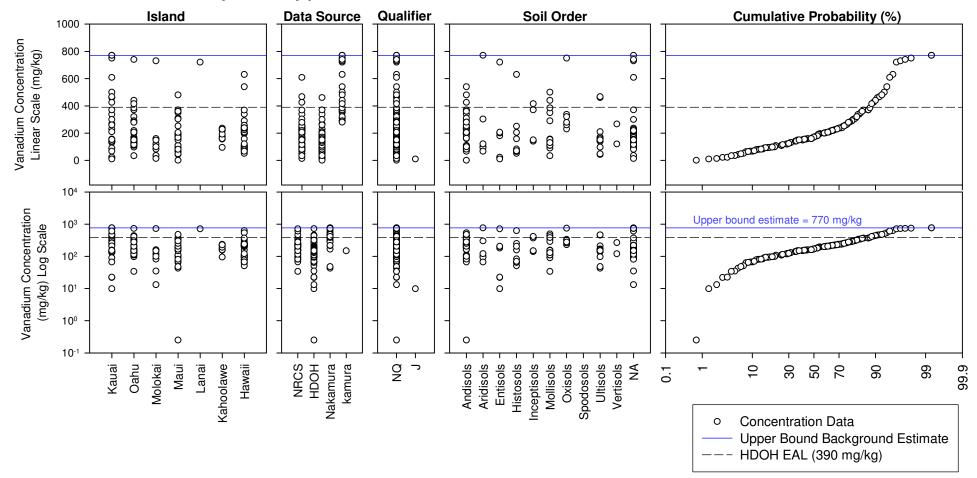


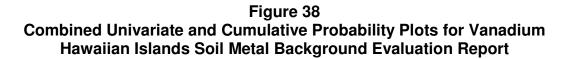


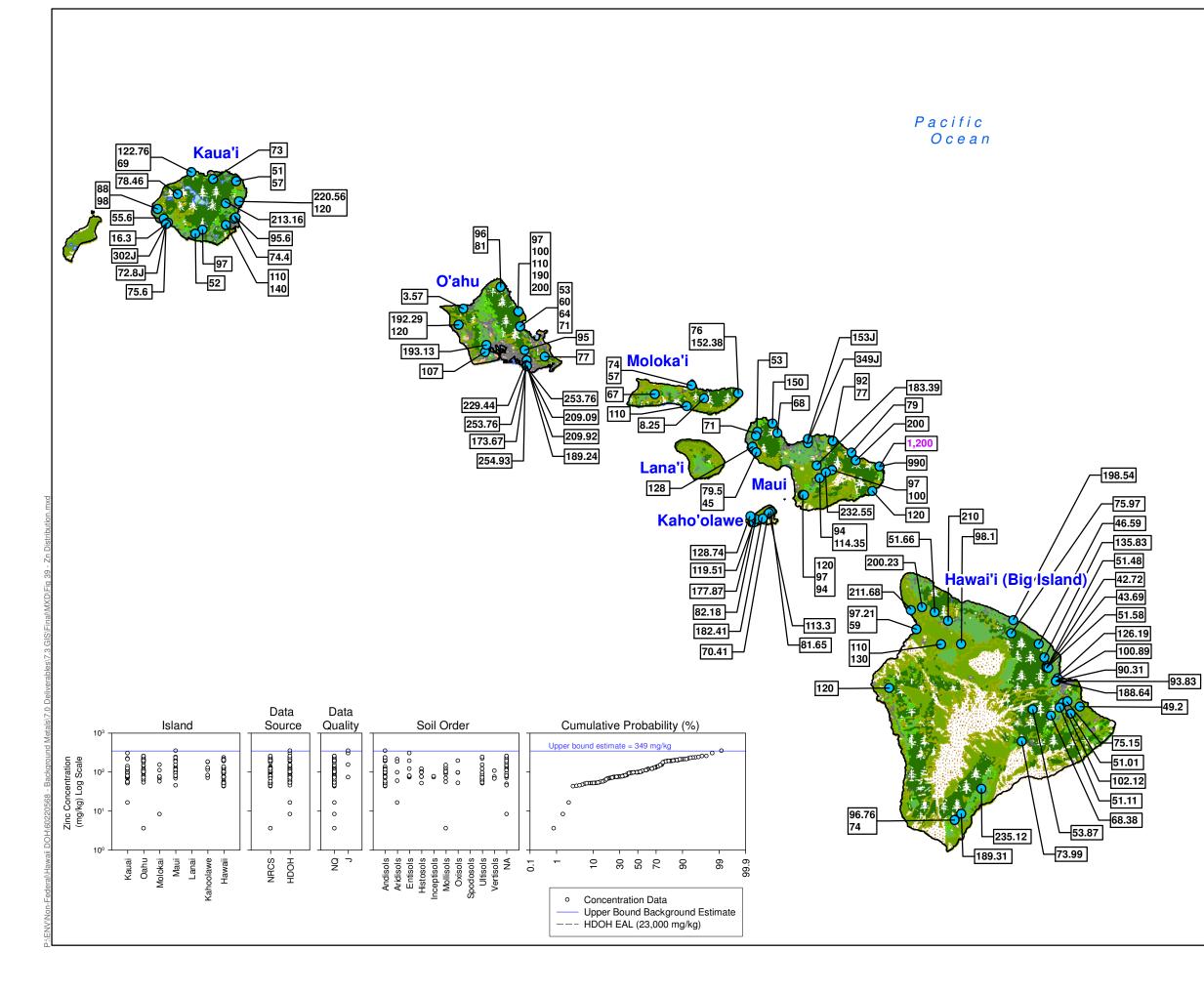


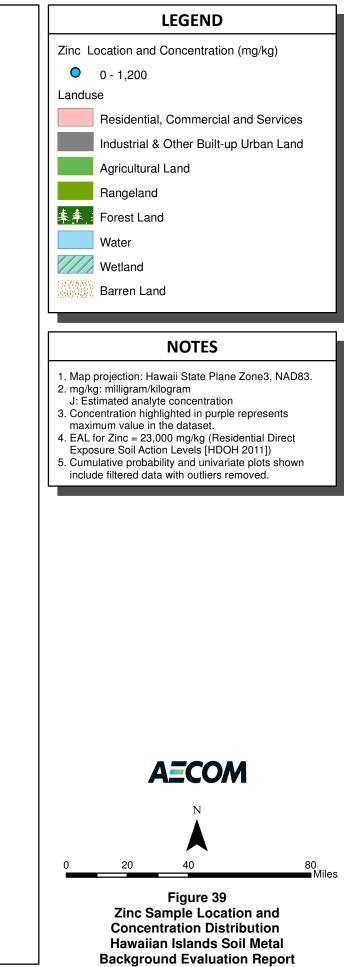
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

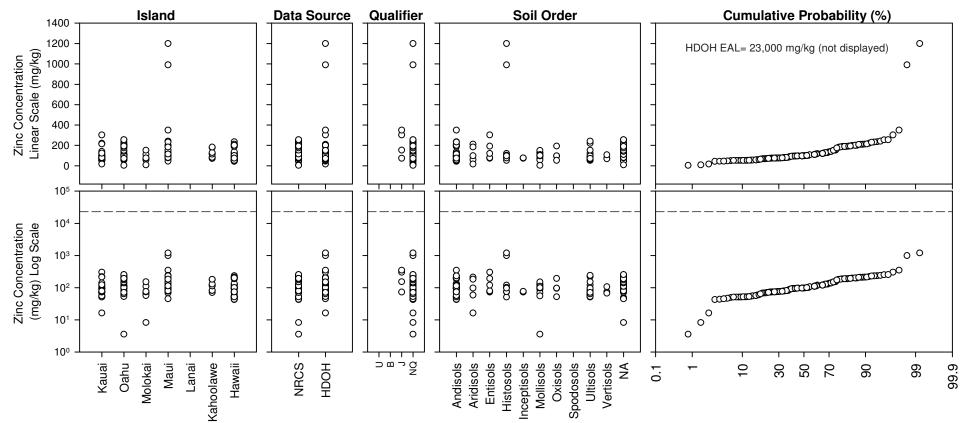




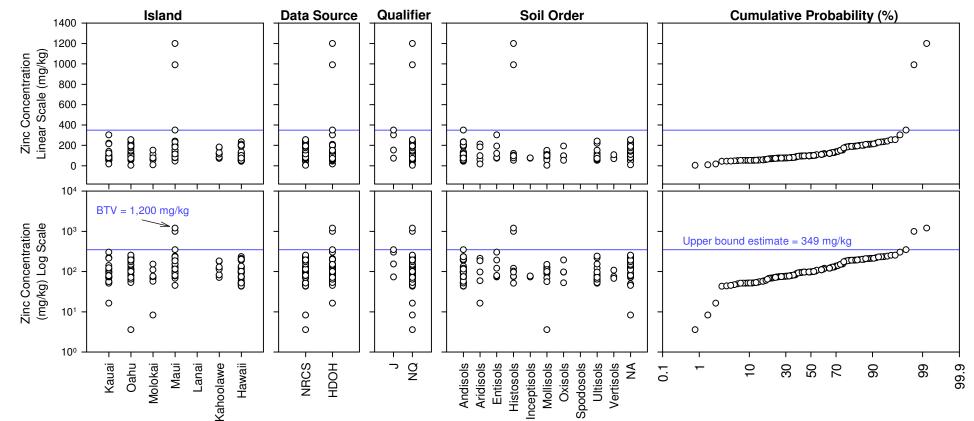








b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

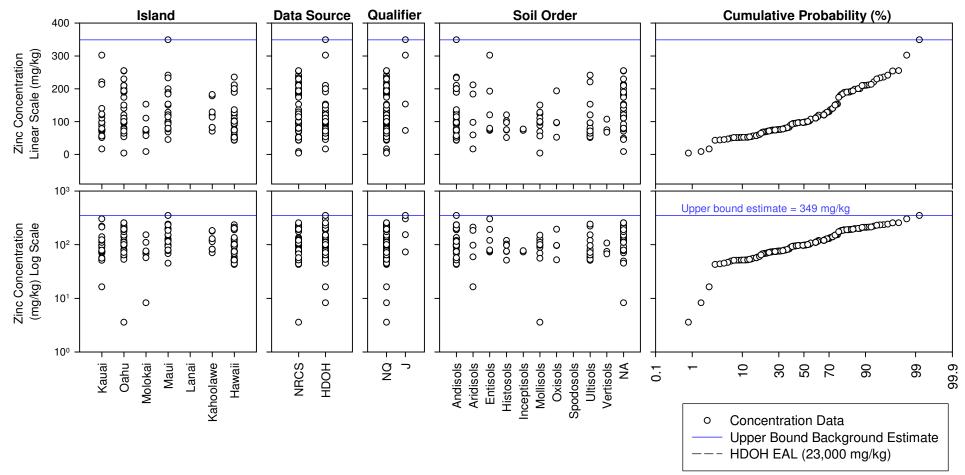
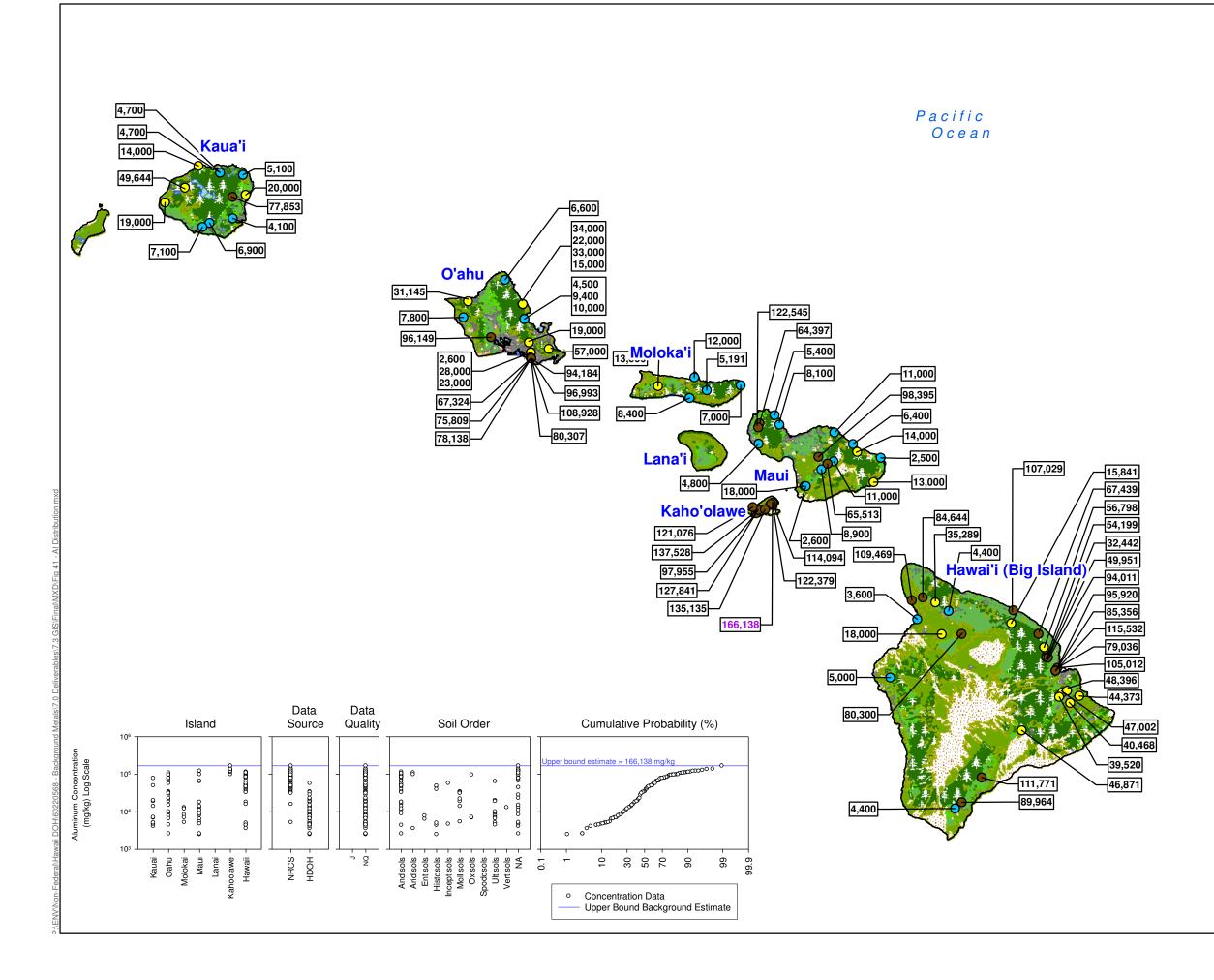
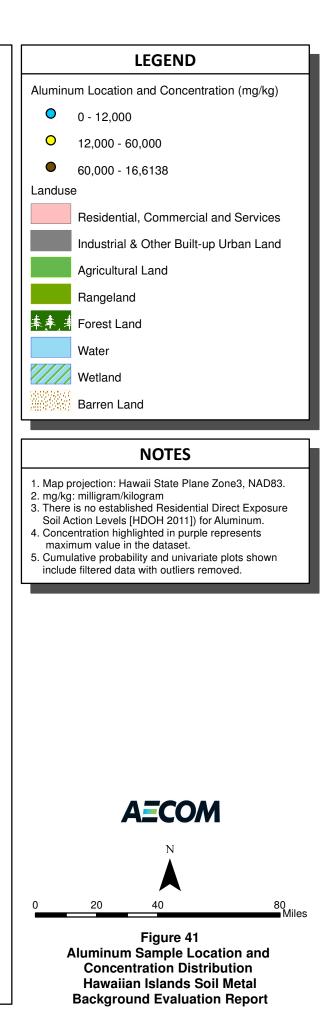
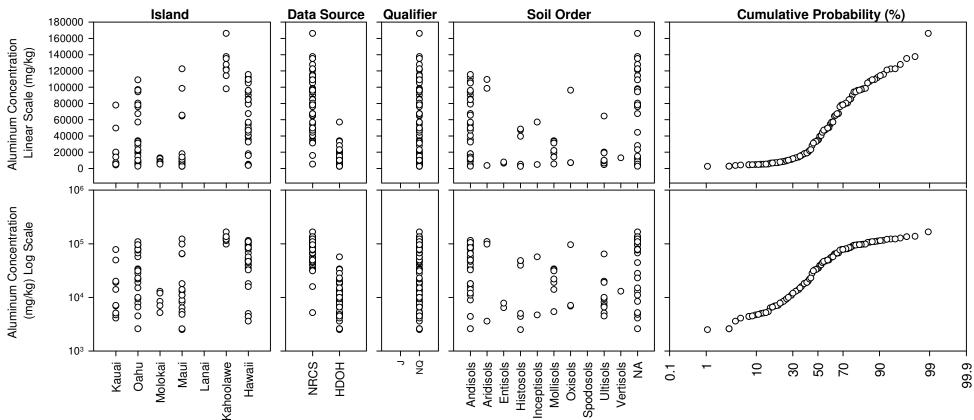


Figure 40 Combined Univariate and Cumulative Probability Plots for Zinc Hawaiian Islands Soil Metal Background Evaluation Report

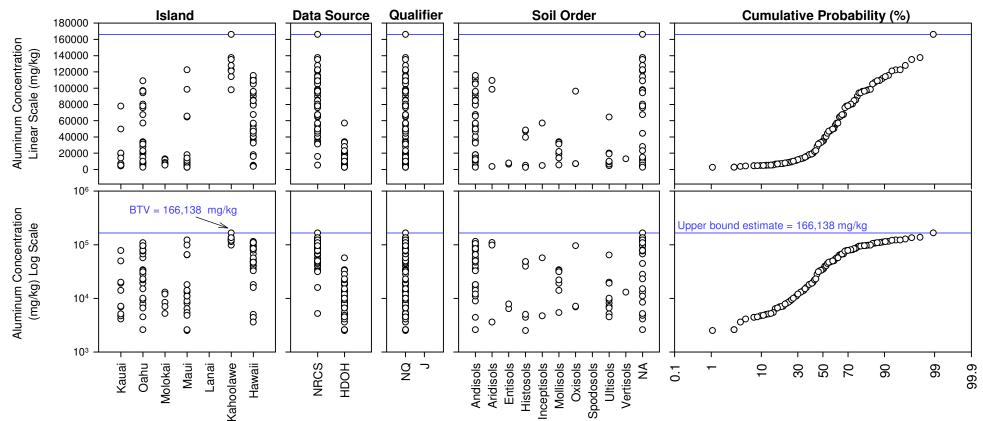


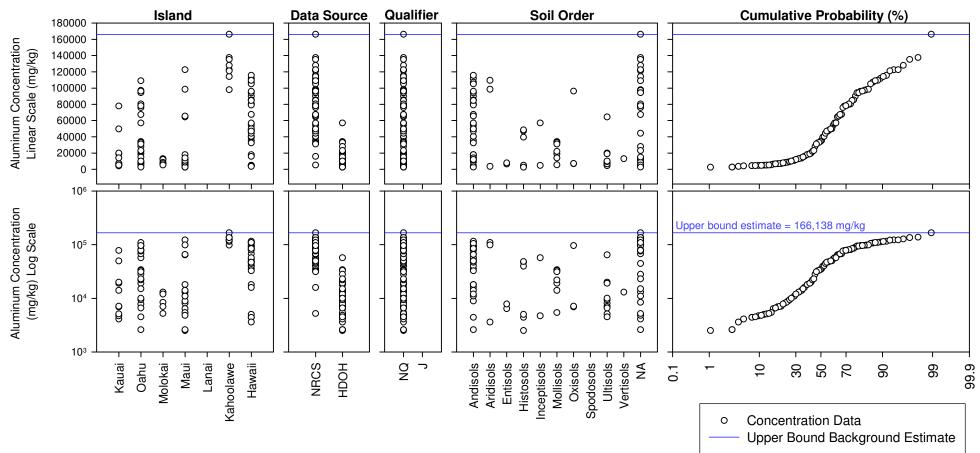


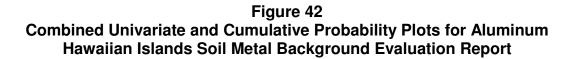


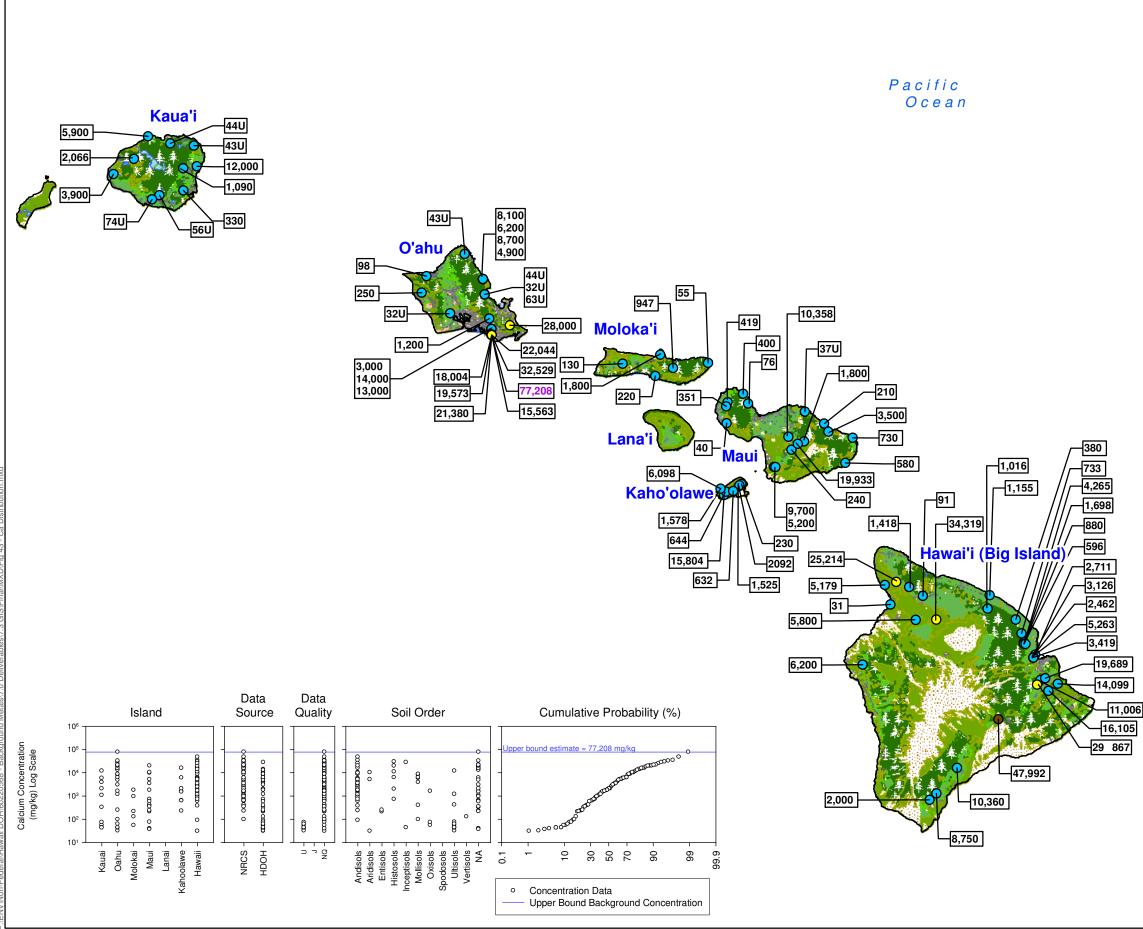


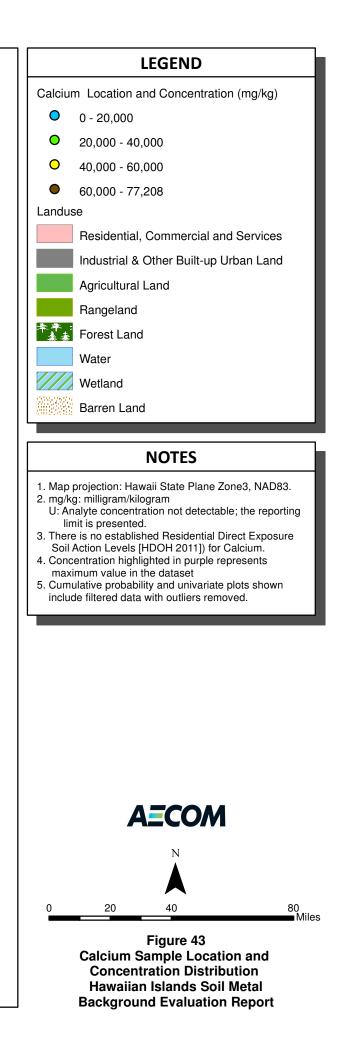
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

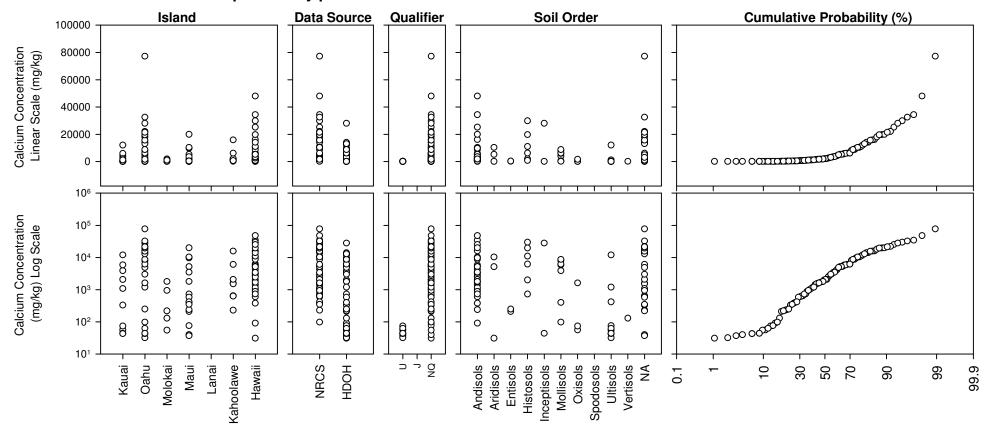




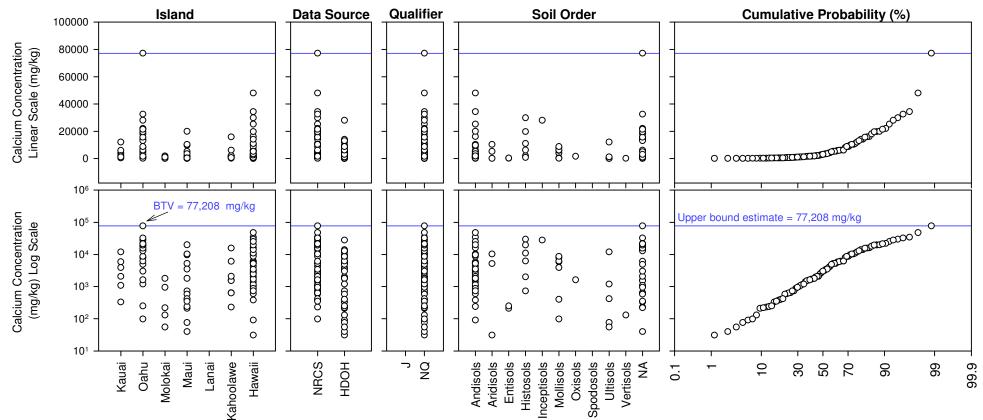


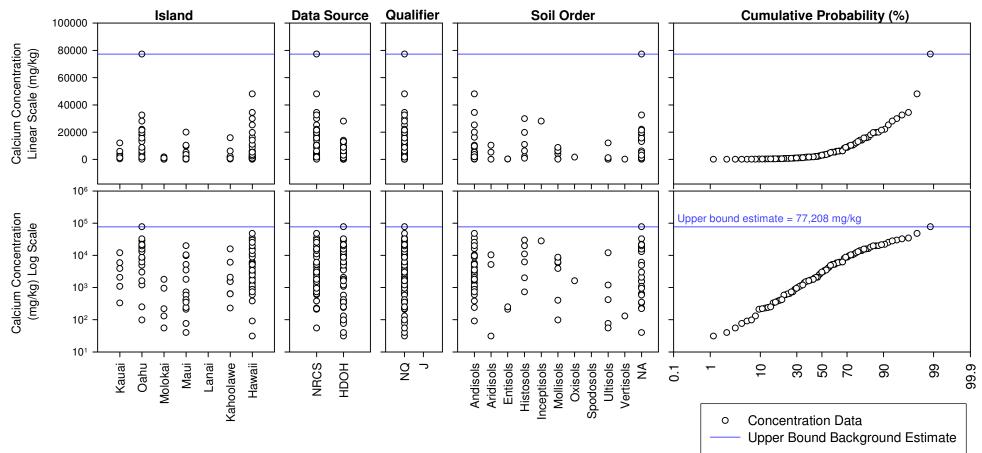


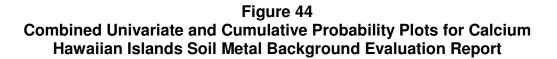


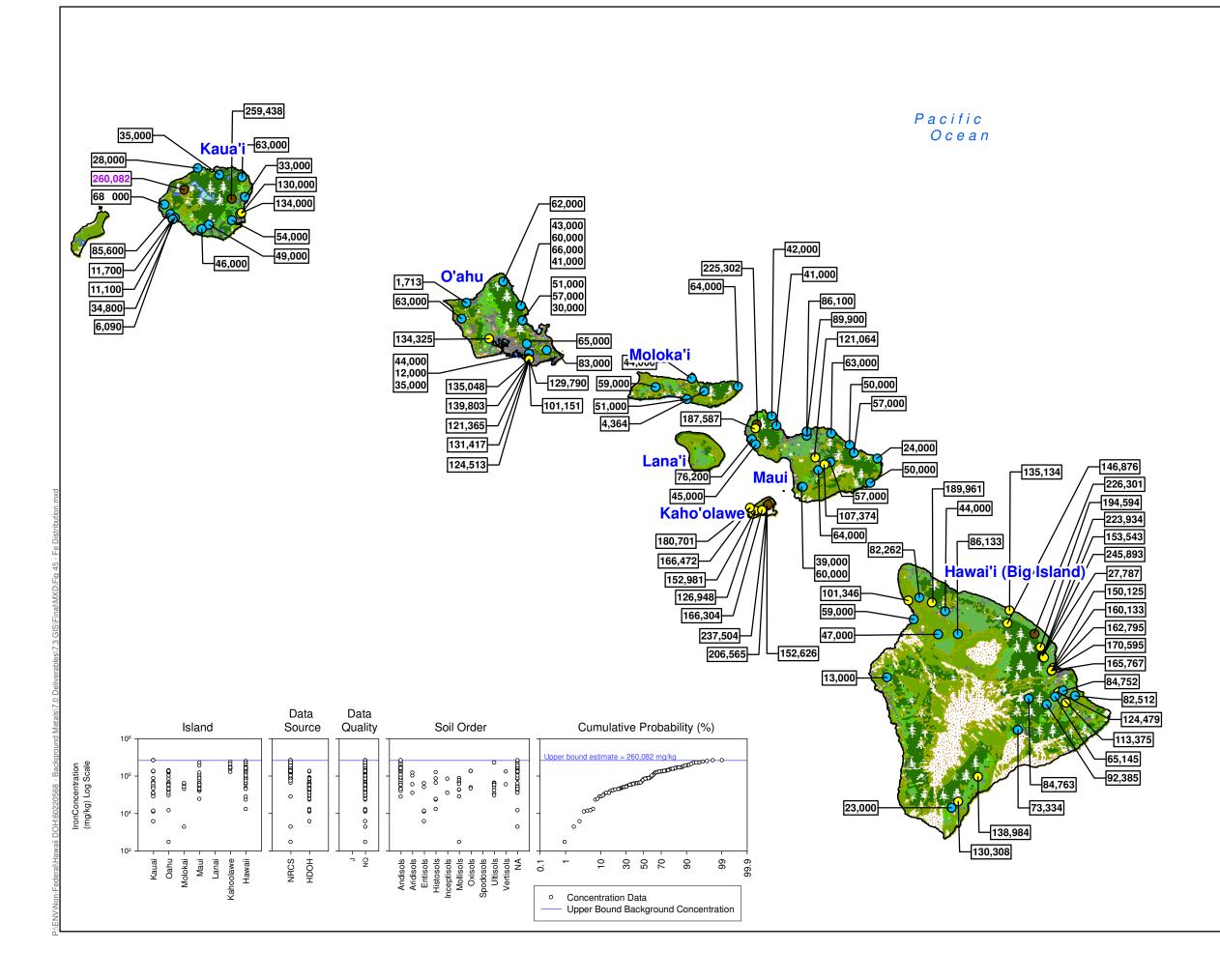


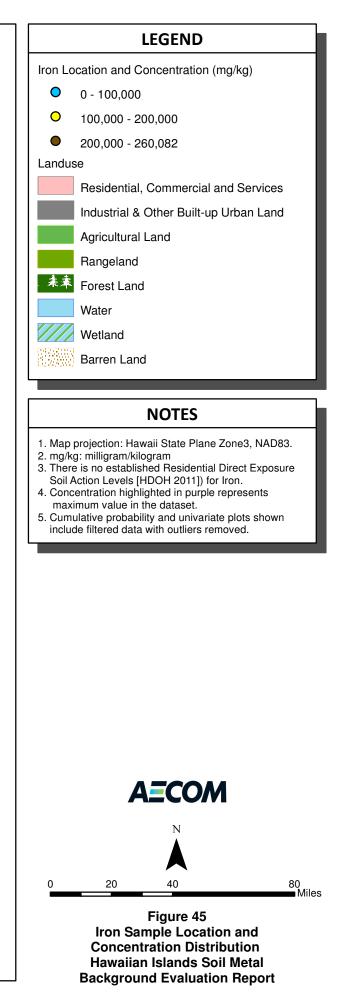
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

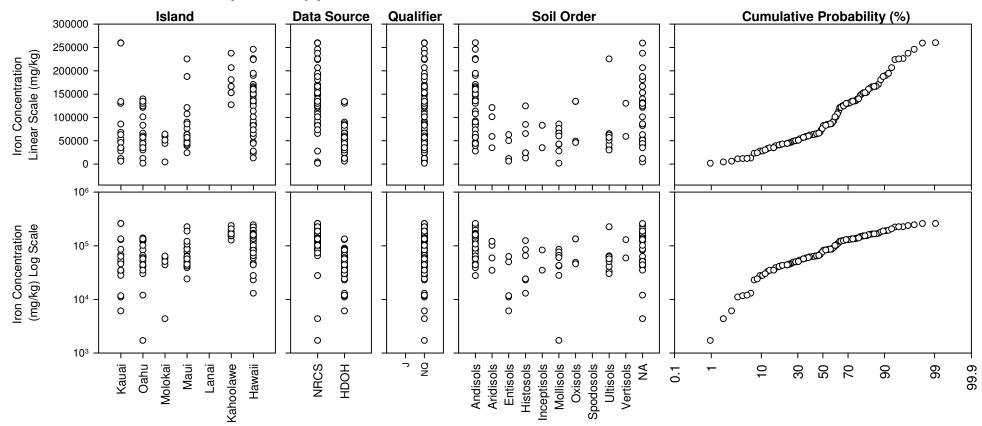




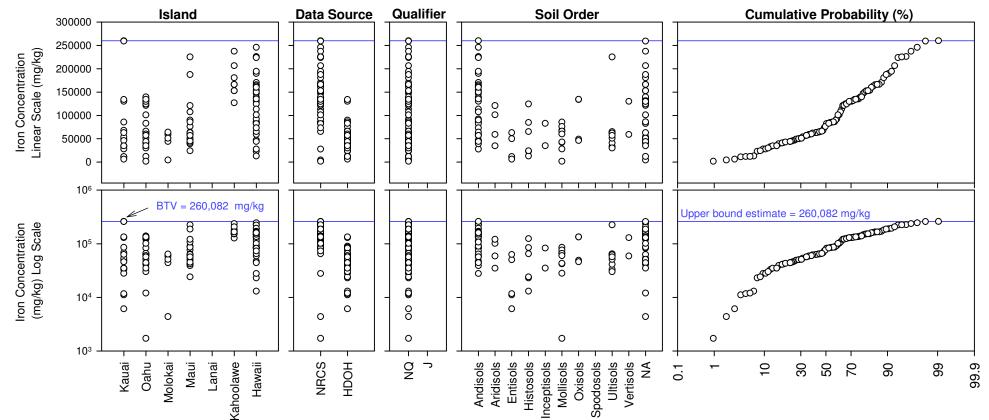








b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

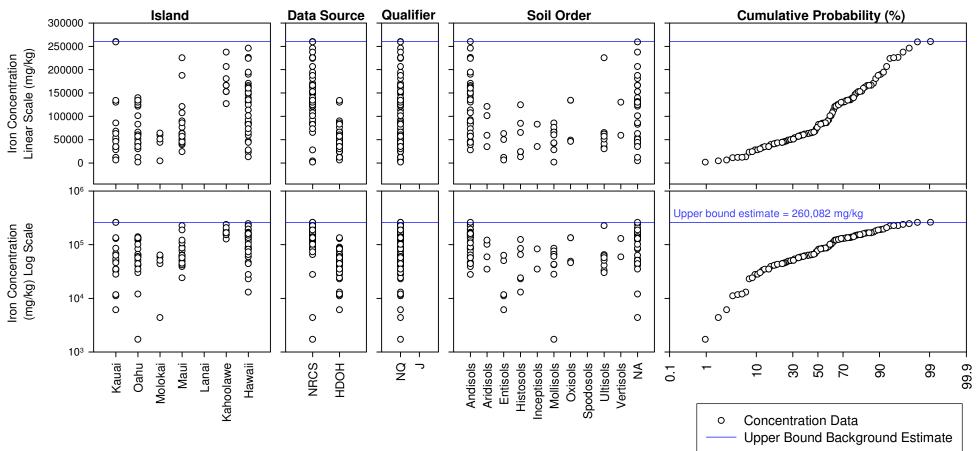
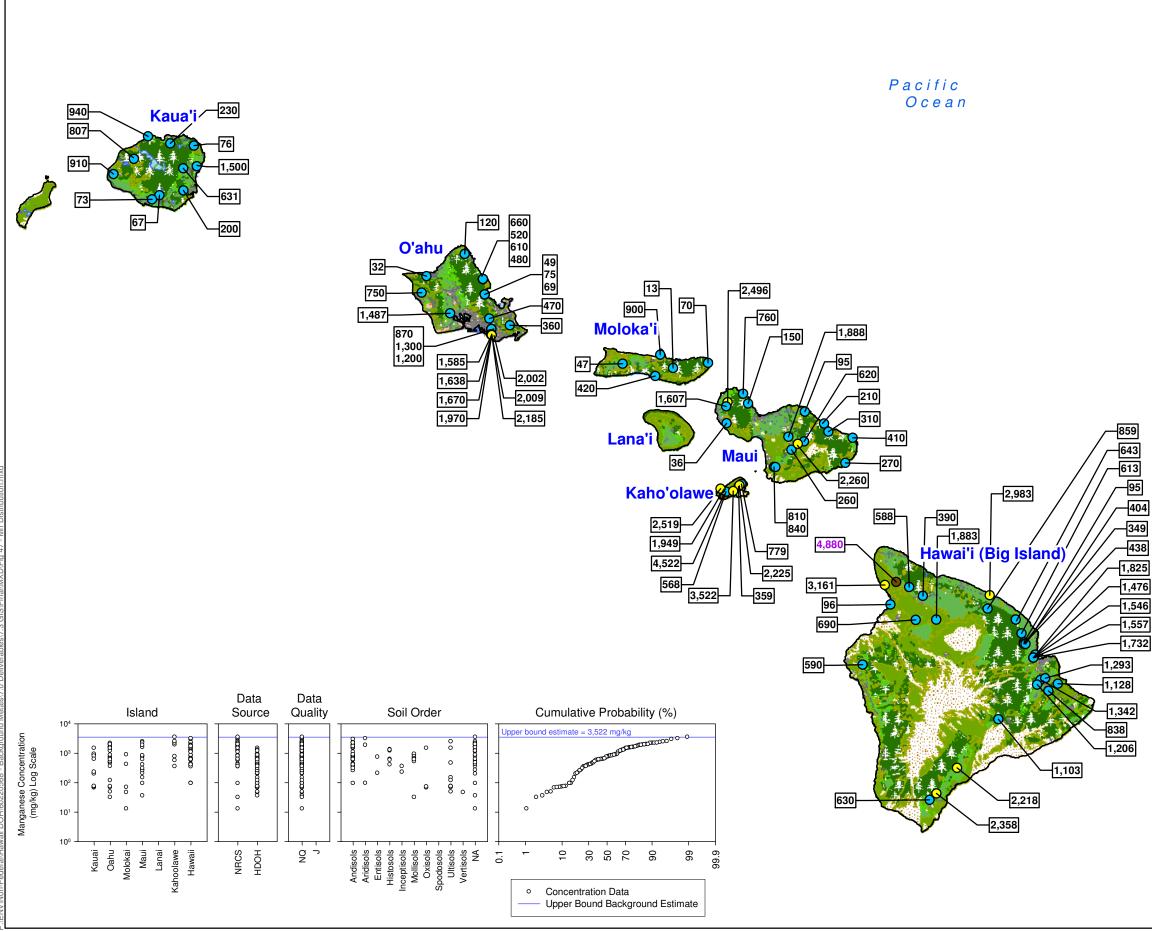
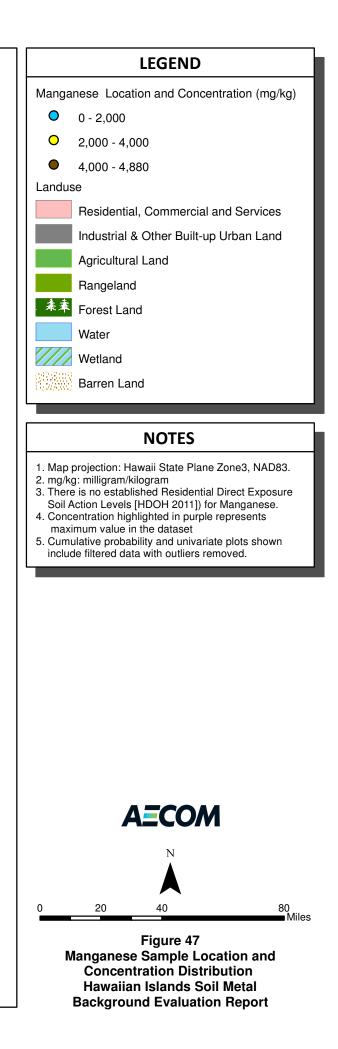
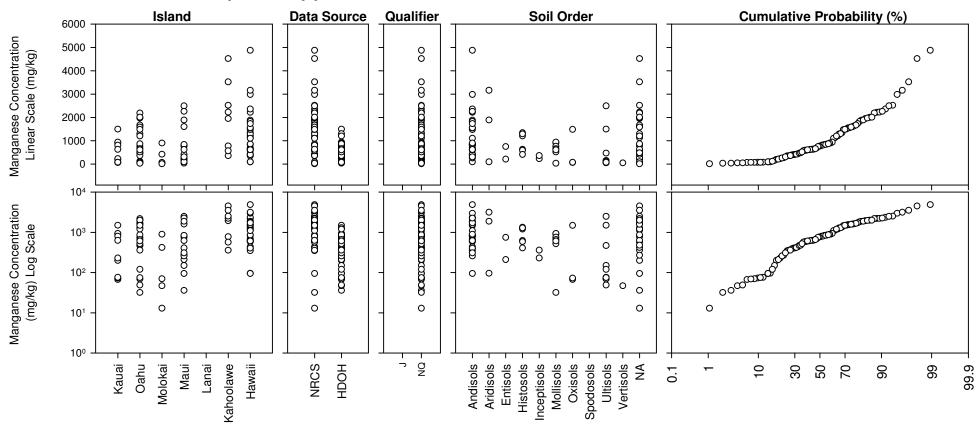


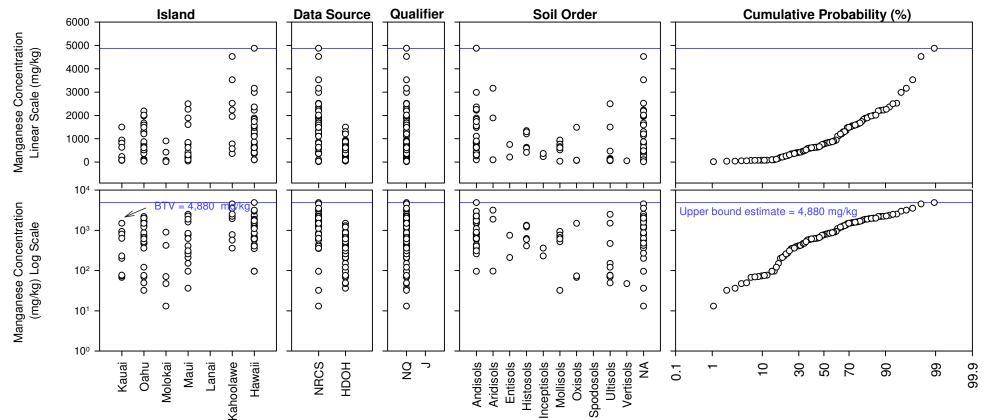
Figure 46 Combined Univariate and Cumulative Probability Plots for Iron Hawaiian Islands Soil Metal Background Evaluation Report

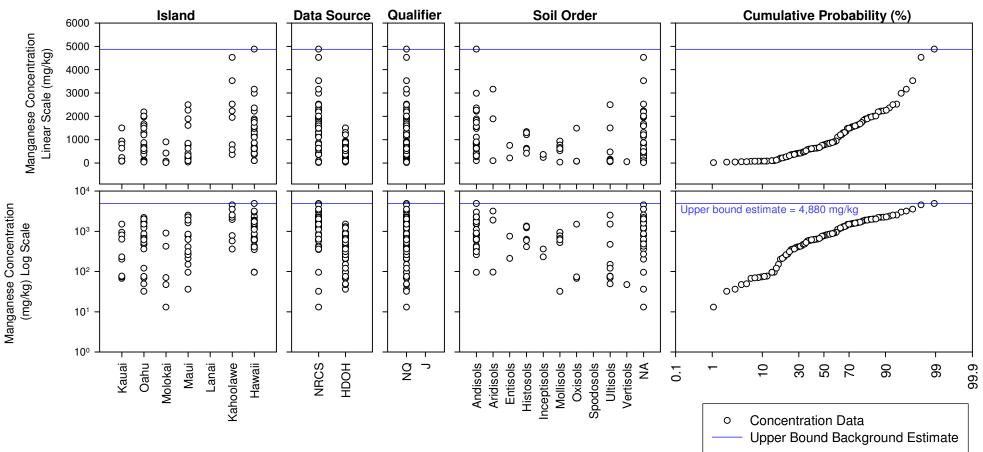


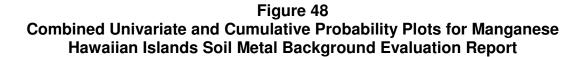


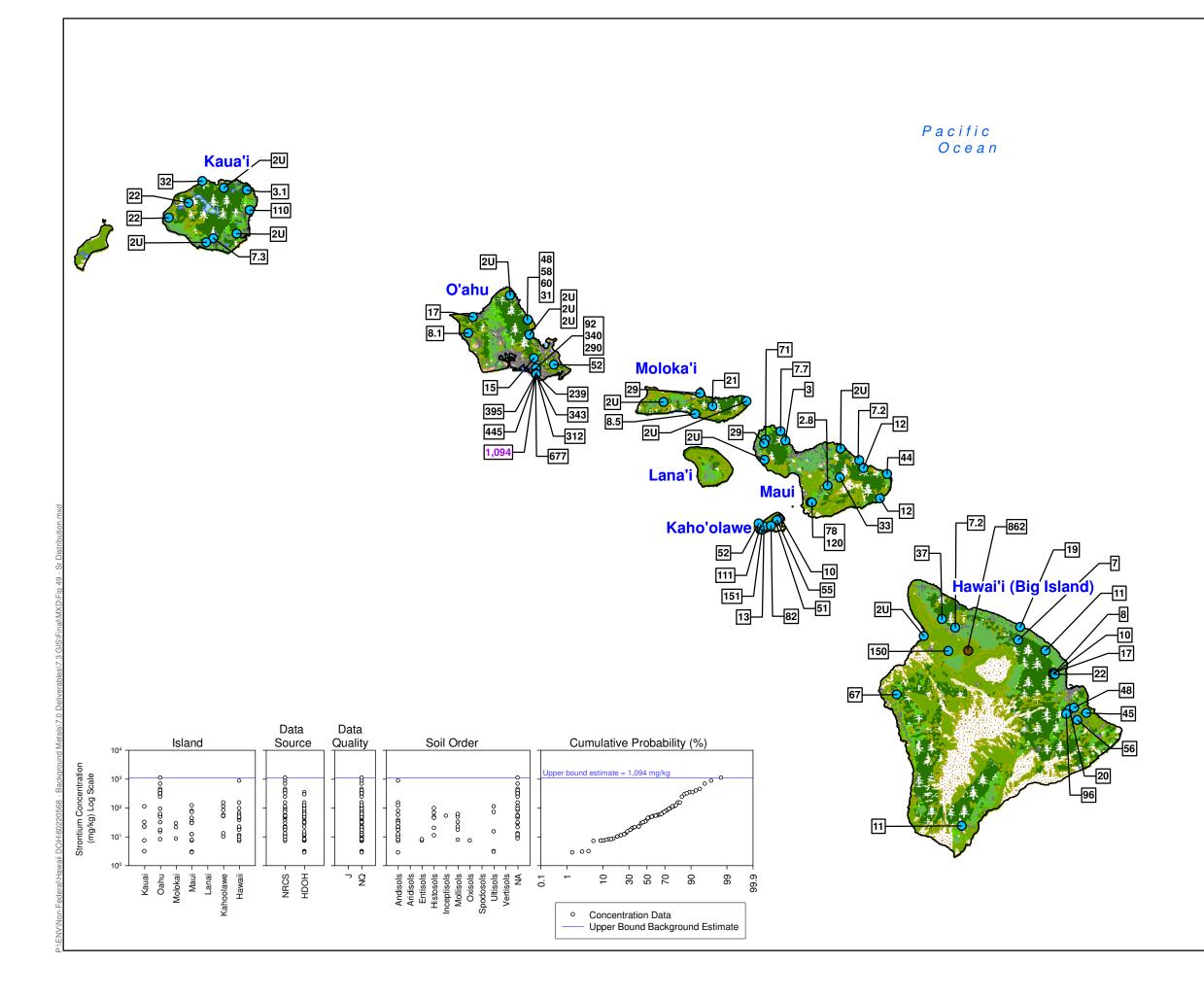


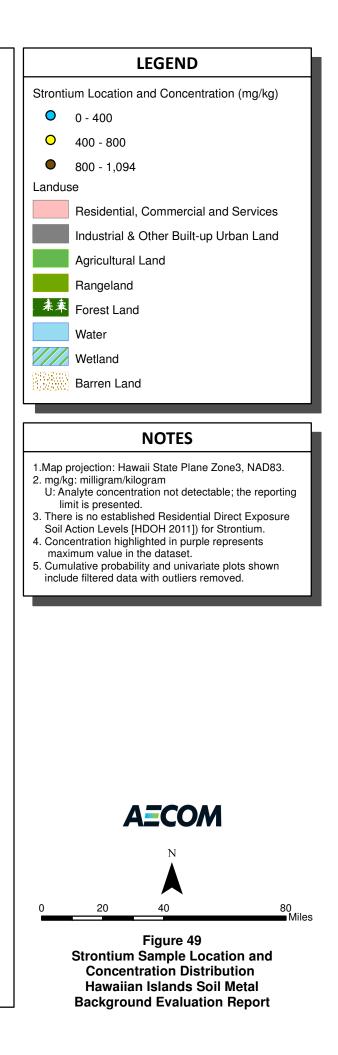
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

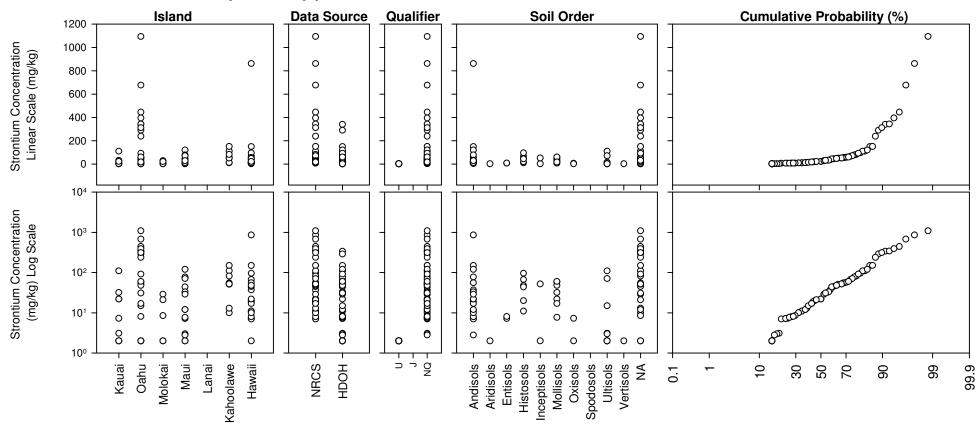




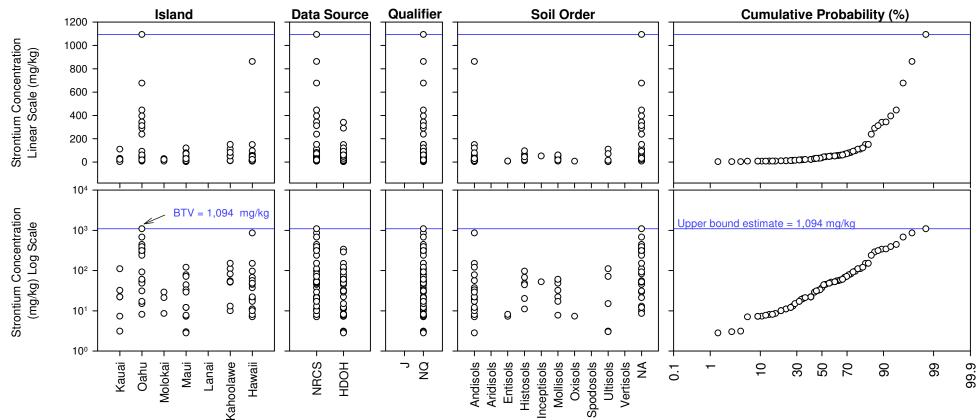








b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

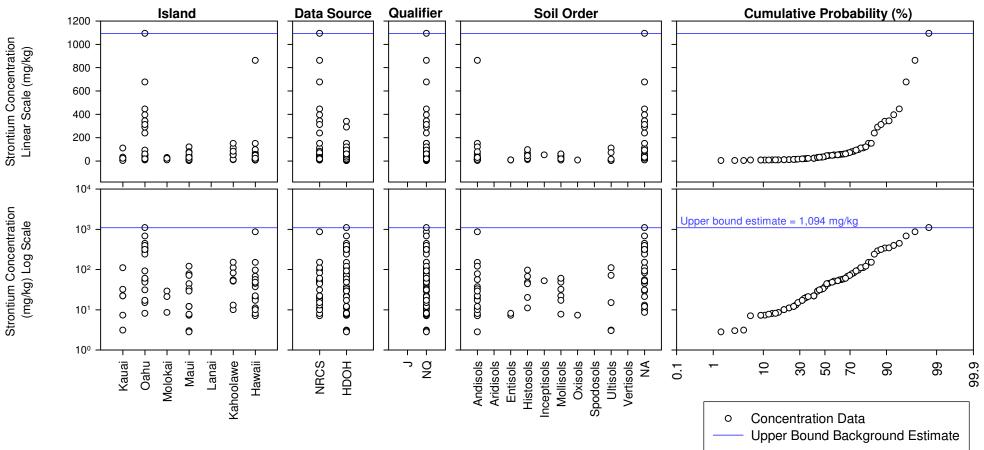
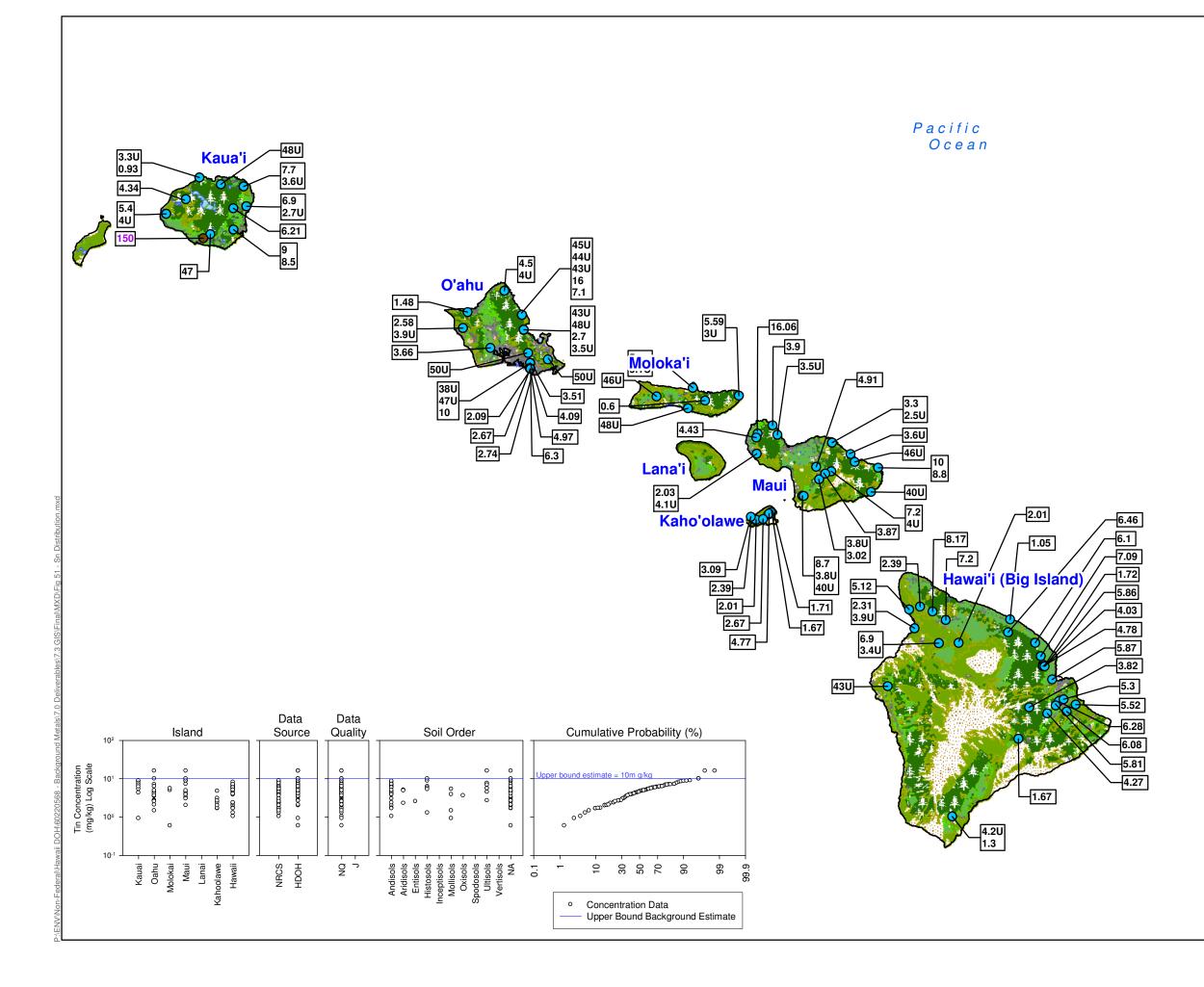
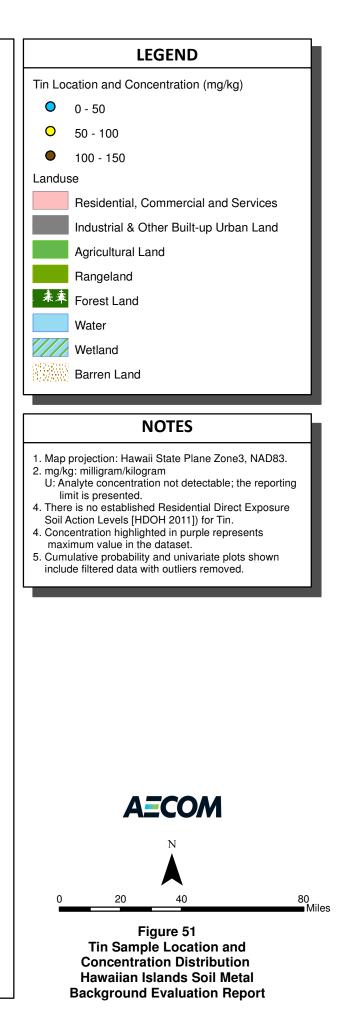
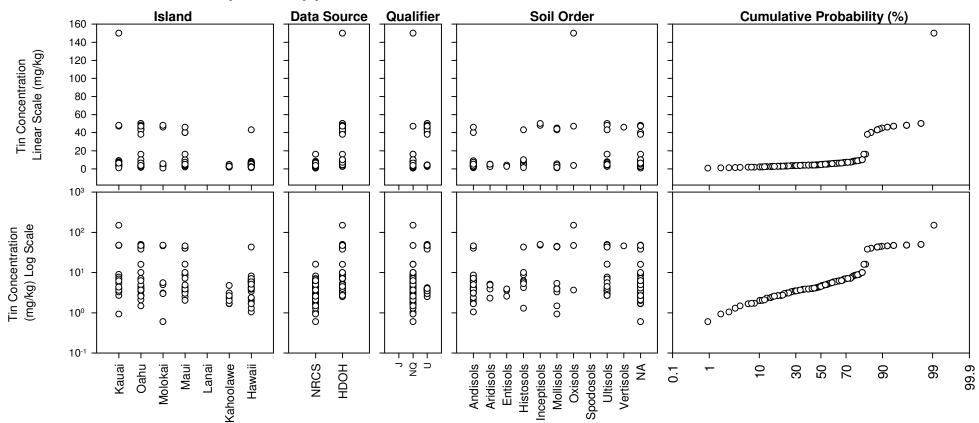




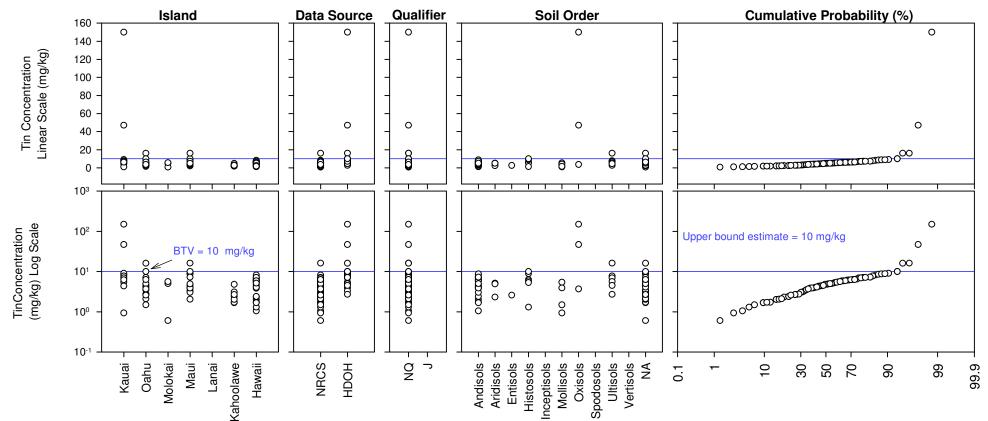
Figure 50 **Combined Univariate and Cumulative Probability Plots for Strontium** Hawaiian Islands Soil Metal Background Evaluation Report







b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

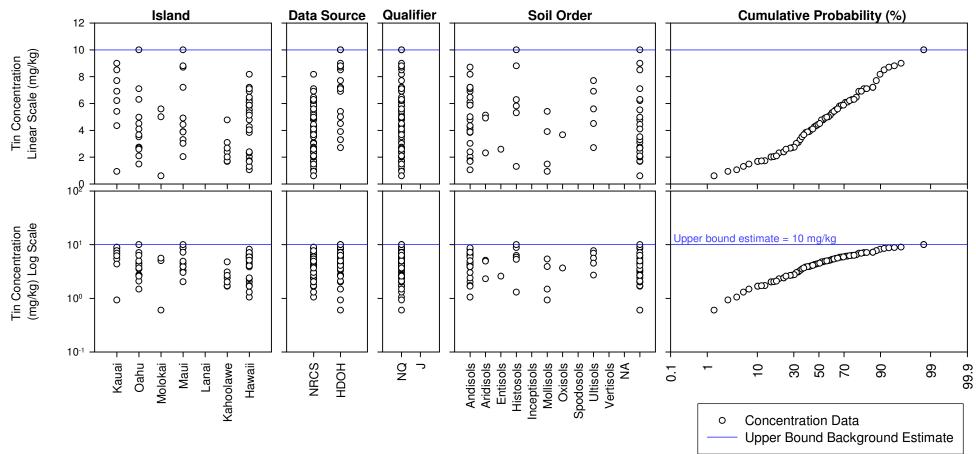
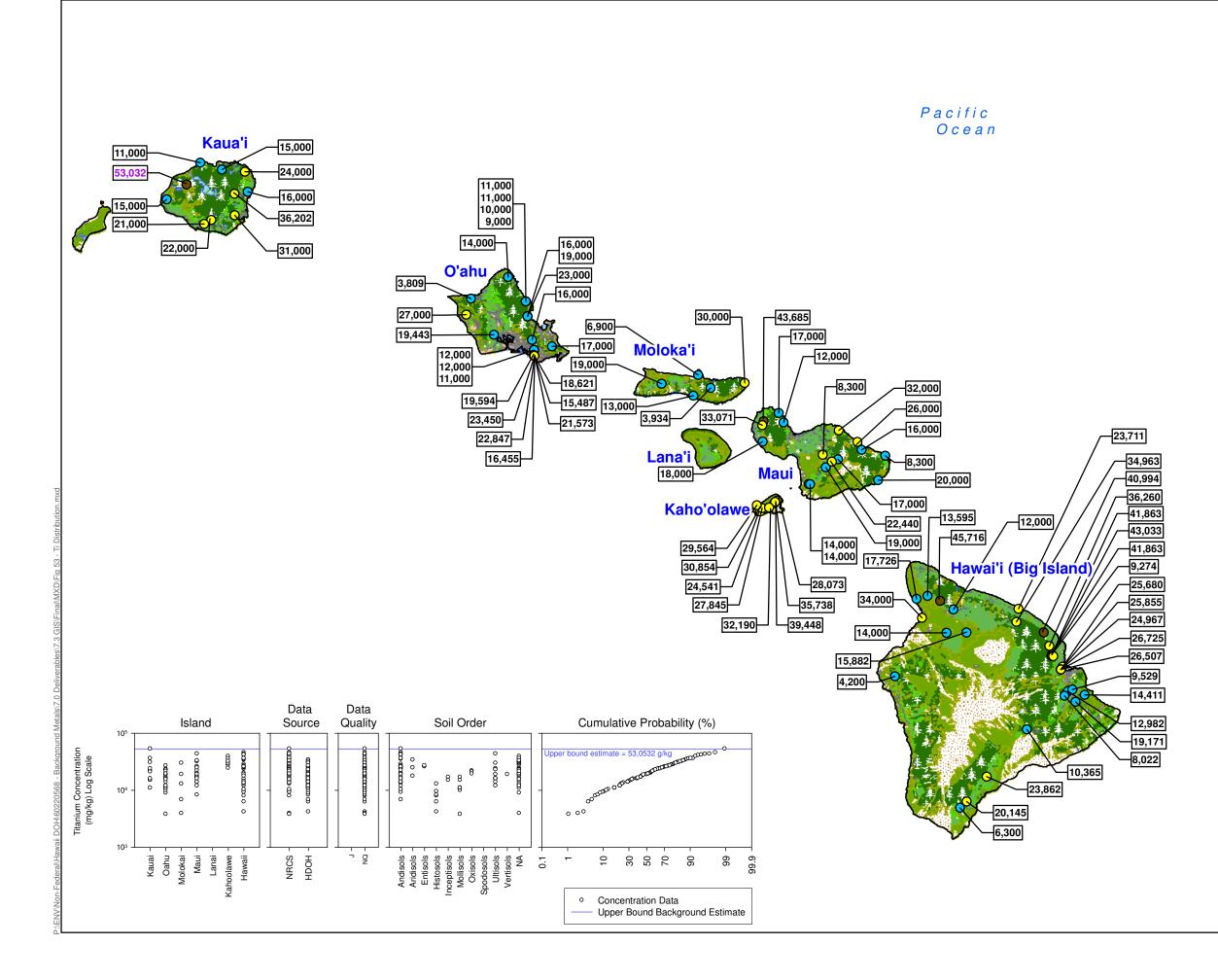
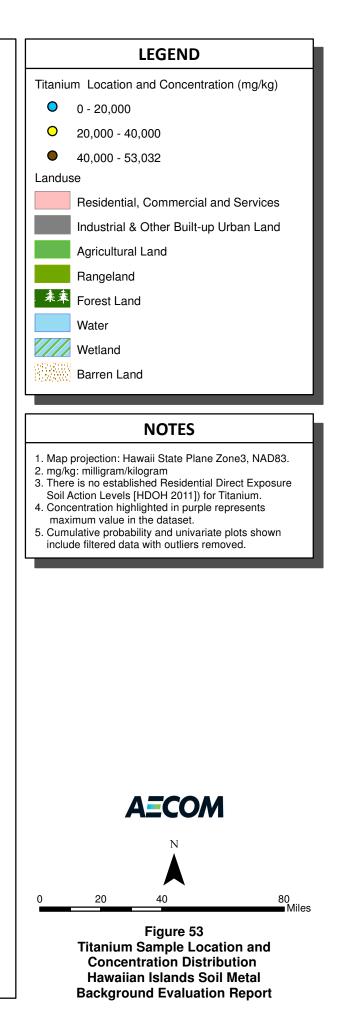
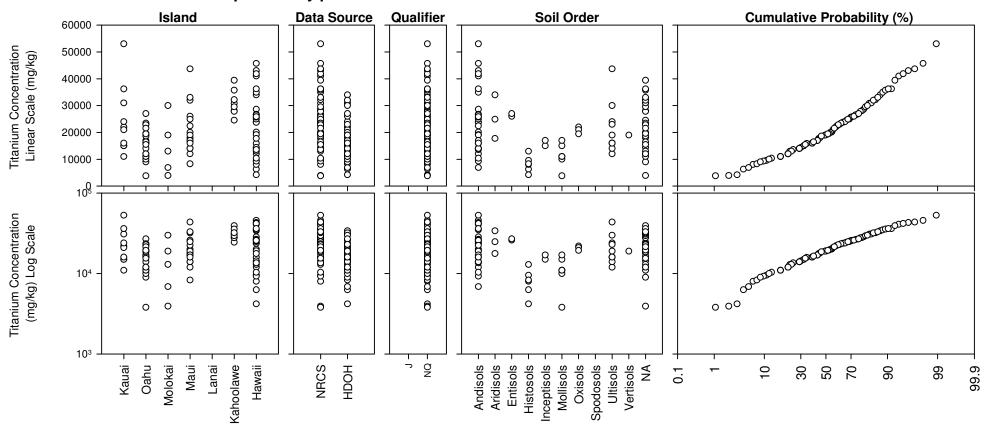


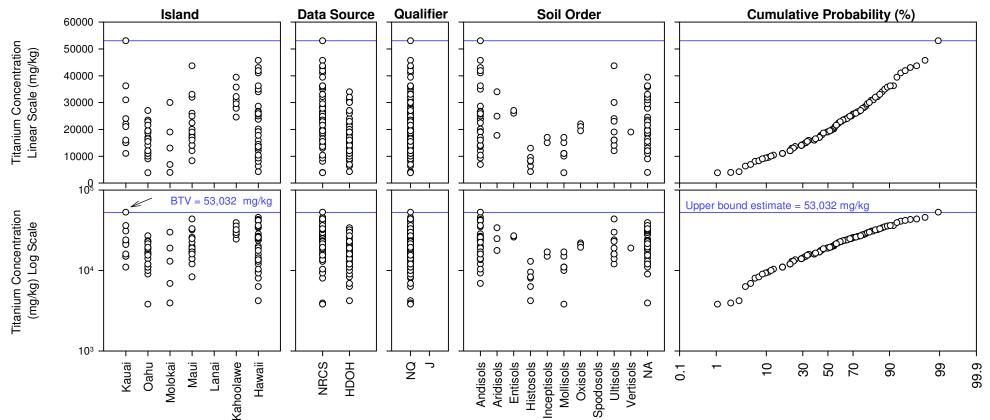
Figure 52 Combined Univariate and Cumulative Probability Plots for Tin Hawaiian Islands Soil Metal Background Evaluation Report

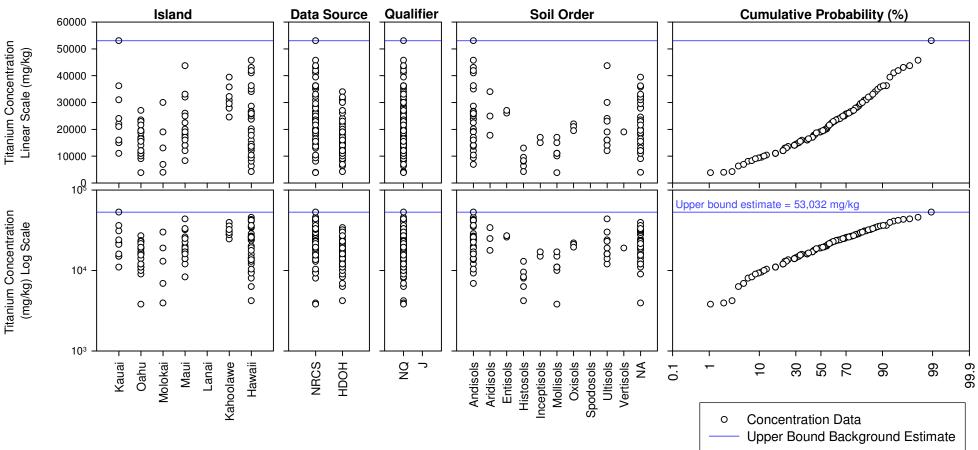


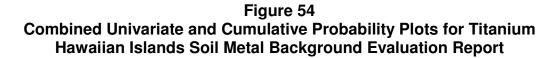


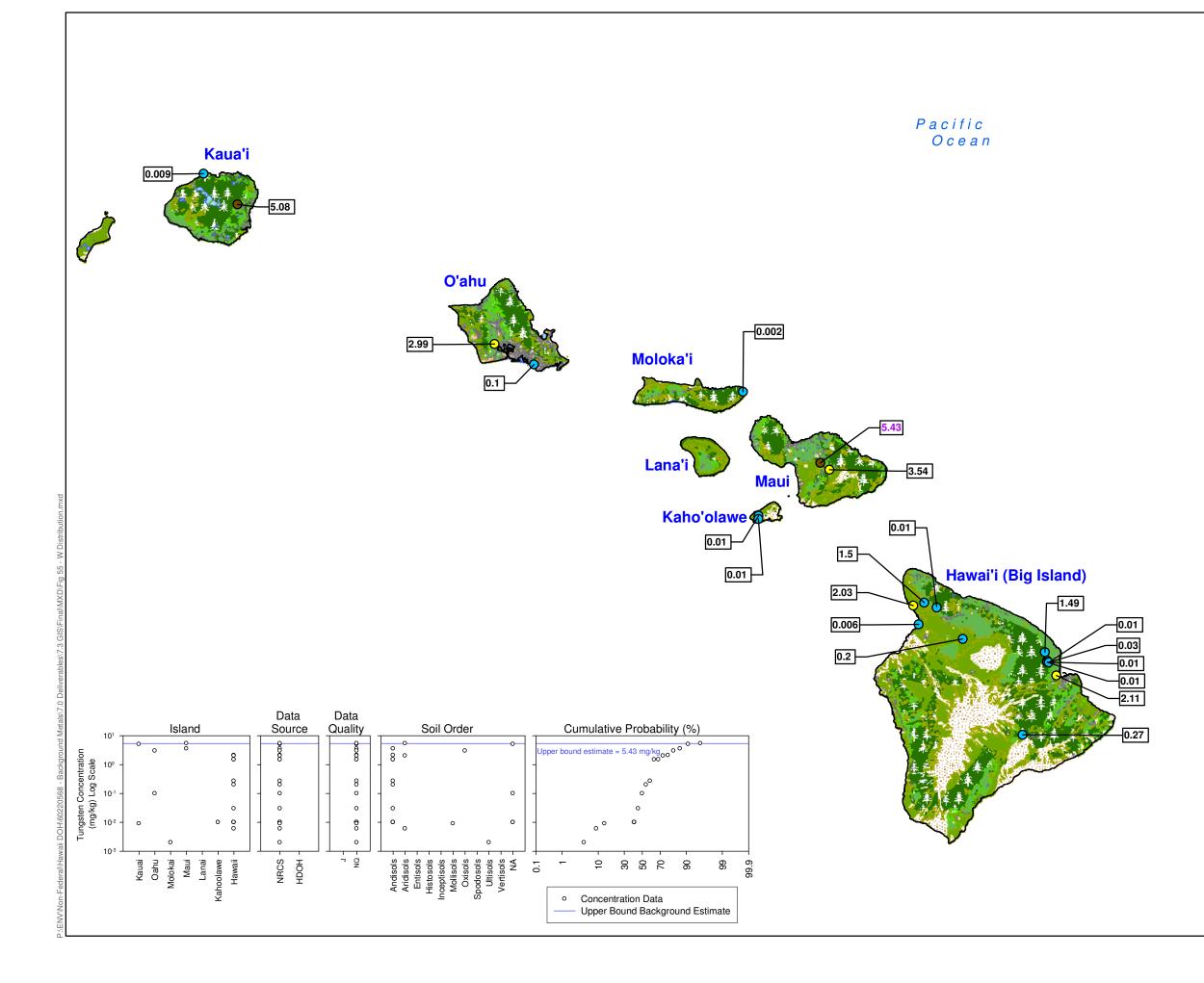


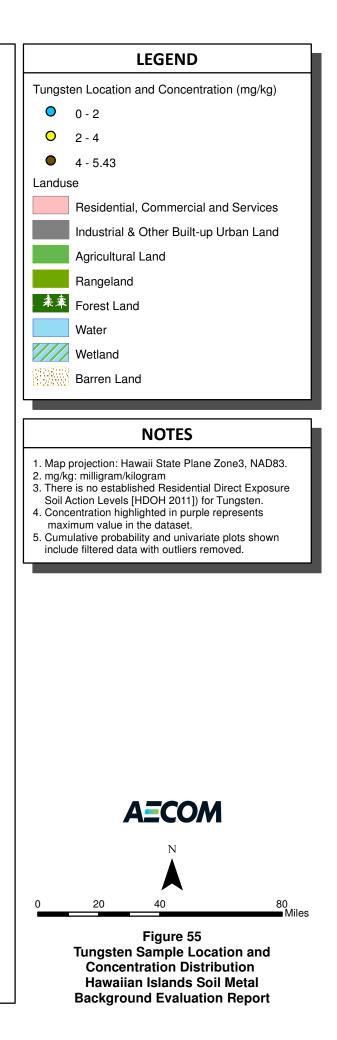
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

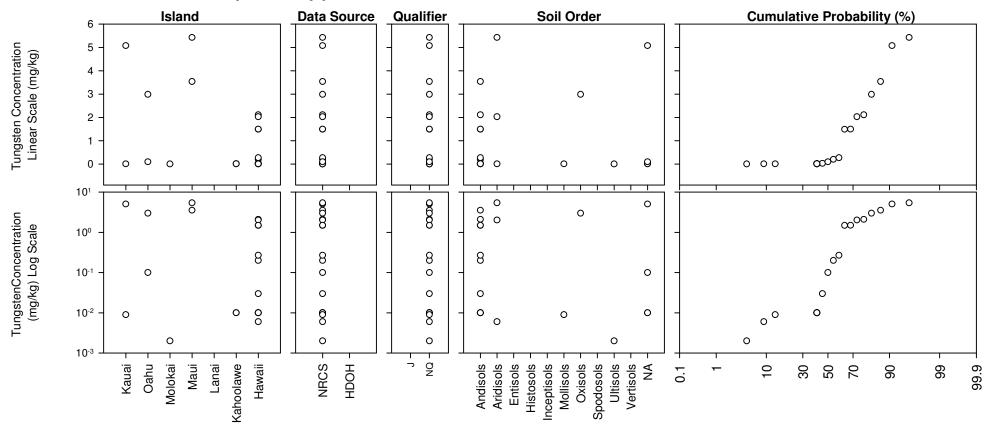




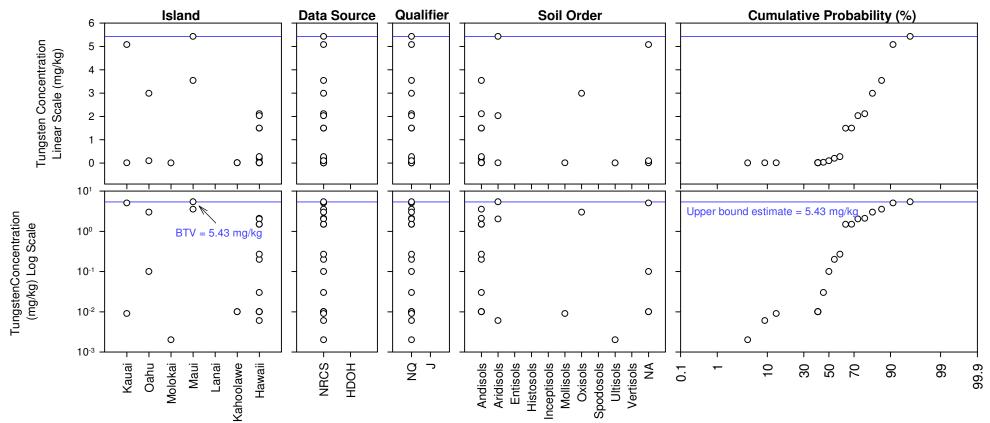








b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

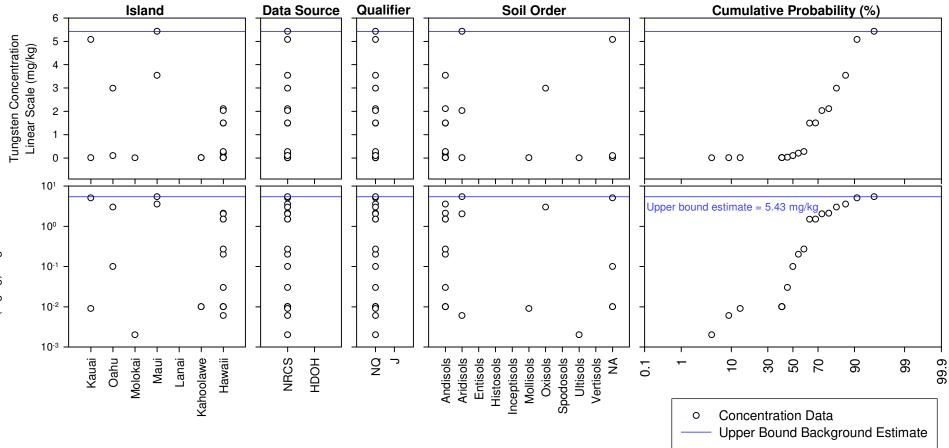
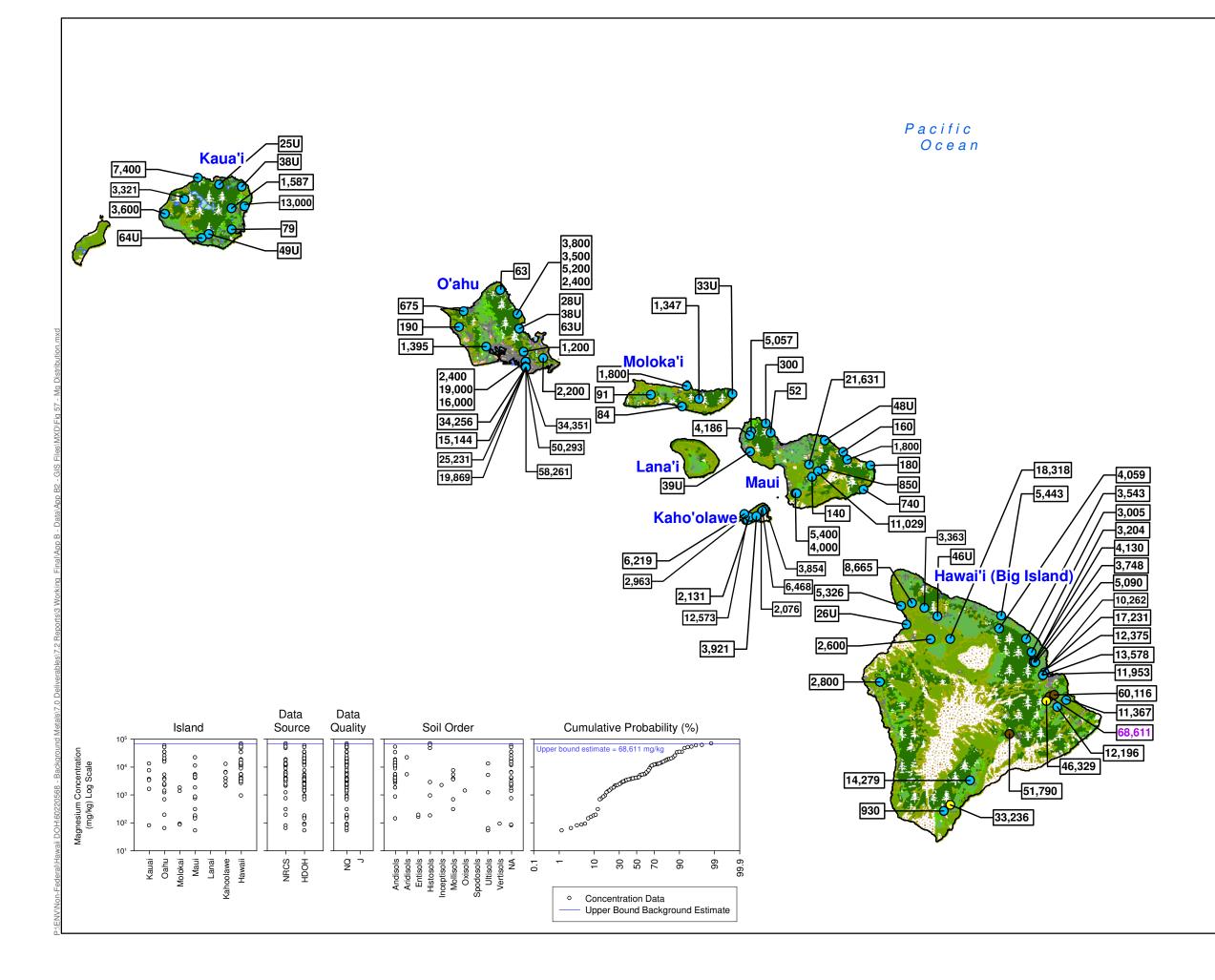
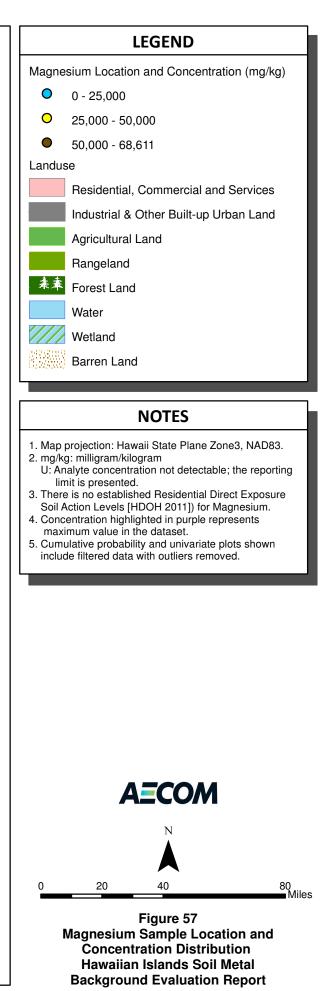
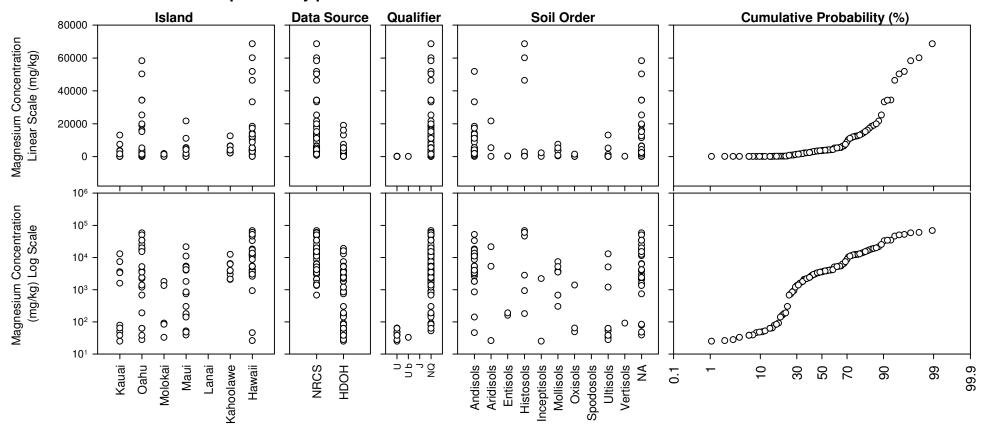




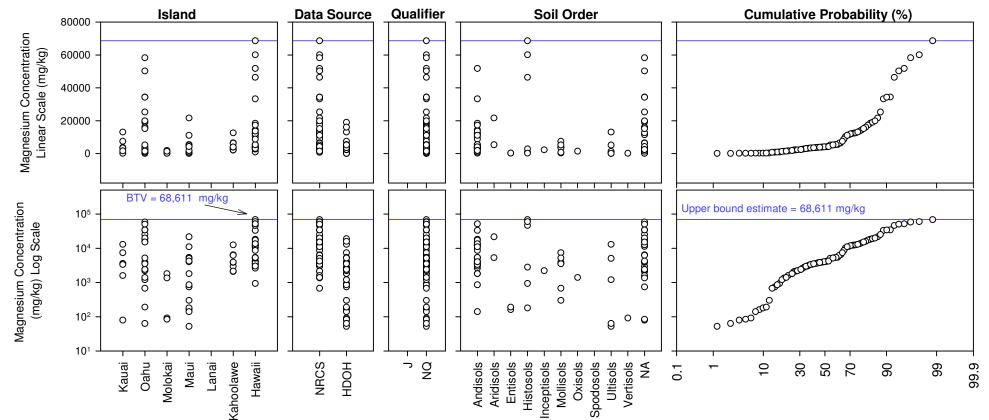
Figure 56 Combined Univariate and Cumulative Probability Plots for Tungsten Hawaiian Islands Soil Metal Background Evaluation Report

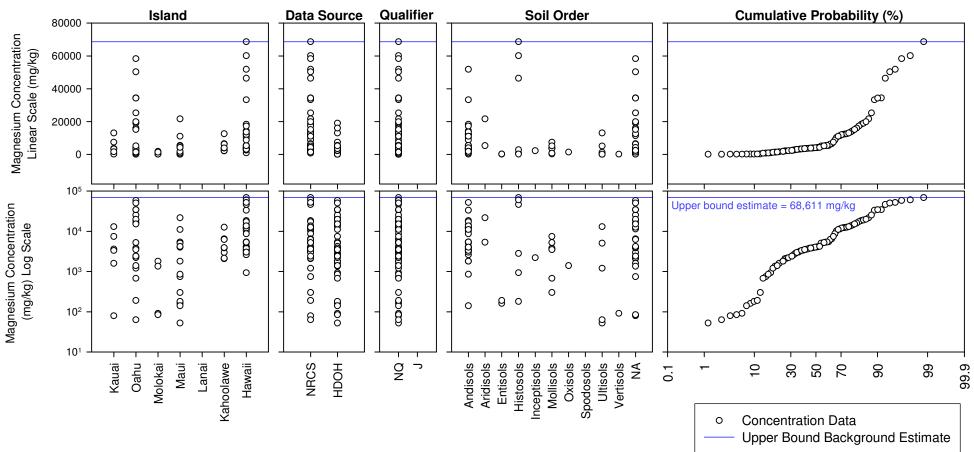


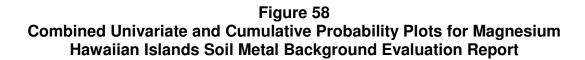


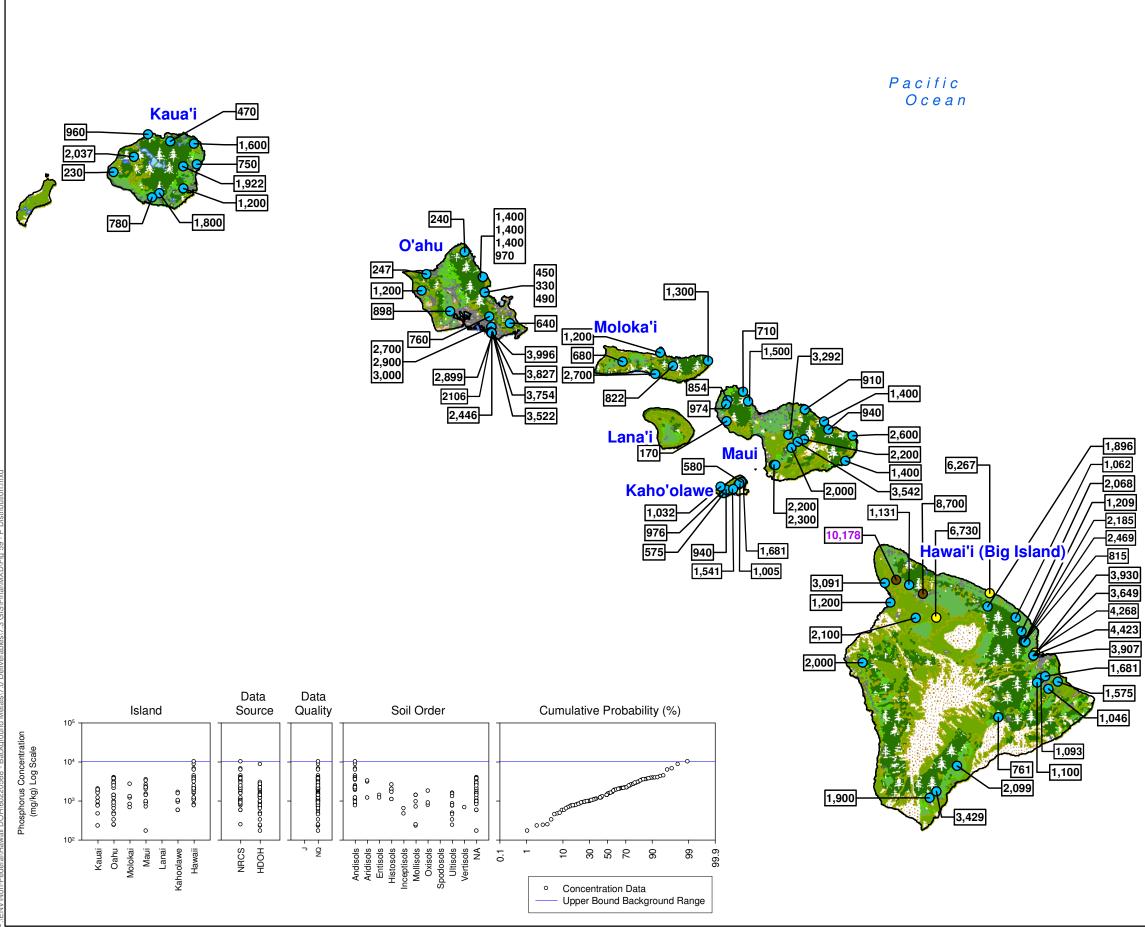


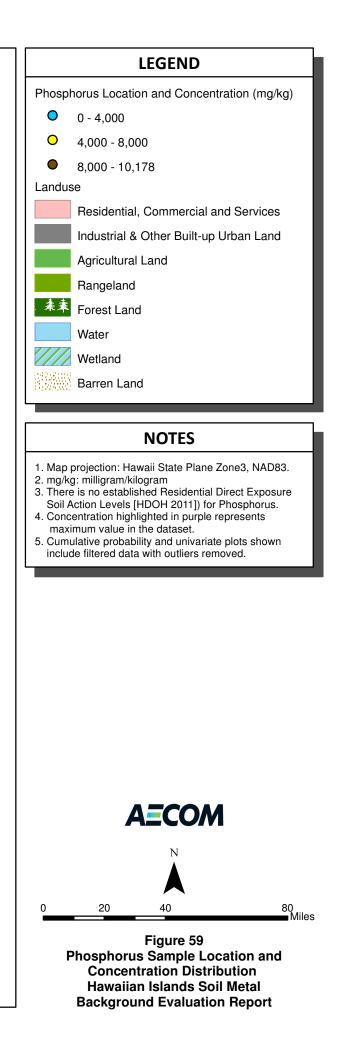
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

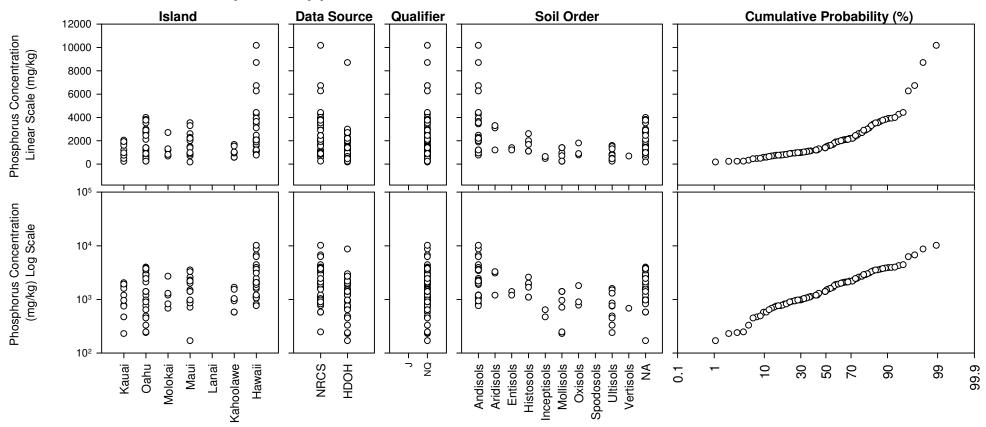






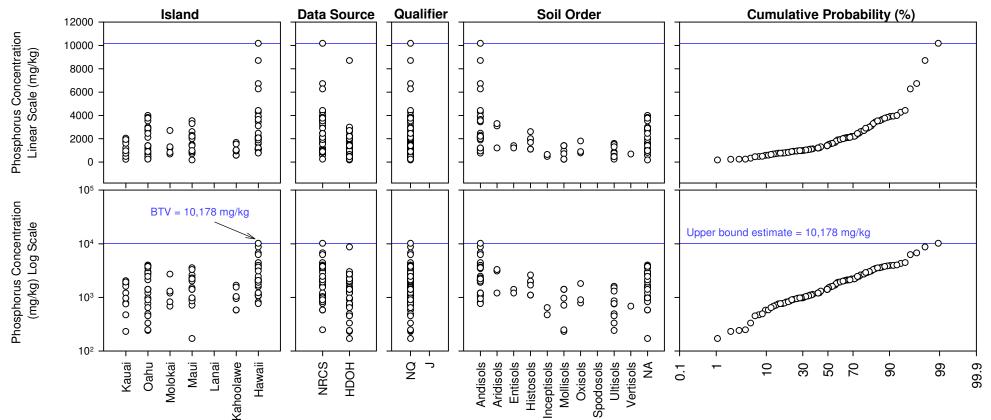






a. Combined univariate and probability plots - all data included.

b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

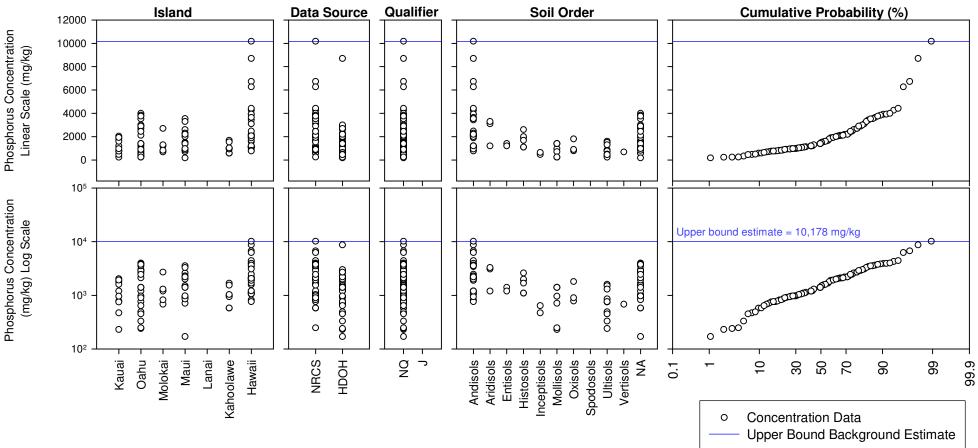
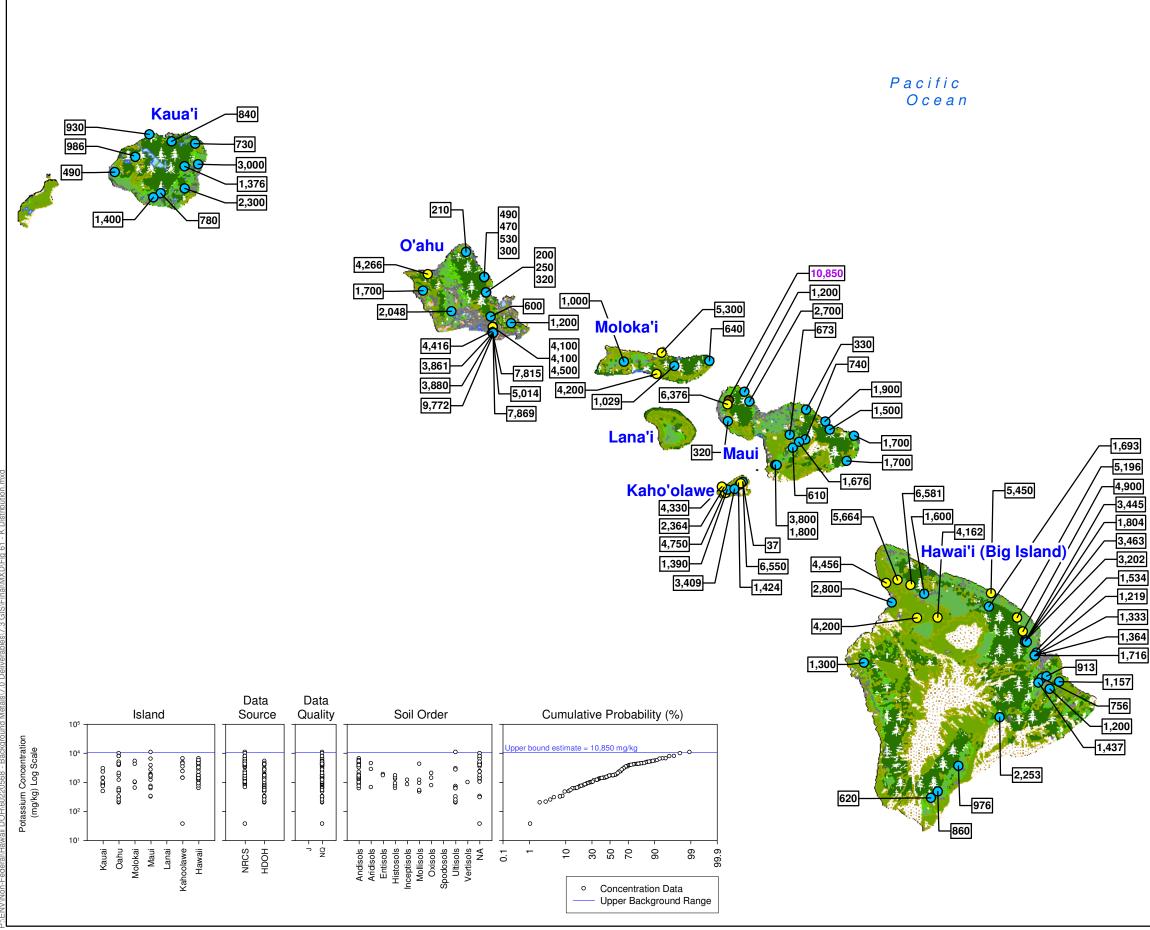
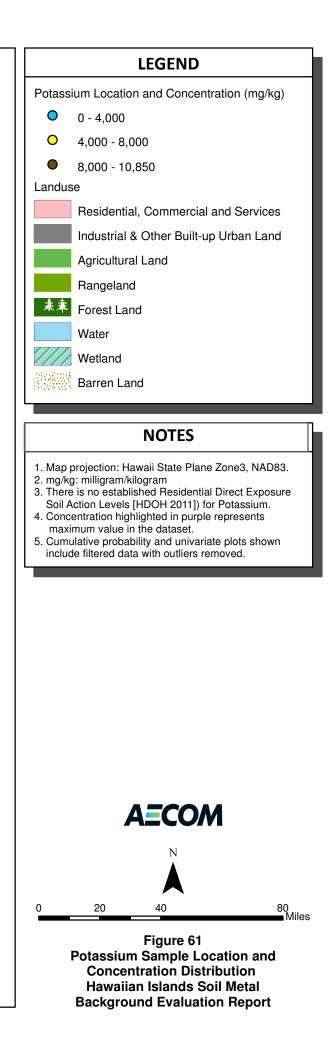
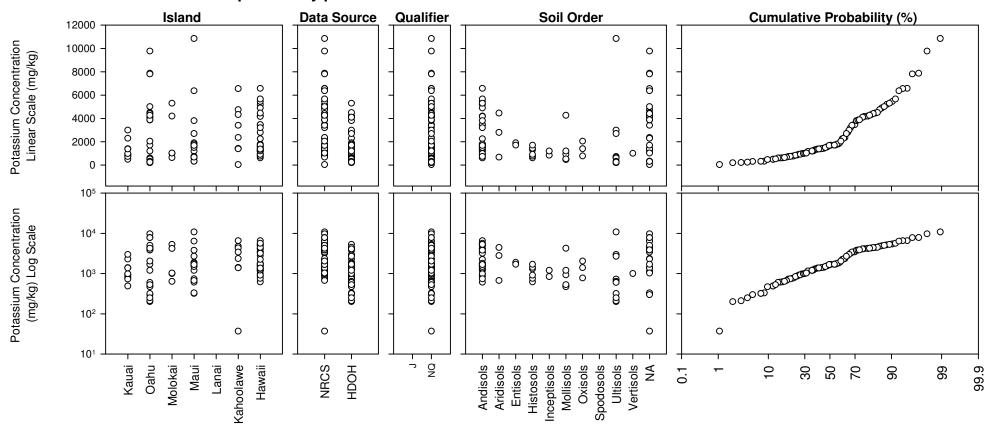




Figure 60 **Combined Univariate and Cumulative Probability Plots for Phosphorus** Hawaiian Islands Soil Metal Background Evaluation Report

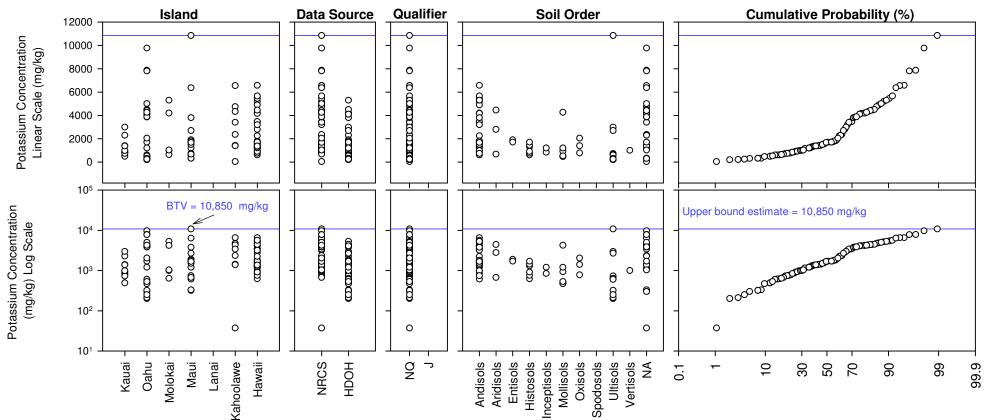




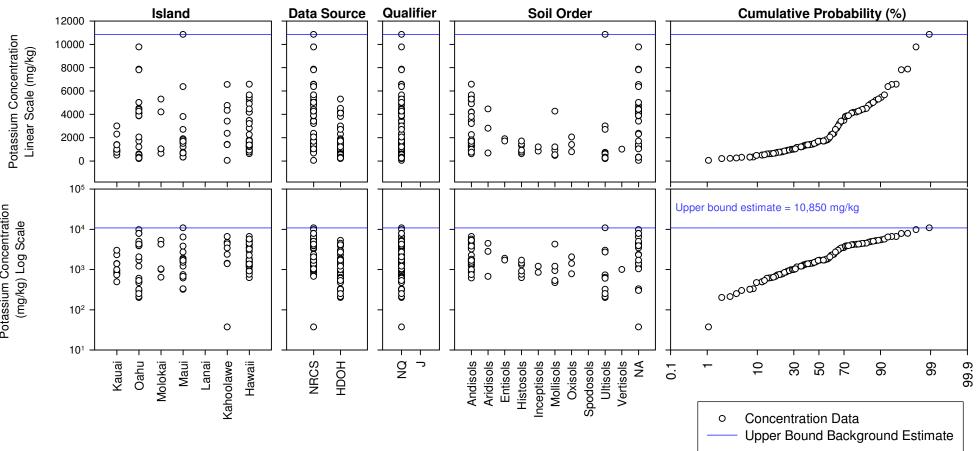


a. Combined univariate and probability plots - all data included.

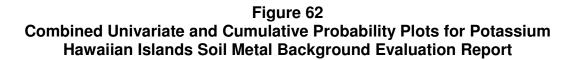
b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)

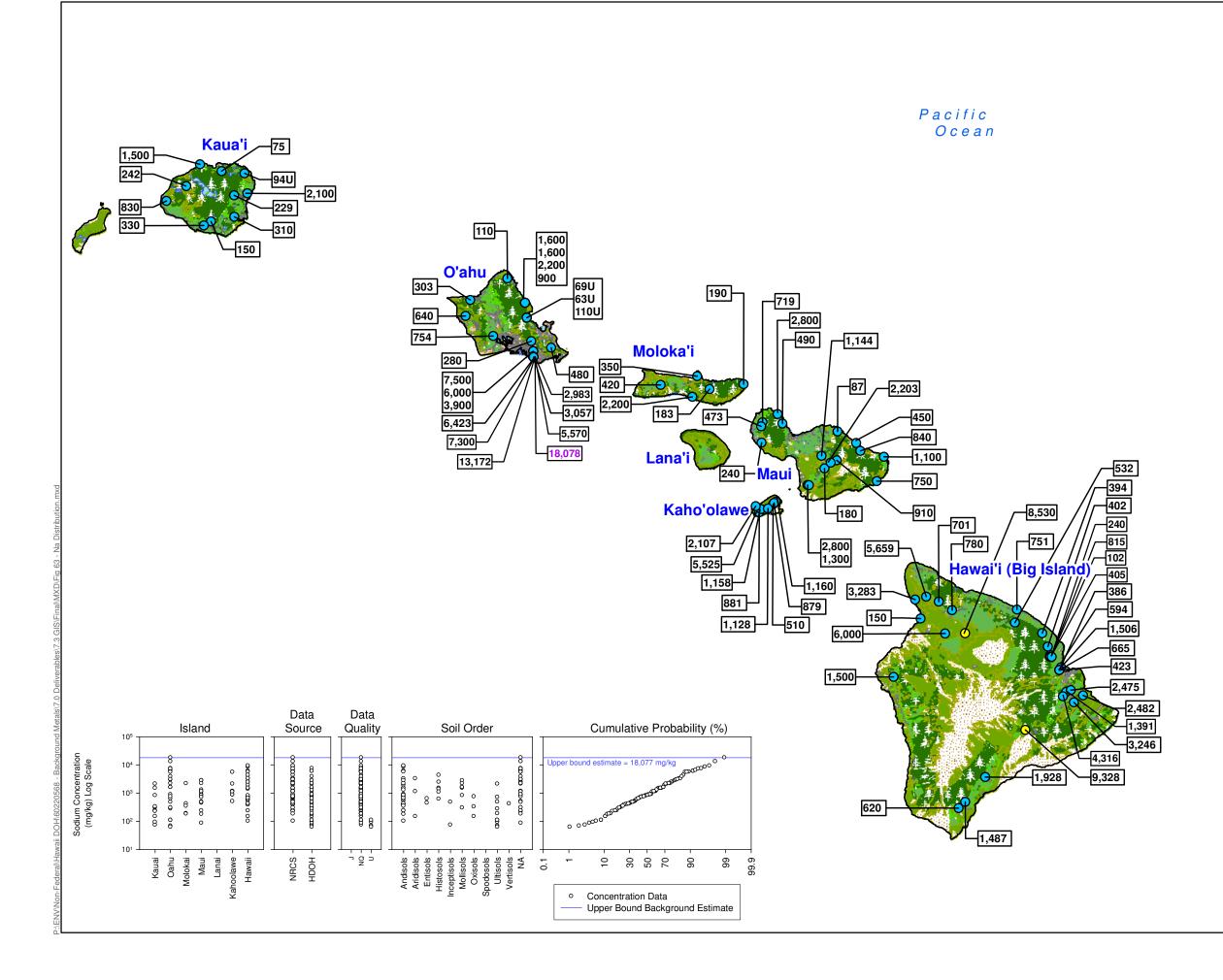


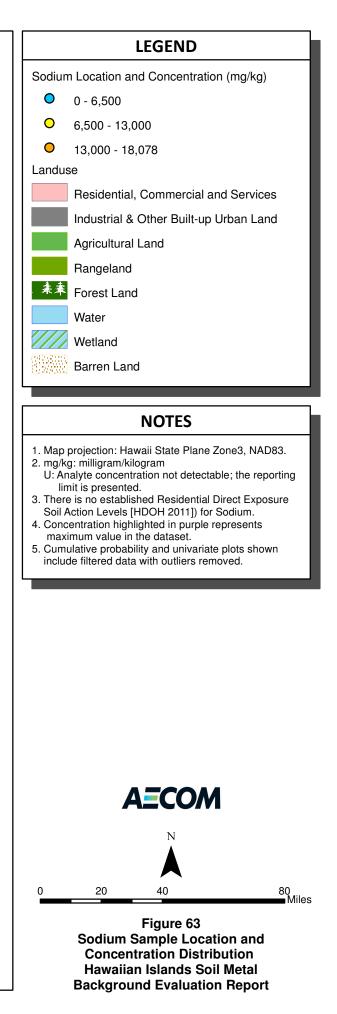
c. Combined univariate and probability plots - filtered data and outliers removed

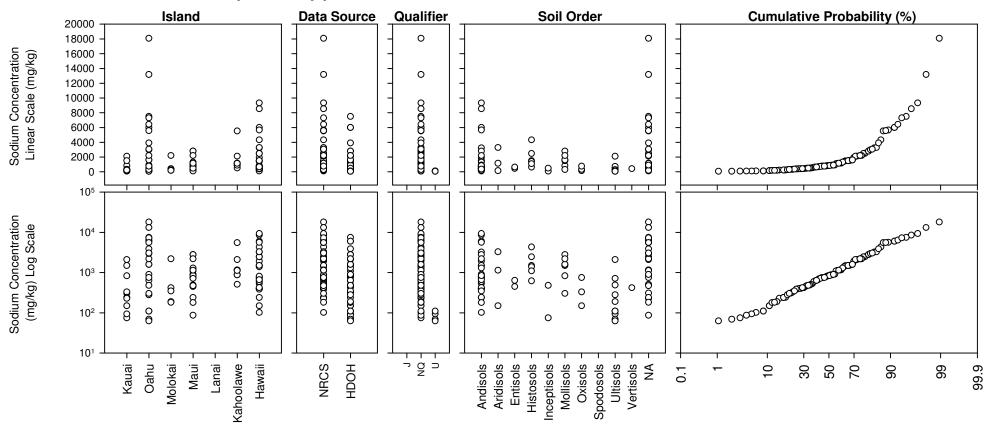






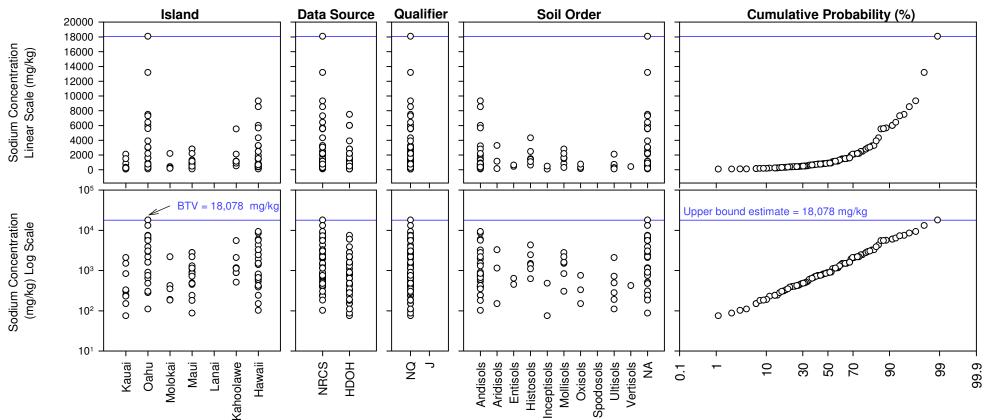






a. Combined univariate and probability plots - all data included.

b. Combined univariate and probability plots - filtered data (non-qualified and J-flagged data only, outliers retained)



c. Combined univariate and probability plots - filtered data and outliers removed

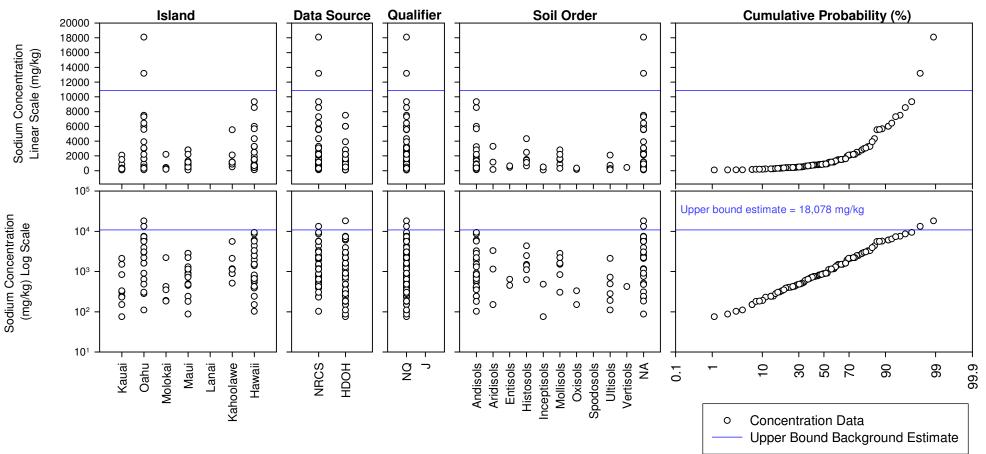
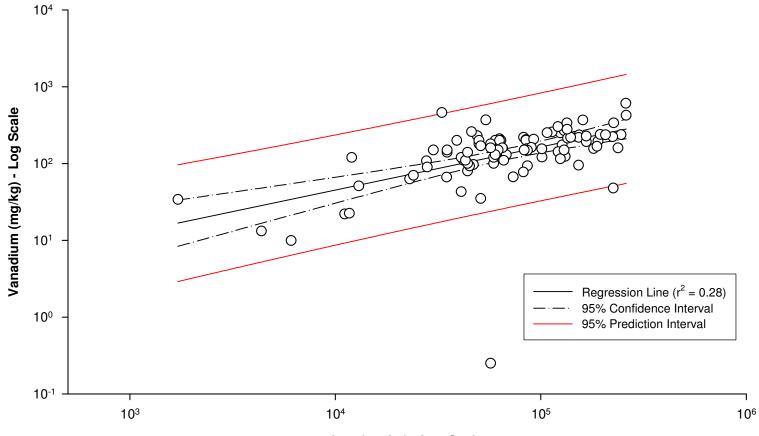
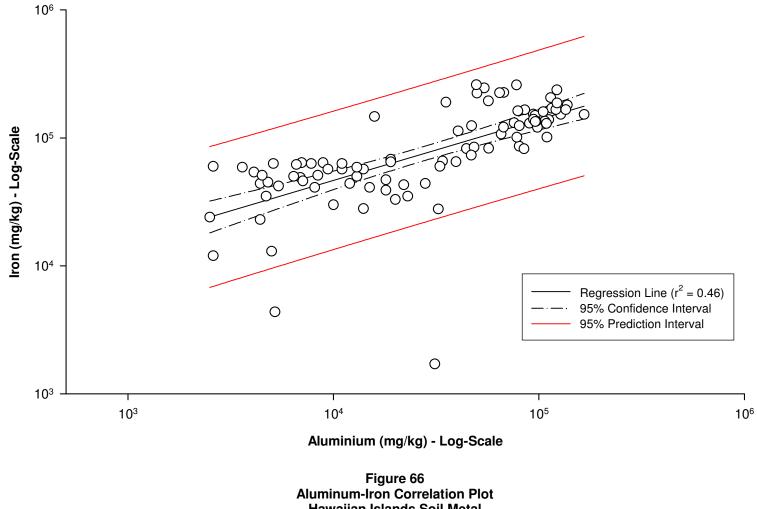


Figure 64 Combined Univariate and Cumulative Probability Plots for Sodium Hawaiian Islands Soil Metal Background Evaluation Report

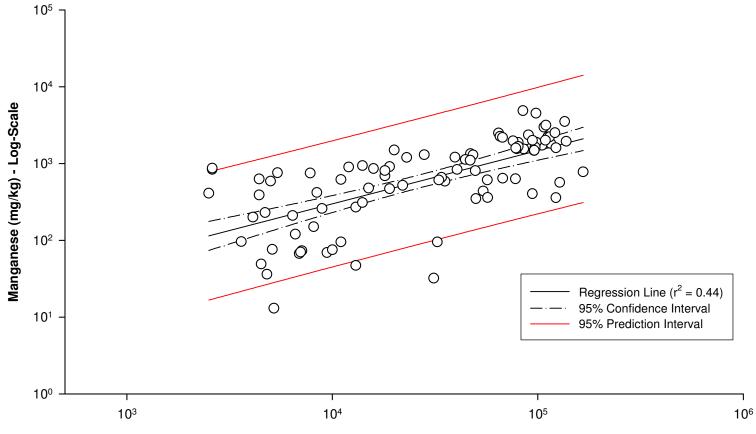


Iron (mg/kg) - Log Scale

Figure 65 Iron-Vanadium Correlation Plot Hawaiian Islands Soil Metal Background Evaluation Report

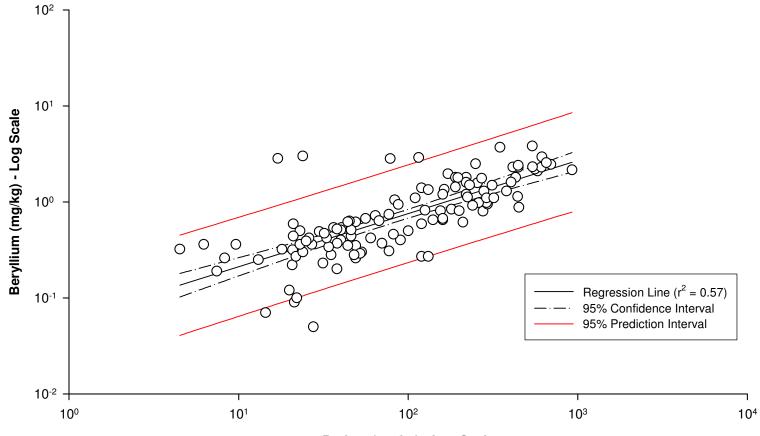


Hawaiian Islands Soil Metal Background Evaluation Report



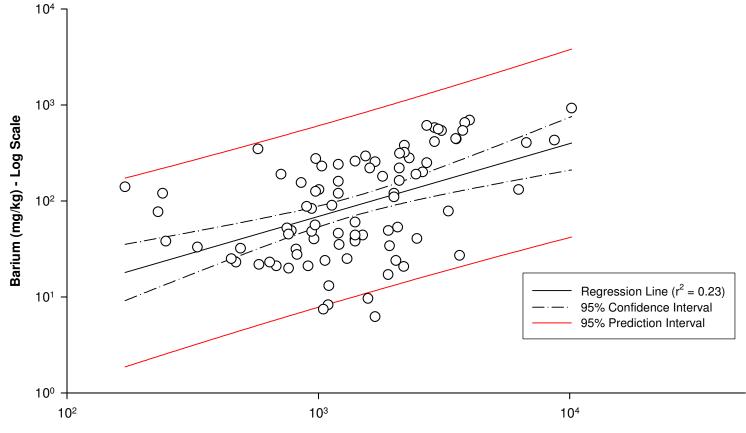
Aluminium (mg/kg) - Log-Scale

Figure 67 Aluminum-Manganese Correlation Plot Hawaiian Islands Soil Metal Background Evaluation Report



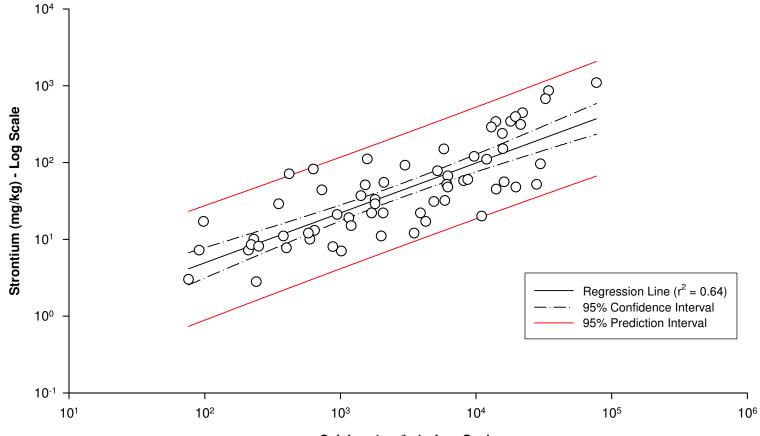
Barium (mg/kg) - Log Scale

Figure 68 Barium-Beryllium Correlation Plot Hawaiian Islands Soil Metal Background Evaluation Report



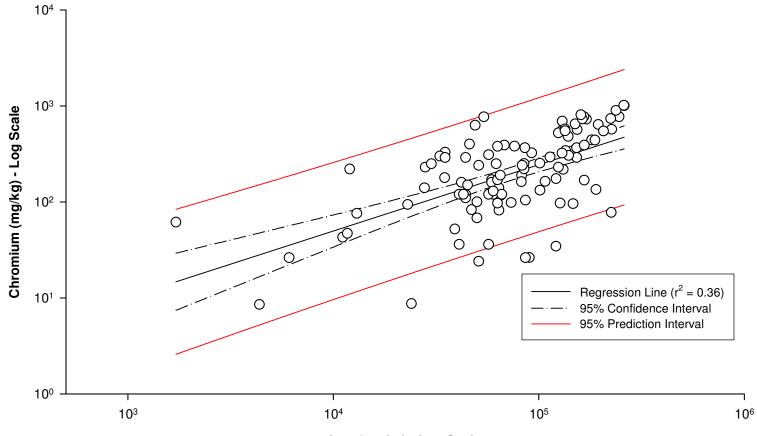
Phosphorus (mg/kg) - Log Scale

Figure 69 Phosphorus-Barium Correlation Plot Hawaiian Islands Soil Metal Background Evaluation Report



Calcium (mg/kg) - Log Scale

Figure 70 Calcium-Strontium Correlation Plot Hawaiian Islands Soil Metal Background Evaluation Report



Iron (mg/kg) - Log Scale

Figure 71 Iron-Chromium Correlation Plot Hawaiian Islands Soil Metal Background Evaluation Report

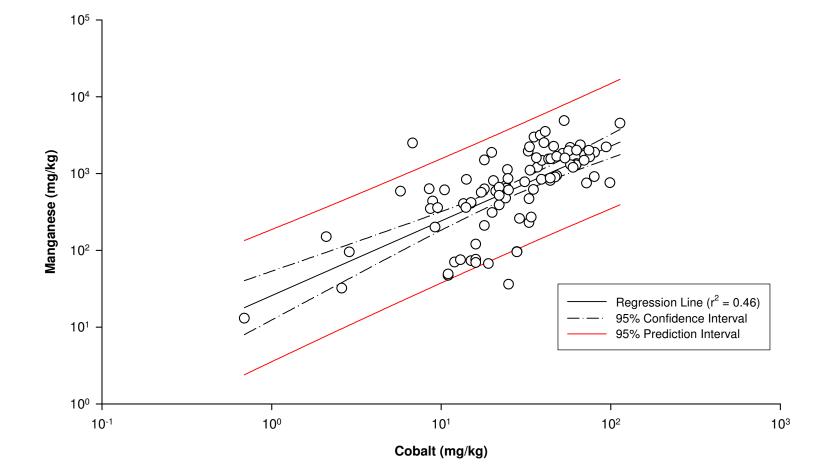
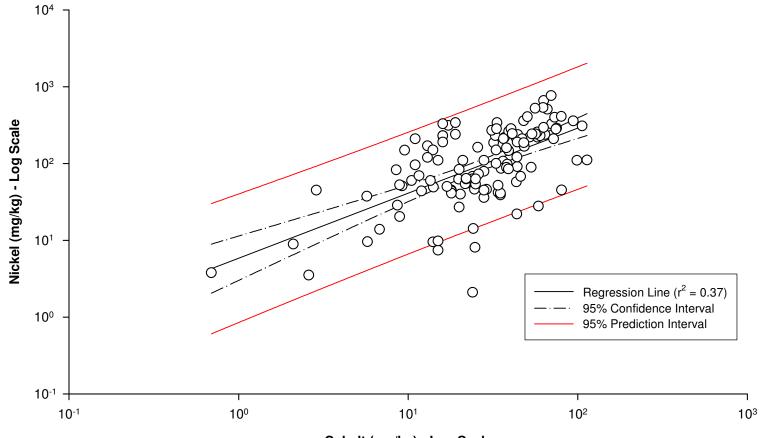


Figure 72 Cobalt-Manganese Correlation Plot Hawaiian Islands Soil Metal Background Evaluation Report



Cobalt (mg/kg) - Log Scale

Figure 73 Cobalt-Nickel Correlation Plot Hawaiian Islands Soil Metal Background Evaluation Report

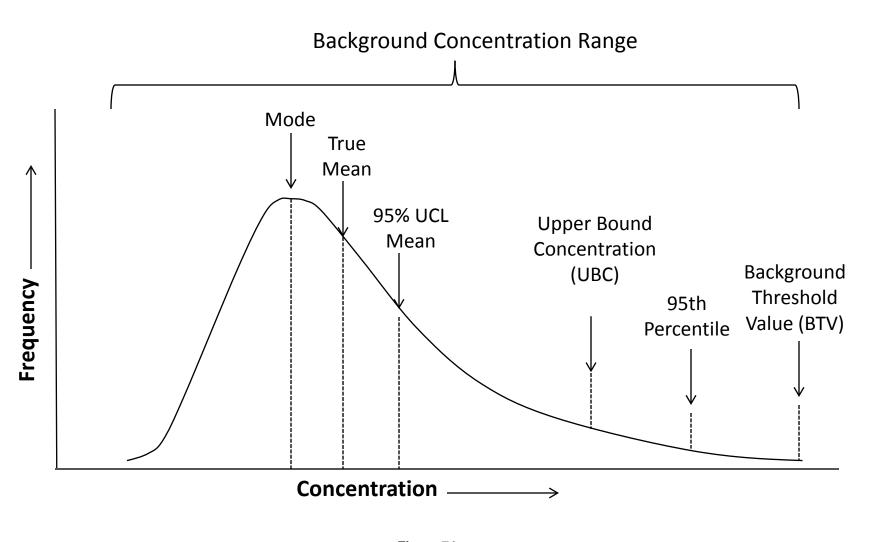


Figure 74 Generalized Log-normal Distribution and Parameters Defined for Background Concentrations Hawaiian Islands Soil Metal Background Evaluation Report

Appendix A PARCCS Report

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ACRONYMS AND ABBREVIATIONS

| ELAP | Environmental Laboratory Accreditation Program |
|--------|---|
| EPA | Environmental Protection Agency, United States |
| HDOH | Hawai'i Department of Health |
| ISM | incremental sampling methodology |
| LCS | laboratory control sample |
| MS | matrix spike |
| MSD | matrix spike duplicate |
| PARCCS | precision, accuracy, representativeness, completeness, comparability, and sensitivity |
| QC | quality control |
| RPD | relative percent difference |
| SDG | sample delivery group |



1.0 INTRODUCTION

This document presents data quality evaluation of soil data collected by the Hawaii Department of Health (HDOH) as part of the Hawaii Islands Soil Metal Background Evaluation Report, prepared for the HDOH. Between November 2009 and April 2010, 43 soil samples were collected from the islands of Hawaii, Maui, Oahu, and Kauai as part of the HDOH background metals study. These soil data are evaluated in this appendix for PARCCS (precision, accuracy, representativeness, comparability, completeness, and sensitivity) parameters. The objective of the data quality evaluation is to determine the usability of the data for the metals background evaluation, based on compliance with the laboratory-specific data quality indicator criteria. These criteria include field and laboratory blanks; the acceptance ranges for matrix spike (MS), matrix spike duplicate (MSD), and laboratory control samples (LCSs); and the relative percent difference (RPD) for MS or LCS duplicates, as specified by analytical method and/or the laboratory. Other aspects of method compliance, including instrument calibration frequency and acceptability, were not evaluated. This evaluation is not based on an independent third-party formal data validation process, and the data were not assigned qualifiers.

2.0 DATA EVALUATION VIA PARCCS

Analytical results for the soil samples were grouped into the following sample delivery groups (SDGs):

- SDG 222607: samples analyzed for 18 trace metals
- SDG 222610: samples analyzed for 10 major metals
- SDG 222611: samples analyzed for 18 trace metals

Analytical results are presented in Attachment A1.

SDG 222607. This SDG includes sample and quality control (QC) analytical results for 43 soil samples submitted on 09/14/2010 for analysis of 18 trace metals (antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, silver, tin, thallium, vanadium, and zinc). Samples were air-dried, and then a 30-gram aliquot was obtained using incremental sampling methodology (ISM). The 30-gram aliquot was reduced to < 75 microns in a puck mill. The analytical volume of 0.5 gram was then collected and used in the U.S. Environmental Protection Agency (EPA) 3051 digestion method and for mercury digestion method. EPA 6010B analytical method was used. All results were reported in dry-weight basis. EPA 6020 method was used for all trace metals analysis except for mercury (EPA 7471A) and tin (EPA 6010B).

SDG 222610. This SDG includes sample and QC analytical results for 43 samples submitted on 09/14/2011 for analysis of 10 major metals (aluminum, calcium, iron, magnesium, manganese, phosphorus, potassium, strontium, sodium, and titanium). Samples were air dried, and then a 30-gram aliquot was obtained using ISM. The 30-gram aliquot was reduced to < 75 microns in a puck mill. The analytical volume of 0.5 gram was then collected and used for the EPA 3052 digestion method. EPA 6010B analytical method was used. All results were reported in dry-weight basis.

SDG 222611. This SDG includes sample and QC analytical results for 12 soil samples representing a subset of the 43 soil samples submitted for analysis using the EPA 3050B digestion method. The objective of this analysis was to evaluate and compare the analytical results between samples prepared using the EPA 3051 and EPA 3050B digestion methods. Samples were air-dried, and a 10-gram aliquot was then obtained using ISM. The 10-gram aliquot was further reduced to < 75 microns in a puck mill. EPA 6020 analytical method was used for all metals except for tin (EPA 6010B). This sample group was not submitted for analysis of mercury. The results of the comparison between the two digestion methods are presented below in Section 3.0.



No data were considered as potentially rejected based on evaluation against the PARCCS criteria, as discussed in detail below.

2.1 PRECISION

Overall precision of the data set is considered acceptable, as all blank samples and LCSs were within acceptable ranges, and most RPDs that were outside acceptance limits were relatively close to their acceptance limits (acceptance limits are presented in Attachment A2). Several metal results should be considered estimates due to MS/MSD and field duplicate sample RPDs outside of acceptance ranges, as noted below.

SDG 222607:

Due to high MS/MSD RPD, silver should be noted as "estimated" in the following samples:

HA04, KA02 KA05, KA06 MA05, MA14, MA19 MO01, MO03 OA01, OA04, OA08, OA10, OA11, OA12, OA13, OA14, OA15, OA16

Due to high MS/MSD RPDs, chromium, cobalt, nickel, and vanadium should be noted as "estimated" in the following samples:

KA01 MA07 OA09

Due to high field sample duplicate RPDs, molybdenum, selenium, and silver should be noted as "estimated" in the following samples:

KA01 MA07 OA09

SDG 222610:

Due to high MS/MSD RPDs, calcium, magnesium, strontium, and sodium should be noted as "estimated" in the following samples:

MA01, MA03

Due to high duplicate sample RPDs, aluminum, calcium, iron, magnesium, and strontium should be noted as "estimated" in the following samples:

KA01 MA07 OA09

SDG 222611:

Due to high MS/MSD RPDs, antimony should be noted as "estimated" in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07



Due to high duplicate sample RPDs, cadmium, selenium, and silver should be noted as "estimated" in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07

Due to no MS/MSD RPD for barium (the lab did not reanalyze an outlier sample, so an RPD could not be calculated) and no duplicate RPDs for antimony and thallium (duplicate results were non-detect, therefore an RPD could not be calculated), each should be noted as "estimated" in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07

2.2 ACCURACY

Several metal results should be considered estimates due to MS and MSD percent recoveries outside of acceptance ranges, which indicates possible matrix interference in sample analyses; these are noted below. Overall accuracy of the data set is considered acceptable as all blanks and LCS results were within acceptance limits, and percent recoveries that were outside acceptance limits were generally relatively close to their acceptance limits (acceptance limits are presented in Attachment A2).

SDG 222607:

Due to high MSD percent recoveries, barium, chromium, nickel, silver, vanadium, and zinc should be noted as "estimated" with a potential high bias in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07

Due to high MS and MSD percent recoveries, nickel, vanadium, and zinc should be noted as "estimated" with a potential high bias in the following samples:

HA04, KA02 KA05, KA06 MA05, MA14, MA19 MO01, MO03 OA01, OA04, OA08, OA10, OA11, OA12, OA13, OA14, OA15, OA16

Due to high MS and MSD percent recoveries, zinc should be noted as "estimated" with a potential high bias in the following samples:

MA01, MA03

Due to high MS and MSD percent recoveries, chromium, and nickel should be noted as "estimated" with a potential high bias in the following samples:



KA01 MA07 OA09

Due to low MS and MSD percent recoveries, arsenic, beryllium, cadmium, molybdenum, selenium, silver, and thallium should be noted as "estimated" with a potential low bias in the following samples:

HA04, KA02 KA05, KA06 MA05, MA14, MA19 MO01, MO03 OA01, OA04, OA08, OA10, OA11, OA12, OA13, OA14, OA15, OA16

Due to low MS and MSD percent recoveries, arsenic, beryllium, cadmium, cobalt, molybdenum, selenium, silver, and thallium should be noted as "estimated" with a potential low bias in the following samples:

MA01 MA03

Due to low MS and MSD percent recoveries, arsenic, barium, beryllium, cobalt, copper, molybdenum, selenium, silver, vanadium, and zinc should be noted as "estimated" with a potential low bias in the following samples:

KA01 MA07 OA09

Silver MS and MSD percent recoveries were relatively high; however, silver results from all SDGs were non-detect except HA05 at 0.4 mg/kg; HA07 at 0.37 mg/kg; MA15 at 2.9 mg/kg; and MO07 at 0.76 mg/kg. There was no impact on ND silver results; however, silver detections should be noted as "estimated" with a potential high bias in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07

SDG 222610:

Due to high MS/MSD percent recoveries for aluminum, calcium, iron, and manganese and high MS recoveries for magnesium and potassium, each should be noted as "estimated" with a potential high bias in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07

Due to high MS/MSD percent recoveries, aluminum, iron, manganese, and titanium should be noted as "estimated" with a potential high bias in the following samples:

HA04, KA02 KA05, KA06



MA05, MA14, MA19 MO01, MO03 OA01, OA04, OA08, OA10, OA11, OA12, OA13, OA14, OA15, OA16

Due to high MS/MSD percent recoveries, aluminum, iron, manganese, and titanium should be noted as "estimated" with a potential high bias in the following samples:

MA01 MA03

Due to high MS/MSD percent recoveries for iron, manganese and low MS/MSD percent recoveries for titanium, each should be noted as "estimated" with a potential high bias in the following samples:

KA01 MA07 OA09

Due to low MSD percent recovery for strontium and low MS/MSD percent recovery for titanium, each should be noted as "estimated" with a potential low bias in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07

Due to low MS/MSD percent recoveries for strontium and titanium, each should be noted as "estimated" with a potential low bias in the following samples:

HA04, KA02 KA05, KA06 MA05, MA14, MA19 MO01, MO03 OA01, OA04, OA08, OA10, OA11, OA12, OA13, OA14, OA15, OA16

SDG 222611:

Due to high MS percent recoveries, barium should be noted as "estimated" with a potential high bias in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07

Due to low MS percent recoveries, arsenic should be noted as "estimated" with a potential low bias in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07



Due to low MSD percent recoveries, nickel, selenium, vanadium, and zinc should be noted as "estimated" with a potential low bias in the following samples:

HA05 KA01, KA03, KA09 MA02, MA04, MA16, MA17 MO02 OA05, OA06, OA07

2.3 REPRESENTATIVENESS

All mercury results should be considered estimates as they were analyzed outside of EPA method holding times. All samples were associated with a method blank in each individual SDG. All blank sample results were at non-detect concentrations with the exception of aluminum in two batches. However, all associated aluminum sample results in these batches were greater than 10 times the blank concentration, so the aluminum detected in the blank sample does not compromise associated sample results. The representativeness of the data is considered acceptable.

2.4 COMPARABILITY

The Environmental Laboratory Accreditation Program (ELAP)-certified laboratory used standard analytical methods for the analyses; results were reported in correct standard units. The overall comparability is considered acceptable when using same methods.

2.5 COMPLETENESS

The completeness level attained for the project was 98%. SDGs 222607 and 222611 had 100% completion of samples analysis per sample collected. SDG 222610 had two metals that were not analyzed where requested: phosphorus was not analyzed in any samples, and titanium was not analyzed in one LCS.

2.6 SENSITIVITY

All reporting limits (RLs) are at acceptable concentrations.

3.0 DIGESTION METHODS COMPARISON

Twelve of the 43 samples were submitted for a separate analysis using the EPA 3050B digestion methods to in order to evaluate concentrations of trace metals obtained using two different digestion methods used (EPA 3051A vs. EPA 3050B) for analysis of trace metals (Attachment A3). Table A3-1 lists the concentrations obtained using the two different methods for the 12 samples, and Table A3-2 lists concentration differences calculated for trace metals analyzed for each sample.

The average concentration difference tabulated in Table A3-2 shows that values obtained using the 3050B digestion method are generally higher in concentrations for antimony, chromium, copper, lead, selenium, and tin; however, concentrations are lower for arsenic, barium, beryllium, cadmium, cobalt, molybdenum, nickel, silver, vanadium, and zinc. Although concentration differences calculated for each sample show some variations, no consistent high or low bias was observed in concentrations derived using the two different digestion methods.

4.0 SUMMARY

Data for the 43 soil samples collected for the Hawaii metals background study was evaluated against the PARCCS criteria for to evaluate data quality and usability. Based on the results of the evaluation, there were no rejected data based on the PARCCS criteria, and the data are suitable to be included as part of the metals background study for the HDOH.



Attachment A1 Analytical Results

Attachment A1 Table A1-1: Summary of analytical results (results in milligram/kilogram)

| Table A1-1: S | uninary of a | analytica | il results | (results in | minigra | n/kilograi | 11) | | | | | | | | | | | | | | | Comula | | | | | | | | | | | | | | | | | | | |
|-------------------------|--------------|---------------------|------------|-------------|---------|------------|--------|--------|--------|--------|-----------|--------|--------|------------|--------|-----------|--------|--------|--------|---------|---------|---------|---------|-------------|-----------|--------|----------|--------|------------|---------|-----------------|--------|-----------|--------|--------|--------|--------|----------|-----------|-----------|--------------------------------|
| Analuta | 4402 | | LLAGE | | | KA01 | KA02 | K402 | KAOF | KA06 | KA07 | K409 | KA00 | MA01 | MA02 | MA02 | MA04 | MAGE | MA07 | MA 10 | MA14 | Sample | | MA 17 | MA 10 | M001 | M002 | M002 | MO07 0/ | | | | 06 0 007 | 0400 | 0 4 00 | 0410 | 0411 | 0412 | 0412 | 0414 | OA15 OA16 |
| Analyte | | | HAUS | TAU0 | HAU7 | KAU I | KAU2 | KA03 | KA05 | KA00 | KAU7 | KAU0 | KA09 | IVIAU I | WIAUZ | IVIAU3 | WA04 | IVIA05 | IVIAU7 | IVIA 12 | IVIA 14 | IVIA 15 | IVIA 10 | IVIA 17 | IVIA 19 | WOUT | WOUZ | WO03 | | | 404 OAU | 5 UA | 06 0A07 | UAUO | UAU9 | UAIU | UATT | UAIZ | UAI3 (| JA14 (| JAIS UAIO |
| SDG 2222607 Antimony | <0.26 | | 0.79 | 1.5 | 0.27 | <0.25 | <0.2E | 0.68 | <0.25 | 0.48 | 0.49 | <0.25 | <0.25 | 0.48 | <0.25 | 0.32 | 0.28 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | 0.27 | 0.55 | <0.25 | 0.20 | <0.25 | <0.25 <0 | .25 <0 | .26 <0.2 | 5 <0. | 25 1.4 | <0.26 | 1.1 | 0.88 | 0.60 | 0.96 | <0.25 < | <0.25 < | <0.25 <0.25 |
| | 0.86 | 0.59 | 2.2 | 1.5 | 1.6 | 1.1 | 3.3 | 8.6 | 2.0 | 6.8 | 8.2 | 1.2 | 2.7 | 3.9 | 1.3 | 3.1 | 1.5 | 2.5 | 1.4 | 0.97 | 1.8 | 1.9 | 1.9 | 2.2 | 3.2 | 1.5 | 5.2 | | 4.1 1 | | .20 <0.23 | | | 4.6 | 3.4 | 47 | 40 | | | | 3.1 2.6 |
| Arsenic Barium | 49 | 120 | 2.2 | 430 | 1.0 | 64 | 3.3 | 70 | 2.0 | 49 | 8.2 52 | 40 | 450 | 3.9 44 | 290 | 3.1 60 | 1.5 | 2.5 | 1.4 | 140 | 280 | 1.9 | 290 | 2.2 | 3.2 48 | 21 | 5.2 | 2.4 | | - | 0 0.44 5 26 | 1. | - | 23 | 580 | 47 | 38 | 58 44 | | | <u>560</u> <u>610</u> |
| Bervllium | <0.26 | | 220 | 430 | 120 | 0.72 | 0.84 | | 0.50 | | 0.29 | 0.40 | 450 | 44 0.35 | 290 | 0.42 | 0.65 | 260 | 190 | 0.65 | 280 | 1.1 | 290 | 0.32 | 48 | 0.59 | 0.67 | | 0.39 1 | | 5 26 63 0.42 | | | 0.36 | 2.1 | 0.51 | 0.52 | | | - | 2.2 2.3 |
| Cadmium | 1.4 | - | 0.88 | 1.0 | 0.42 | <0.25 | <0.25 | | | | | | 0.00 | 0.35 | 0.98 | <0.25 | 0.85 | 0.98 | 0.47 | <0.25 | 0.33 | 0.30 | 0.72 | <0.25 | 0.28 | <0.25 | | | 0.00 | | .26 <0.2 | | | <0.26 | | | < 0.32 | 0.0- | | 0.00 | <0.25 <0.25 |
| Chromium | 94 | 76 | 140 | 120 | 170 | 500 | 630 | 670 | 330 | | 300 | 230 | 330 | 36 | 150 | 100 | 35 | 68 | 160 | 150 | 120 | 82 | 93 | <0.23 89 | 120 | 160 | 100 | | 140 1 | | 20 <0.2 | | - | 240 | | 120 | 120 | | | | 290 290 |
| Cobalt | 18 | 21 | 28 | 22 | 28 | 73 | 19 | 20 | 33 | 15 | 18 | 48 | 19 | 2.1 | 38 | 100 | 14 | 34 | 99 | 25 | 39 | 29 | 35 | 28 | 20 | 100 | 38 | 15 | 140 1 | 2 3 | | 23 | | 14 | - | 22 | 22 | 25 | | | <u>290</u> <u>290</u> 58 60 |
| Copper | 60 | 63 | 46 | 22 | 43 | 100 | 72 | 110 | 100 | - | 67 | 58 | 61 | 8.2 | 39 | 24 | 27 | 27 | 88 | 48 | 43 | 25 | 25 | 43 | 140 | 120 | 49 | 10 | 12 7 | | 10 130 | | | 14 | 44 | 83 | 80 | 79 | | | 45 48 |
| Lead | 3.9 | 12 | 10 | 33 | 2.9 | 2.2 | 7.7 | 110 | 5.9 | | 20 | 4.4 | 4.7 | 13 | 8.4 | 7.8 | 24 | 5.8 | 2.6 | 1.5 | 3.2 | 4.3 | 4.2 | 5.7 | 5.4 | 4.1 | 49 | 10 | 8.7 3 | · · | 2 3.0 | 10 | 3 430 | 7.8 | | 10 | 11 | 22 | 100 | 01 | 6.2 7.8 |
| Mercury | 0.088 | | 0.043 | 0.67 | <0.021 | | | 0.40 | | | 0.30 | 0.036 | 0.20 | 0.54 | 0.11 | 0.39 | 0.14 | | 0.029 | <0.02 | 0.16 | 0.39 | 0.056 | <0.02 | 0.31 | 0.39 | | | 0.57 0. | - | | 2 <0. | | 0.10 | | | | 0.077 | | | <0.020 <0.021 |
| Molvbdenum | 0.49 | 0.47 | 1.1 | 0.78 | 0.47 | 0.69 | 0.83 | | 0.62 | | 4.0 | 0.66 | 0.20 | <0.25 | 0.81 | 1.5 | 0.70 | 0.12 | <0.25 | <0.02 | <0.25 | 1.1 | 1.2 | 0.85 | 1.4 | <0.25 | | | 1.5 0. | | .26 <0.2 | | | <0.26 | | <0.25 | <0.25 | | | | 1.0 1.5 |
| Nickel | 45 | 110 | 79 | 55 | 110 | 400 | 340 | | 150 | - | 44 | 360 | 240 | 8.9 | 89 | 41 | 9.5 | 42 | 110 | 54 | 85 | 46 | 39 | 36 | 27 | 96 | 160 | 9.8 | 44 2 | | 0 170 | | | 150 | - | 63 | 64 | | 0.20 | 0.20 | 220 230 |
| Selenium | 2.7 | - | 0.84 | 0.76 | 0.28 | 0.95 | | 3.4 | 3.9 | - | 4.5 | 0.50 | 3.0 | 1.2 | 0.42 | 2.1 | 0.42 | 1.3 | 0.37 | 0.51 | 0.44 | 0.93 | 0.52 | 2.9 | 1.5 | 0.64 | 1.1 | | 2.9 1 | - | .2 0.83 | | | 1.5 | | 0.77 | 0.73 | | | - | <0.25 <0.25 |
| Silver | <0.26 | - | | <0.25 | 0.37 | <0.25 | | <0.27 | | - | | | | | <0.25 | | <0.25 | - | 0.27 | <0.25 | | 2.9 | <0.25 | | 0.30 | 0.30 | | <0.25 | - | | .26 <0.2 | | | <0.26 | | <0.25 | | | | <0.25 | |
| Tin | <4.2 | <43 | <3.4 | 7.2 | <3.9 | <4 | 47 | | <48 | | <2.7 | <3.3 | <3.6 | <3.5 | <3.8 | <3.6 | 8.8 | | 3.9 | <4.1 | <40 | <3.8 | <4 | <2.5 | <46 | <46 | <3.1 | <48 | | | 50 <3.5 | | | <50 | | <45 | <43 | | | | <38 <47 |
| Thallium | <0.25 | | | | | | | <0.25 | | | | | | <0.25 | <0.25 | <0.25 | <0.25 | | <0.25 | <0.25 | - | <0.25 | | <0.25 | <0.25 | | . | | - | | .25 <0.2 | | | | | | | | | <0.25 < | |
| Vanadium | 63 | 51 | 110 | 80 | 100 | 140 | 230 | | 140 | | 460 | 90 | 140 | 43 | 160 | 180 | 65 | 200 | 110 | 93 | 200 | 200 | 190 | 110 | 180 | 120 | 82 | | 160 20 | | 50 140 | | | 150 | | 110 | 110 | | | | 140 150 |
| Zinc | 74 | 120 | 130 | 210 | 59 | 98 | 97 | 140 | 73 | 52 | 120 | 69 | 57 | 68 | 97 | 79 | 990 | 120 | 150 | 45 | 94 | 94 | 100 | 77 | 200 | 67 | 57 | 110 | 76 1 | | | 81 | - | 77 | 110 | 97 | 110 | | | | 140 150 |
| SDG 222610 (| | | | 1 | | 1 | 1 | | | | | | | | | | | | | | | | | | | 1 | | | | | | | | 1 | | | 1 | | | | |
| Aluminum | 4,400 | | 18.000 | 4.400 | 3.600 | 19.000 | 6.900 | 4.100 | 4.700 | 7.100 | 20.000 | 14.000 | 5,100 | 8.100 | 18.000 | 6.400 | 2.500 | 13.000 | 5.400 | 4.800 | 26.000 | 8,900 | 11.000 | 11.000 | 14.000 | 13.000 | 12.000 | 8.400 | 7.000 7.8 | 00 19. | 000 4.500 | 6.60 | 0 15.000 | 57.000 | 2.600 | 34.000 | 22.000 | 33.000 | 9.400 10 | 10.000 28 | 8.000 23.000 |
| Calcium | 2.000 | 6,200 | 5.800 | 91 | 31 | 3,900 | <56 | 330 | <44 | 1 | 12.000 | 5.900 | <43 | 76 | 9,700 | 210 | 730 | 580 | 400 | 40 | 5.200 | 240 | 1.800 | <37 | 3.500 | 130 | 1.800 | 220 | 55 2 | 50 1.2 | 00 <32 | <4 | 3 4.900 | 28,000 | 3.000 | 8,100 | 6.200 | 8,700 | <48 | <44 14 | 4.000 13.000 |
| Iron | 23.000 | 13.000 | 47.000 | 44.000 | 59.000 | 68.000 | 49.000 | 54,000 | 35,000 | 46.000 | 33,000 | 28.000 | 63.000 | 41.000 | 39.000 | 50,000 | 24.000 | 50.000 | 42.000 | 45.000 | 60.000 | 64.000 | 57.000 | 63.000 | 57.000 | 59.000 | 44.000 | 51.000 | 64.000 63. | 00 65. | 000 51.00 | 0 62.0 | 00 41.000 | 83.000 | 12.000 | 66.000 | 43.000 | 60.000 / | 57.000 30 | 30.000 44 | 4,000 35,000 |
| Magnesium | 930 | 2,800 | 2,600 | <46 | <26 | 3,600 | <49 | 79 | <25 | | 13,000 | 7,400 | <38 | 52 | 5,400 | 160 | 180 | 740 | 300 | <39 | 4,000 | 140 | 850 | <48 | 1,800 | 91 | 1,800 | 84 | <33 1 | 0 1,2 | 00 <28 | 63 | 2,400 | 2,200 | 2,400 | 3,800 | 3,500 | 5,200 | <63 | <38 19 | 9,000 16,000 |
| Manganese | 630 | 590 | 690 | 390 | 96 | 910 | 67 | 200 | 230 | 73 | 1,500 | 940 | 76 | 150 | 810 | 210 | 410 | 270 | 760 | 36 | 840 | 260 | 620 | 95 | 310 | 47 | 900 | 420 | 70 7 | 60 47 | 70 49 | 12 | 0 480 | 360 | 870 | 660 | 520 | 610 | 69 | 75 1 | 1,300 1,200 |
| Phosphorus | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA | NA N | A N | IA NA | N | A NA | NA | NA | NA | NA | NA | NA | NA | NA NA |
| Potassium | 620 | 1,300 | 4,200 | 1,600 | 2,800 | 490 | 780 | 2,300 | 840 | 1,400 | 3,000 | 930 | 730 | 2,700 | 3,800 | 1,900 | 1,700 | 1,700 | 1,200 | 320 | 1,800 | 610 | 740 | 330 | 1,500 | 1,000 | 5,300 | 4,200 | 640 1,7 | 00 60 | 00 200 | 21 | 300 | 1,200 | 4,100 | 490 | 470 | 530 | 320 | 250 4 | 4,500 4,100 |
| Strontium | 11 | 67 | 150 | 7.2 | <2 | 22 | 7.3 | <2 | <2 | <2 | 110 | 32 | 3.1 | 3.0 | 120 | 7.2 | 44 | 12 | 7.7 | <2 | 78 | 2.8 | 33 | <2 | 12 | <2 | 29 | 8.5 | <2 8 | 1 1 | 5 <2 | < | 2 31 | 52 | 92 | 58 | 48 | 61 | <2 | <2 | 340 290 |
| Sodium | 620 | 1,500 | 6,000 | 780 | 150 | 830 | 150 | 310 | 75 | 330 | 2,100 | 1,500 | <94 | 490 | 2,800 | 450 | 1,100 | 750 | 2,800 | 240 | 1,300 | 180 | 910 | 87 | 840 | 420 | 350 | 2,200 | 190 64 | 0 28 | 30 <69 | 11 | 0 900 | 480 | 3,900 | 1,600 | 1,600 | 2,200 | <110 | <63 7 | 7,500 6,000 |
| Titanium | 6,300 | 4,200 | 14,000 | 12,000 | 34,000 | 15,000 | 22,000 | 31,000 | 15,000 | 21,000 | 16,000 | 11,000 | 24,000 | 12,000 | 14,000 | 26,000 | 8,300 | 20,000 | 17,000 | 18,000 | 14,000 | 19,000 | 17,000 | 32,000 | 16,000 | 19,000 | 6,900 | 13,000 | 30,000 27, | 000 16, | 000 23,00 | 0 14,0 | 9,000 | 17,000 | 11,000 | 10,000 | 11,000 | 11,000 1 | 19,000 10 | 16,000 12 | 2,000 12,000 |
| SDG 222610 (| 10 grams al | iquot) ^a | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Antimony | NA | NA | <0.25 | NA | NA | <0.25 | NA | 0.43 | NA | NA | NA | NA | <0.25 | NA | <0.25 | NA | <0.25 | NA | NA | NA | NA | NA | <0.25 | <0.25 | NA | NA | <0.25 | NA | NA N | A N | IA <0.2 | 5 <0. | 25 1.0 | NA | NA | NA | NA | NA | NA | NA | NA NA |
| Arsenic | NA | NA | 2.2 | NA | NA | 1.7 | NA | 5.8 | NA | NA | NA | NA | 2.1 | NA | 2.5 | NA | 2.6 | NA | NA | NA | NA | NA | 2.3 | 1.1 | NA | NA | 7.6 | NA | NA N | A N | IA 0.42 | 1.4 | 100 | NA | NA | NA | NA | NA | NA | NA | NA NA |
| Barium | NA | NA | 220 | NA | NA | 77 | NA | 46 | NA | NA | NA | NA | 220 | NA | 380 | NA | 200 | NA | NA | NA | NA | NA | 320 | 21 | NA | NA | 240 | NA | NA N | A N | IA 33 | 12 | 0 56 | NA | NA | NA | NA | NA | NA | NA | NA NA |
| Beryllium | NA | NA | 1.6 | NA | NA | 0.74 | NA | 0.44 | NA | NA | NA | NA | 1.2 | NA | 1.3 | NA | 0.81 | NA | NA | NA | NA | NA | 1.1 | 0.44 | NA | NA | 0.92 | NA | | | IA 0.42 | | | NA | NA | NA | NA | NA | NA | | NA NA |
| Cadmium | NA | NA | 1.5 | NA | NA | <0.25 | NA | 0.51 | NA | NA | NA | NA | 0.27 | NA | 0.49 | NA | 1.0 | NA | NA | NA | NA | NA | 0.96 | 0.40 | NA | NA | 1.1 | NA | | | IA <0.2 | | - | NA | NA | NA | NA | NA | NA | | NA NA |
| Chromium | NA | NA | 83 | NA | NA | 390 | NA | - | NA | NA | NA | NA | 380 | NA | 52 | NA | 8.7 | NA | NA | NA | NA | NA | 36 | 97 | NA | NA | 110 | NA | NA N | A N | IA 240 | 25 | 0 120 | NA | NA | NA | NA | NA | NA | NA | NA NA |
| Cobalt | NA | NA | 24 | NA | NA | 80 | NA | | NA | | NA | NA | 16 | NA | 44 | NA | 15 | NA | NA | NA | NA | NA | 35 | 28 | NA | NA | 47 | NA | NA N | | IA 11 | 16 | | NA | | NA | NA | | | | NA NA |
| Copper | NA | NA | 46 | NA | NA | 76 | NA | | NA | | NA | NA | 56 | NA | 50 | NA | 35 | NA | NA | NA | NA | NA | 29 | 51 | NA | NA | 56 | NA | | | IA 140 | | | NA | NA | NA | NA | | | | NA NA |
| Lead | NA | NA | 11 | NA | NA | 2.3 | NA | | NA | | NA | NA | 5.9 | NA | 11 | NA | 32 | NA | NA | NA | NA | NA | 5.2 | 7.9 | NA | NA | 22 | NA | | | IA 3.7 | | | NA | NA | NA | NA | NA | | | NA NA |
| Molybdenum | NA | NA | 0.57 | NA | NA | <0.42 | | 3.5 | NA | | NA | NA | 0.91 | NA | 0.74 | NA | 0.80 | NA | NA | NA | NA | NA | 1.4 | 0.81 | NA | NA | 1.0 | NA | | | IA <0.4 | - | - | NA | | NA | NA | | | | NA NA |
| Nickel | NA | NA | 68 | NA | NA | 410 | NA | 51 | NA | | NA | NA | 230 | NA | 91 | NA | 7.4 | NA | NA | NA | NA | NA | 41 | 45 | NA | NA | 210 | NA | | | IA 210 | | | NA | NA | NA | NA | NA | | | NA NA |
| Selenium | NA | NA | 0.74 | NA | NA | 1.0 | NA | | NA | | NA | NA | 1.8 | NA | 0.46 | NA | 0.89 | NA | NA | NA | NA | NA | 0.54 | 1.6 | NA | NA | 1.5 | NA | | | IA 0.72 | | | NA | | NA | NA | | | | NA NA |
| Silver | NA | NA | 1.0 | NA | NA | <0.25 | NA | 0.35 | NA | | NA | NA | 0.91 | NA | 0.76 | NA | <0.25 | NA | NA | NA | NA | NA | 0.41 | 1.5 | NA | NA | 0.34 | NA | | | IA 0.31 | 0.3 | | NA | NA | NA | NA | | | | NA NA |
| Tin | NA | NA | 6.9 | NA | NA | 5.4 | NA | | NA | | NA | NA | 7.7 | NA | 8.7 | NA | 10 | NA | NA | NA | NA | NA | 7.2 | 3.3 | NA | NA | 5.0 | NA | | | IA 2.7 | 4. | | NA | | NA | NA | | | | NA NA |
| Thallium | NA | | <0.25 | NA | NA | <0.25 | | <0.25 | | | NA | NA | <0.25 | NA | <0.25 | NA | <0.25 | NA | NA | NA | NA | NA | <0.25 | | NA | NA | <0.25 | NA | | | A <0.2 | | | | | NA | NA | | | | NA NA |
| Vanadium | NA | | 97 | NA | NA | 130 | NA | 370 | NA | | NA | NA | 210 | NA | 200 | NA | 70 | NA | NA | NA | NA | NA | 190 | 180 | NA | NA | 100 | NA | | | IA 170 | | | NA | NA | NA | NA | | | | NA NA |
| Zinc | NA | NA | 110 | NA | NA | 88 | NA | 110 | NA | NA | NA | NA | 51 | NA | 120 | NA | 1,200 | NA | NA | NA | NA | NA | 97 | 92 | NA | NA | 74 | NA | NA N | A N | IA 53 | 96 | 200 | NA | NA | NA | NA | NA | NA | NA | NA NA |

 ZINC
 NA
 N

NA not analyzed

Attachment A2 Acceptance Limits

Attachment A2 HDOH Background Metals Results - Curtis and Tompkins Laboratory In-house Limits

LCS Percent Recovery Limits

| Analyte | Limits |
|------------|--------|
| Antimony | 80–120 |
| Arsenic | 80–120 |
| Barium | 79–120 |
| Beryllium | 75–123 |
| Cadmium | 80–120 |
| Chromium | 80–120 |
| Cobalt | 80–120 |
| Copper | 78–120 |
| Lead | 80–120 |
| Mercury | 80–120 |
| Molybdenum | 77–120 |
| Nickel | 80–120 |
| Selenium | 80–120 |
| Silver | 80–120 |
| Tin | 80–120 |
| Thallium | 77–120 |
| Vanadium | 80–120 |
| Zinc | 78–120 |

| | , |
|------------|--------|
| Analyte | Limits |
| Antimony | 18–120 |
| Arsenic | 72-120 |
| Barium | 53–137 |
| Beryllium | 75–123 |
| Cadmium | 77–120 |
| Chromium | 58–133 |
| Cobalt | 70–120 |
| Copper | 55–133 |
| Lead | 65–126 |
| Mercury | 70–131 |
| Molybdenum | 66–120 |
| Nickel | 59–133 |
| Selenium | 76–120 |
| Silver | 74–120 |
| Tin | 60–120 |
| Thallium | 74–120 |
| Vanadium | 59–131 |
| Zinc | 47–141 |
| | |

Duplicate Relative Percent Difference Limits

| Analyte | Limits |
|------------|--------|
| Antimony | 36 |
| Arsenic | 30 |
| Barium | 31 |
| Beryllium | 20 |
| Cadmium | 27 |
| Chromium | 35 |
| Cobalt | 22 |
| Copper | 51 |
| Lead | 23 |
| Mercury | 20 |
| Molybdenum | 26 |
| Nickel | 32 |
| Selenium | 20 |
| Silver | 25 |
| Tin | 35 |
| Thallium | 20 |
| Vanadium | 26 |
| Zinc | 40 |

| Analyte | Limits |
|------------|--------|
| Antimony | 36 |
| Arsenic | 30 |
| Barium | 31 |
| Beryllium | 20 |
| Cadmium | 27 |
| Chromium | 35 |
| Cobalt | 22 |
| Copper | 51 |
| Lead | 23 |
| Mercury | 36 |
| Molybdenum | 26 |
| Nickel | 32 |
| Selenium | 20 |
| Silver | 25 |
| Tin | 35 |
| Thallium | 20 |
| Vanadium | 26 |
| Zinc | 40 |

| LCS | laboratory control sample |
|-----|---------------------------|
| MS | matrix spike |
| MSD | matrix spike duplicate |

MS/MSD Percent Recovery Limits

| Vanadium | 59–131 |
|-----------------|---------------------------|
| Zinc | 47–141 |
| | |
| | |
| | |
| | |
| | |
| MS/MSD Relative | Percent Difference Limits |
| | |
| | |

Attachment A3 EPA 3051 and 3050B Digestion Methods Comparison

Attachment A3

| | H | 405 | ĸ | 401 | ĸ | 403 | K/ | 409 | M | 402 | M | ۹04 | MA | A16 | M | A 17 | MO02 | | OA05 | | OA06 | | 0 | A07 |
|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------------|-------|-------|-------|-------|-------|-------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Element | 3051 | 3050B | 3051 | 3050B | 3051 | 3050B | 3051 | 3050B | 3051 | 3050B | 3051 | 3050B | 3051 | 3050B | 3051 | 3050B |
| Antimony | 0.79 | 0.25 | <0.25 | <0.25 | 0.68 | 0.43 | <0.25 | <0.25 | <0.25 | <0.25 | 0.28 | <0.25 | <0.25 | <0.25 | 0.27 | <0.25 | 0.29 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | 1.4 | 1.0 |
| Arsenic | 2.2 | 2.2 | 1.1 | 1.7 | 8.6 | 5.8 | 2.7 | 2.1 | 1.3 | 2.5 | 1.5 | 2.6 | 1.9 | 2.3 | 2.2 | 1.1 | 5.2 | 7.6 | 0.44 | 0.42 | 1.2 | 1.4 | 81 | 100 |
| Barium | 220 | 220 | 64 | 77 | 70 | 46 | 450 | 220 | 290 | 380 | 160 | 200 | 290 | 320 | 18 | 21 | 160 | 240 | 26 | 33 | 100 | 120 | 46 | 56 |
| Beryllium | 1.8 | 1.6 | 0.72 | 0.74 | 0.37 | 0.44 | 0.88 | 1.2 | 0.98 | 1.3 | 0.65 | 0.81 | 1.1 | 1.1 | 0.32 | 0.44 | 0.67 | 0.92 | 0.42 | 0.42 | 0.50 | 0.59 | 0.51 | 0.67 |
| Cadmium | 0.88 | 1.5 | <0.25 | <0.25 | <0.27 | 0.51 | <0.25 | 0.27 | 0.35 | 0.49 | 0.92 | 1.0 | 0.72 | 0.96 | <0.25 | 0.40 | 0.71 | 1.1 | <0.25 | <0.25 | <0.25 | <0.25 | 2.1 | 4.3 |
| Chromium | 140 | 83 | 500 | 390 | 670 | 770 | 330 | 380 | 150 | 52 | 35 | 8.7 | 93 | 36 | 89 | 97 | 100 | 110 | 230 | 240 | 230 | 250 | 130 | 120 |
| Cobalt | 28 | 24 | 73 | 80 | 20 | 9.2 | 19 | 16 | 38 | 44 | 14 | 15 | 35 | 35 | 28 | 28 | 38 | 47 | 13 | 11 | 16 | 16 | 26 | 24 |
| Copper | 46 | 46 | 100 | 76 | 110 | 68 | 61 | 56 | 39 | 50 | 27 | 35 | 25 | 29 | 43 | 51 | 49 | 56 | 130 | 140 | 160 | 200 | 450 | 210 |
| Lead | 10 | 11 | 2.2 | 2.3 | 380 | 39 | 4.7 | 5.9 | 8.4 | 11 | 24 | 32 | 4.2 | 5.2 | 5.7 | 7.9 | 14 | 22 | 3.0 | 3.7 | 1.8 | 2.3 | 53 | 46 |
| Molybdenum | 1.1 | 0.57 | 0.69 | <0.42 | 2.7 | 3.5 | 0.80 | 0.91 | 0.81 | 0.74 | 0.70 | 0.80 | 1.2 | 1.4 | 0.85 | 0.81 | 0.63 | 1.0 | <0.25 | <0.4 | <0.25 | <0.41 | 0.53 | <0.4 |
| Nickel | 79 | 68 | 400 | 410 | 84 | 51 | 240 | 230 | 89 | 91 | 9.5 | 7.4 | 39 | 41 | 36 | 45 | 160 | 210 | 170 | 210 | 230 | 330 | 73 | 90 |
| Selenium | 0.84 | 0.74 | 0.95 | 1.0 | 3.4 | 1.1 | 3.0 | 1.8 | 0.42 | 0.46 | 0.42 | 0.89 | 0.52 | 0.54 | 2.9 | 1.6 | 1.1 | 1.5 | 0.83 | 0.72 | 0.34 | 0.33 | 0.68 | 0.88 |
| Silver | 0.40 | 1.0 | <0.25 | <0.25 | <0.27 | 0.35 | <0.25 | 0.91 | <0.25 | 0.76 | <0.25 | <0.25 | <0.25 | 0.41 | 0.55 | 1.5 | <0.25 | 0.34 | <0.25 | 0.31 | <0.25 | 0.33 | <0.28 | 0.33 |
| Tin | 3.4 | 6.9 | <4 | 5.4 | 8.5 | 9.0 | <3.6 | 7.7 | <3.8 | 8.7 | 8.8 | 10 | <4 | 7.2 | <2.5 | 3.3 | <3.1 | 5.0 | <3.5 | 2.7 | <4 | 4.5 | 16 | 7.1 |
| Thallium | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 | <0.25 |
| Vanadium | 110 | 97 | 140 | 130 | 300 | 370 | 140 | 210 | 160 | 200 | 65 | 70 | 190 | 190 | 110 | 180 | 82 | 100 | 140 | 170 | 97 | 150 | 120 | 120 |
| Zinc | 130 | 110 | 98 | 88 | 140 | 110 | 57 | 51 | 97 | 120 | 990 | 1,200 | 100 | 97 | 77 | 92 | 57 | 74 | 60 | 53 | 81 | 96 | 190 | 200 |

Table A3-1. Comparison of analytical results using the EPA 3051 and EPA 3050B digestion methods

N/A - 10-gram aliquot samples were not submitted for mercury analysis

| Element | HA05 | KA01 | KA03 | KA09 | MA02 | MA04 | MA16 | MA17 | MO02 | OA05 | OA06 | OA07 | AVERAGE |
|------------|-------|--------|---------|--------|--------|---------|--------|--------|--------|--------|---------|--------|---------|
| Antimony | 0.54 | N/A | 0.25 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | 0.40 | 0.40 |
| Arsenic | 0.00 | -0.60 | 2.80 | 0.60 | -1.20 | -1.10 | -0.40 | 1.10 | -2.40 | 0.02 | -0.20 | -19.00 | -1.70 |
| Barium | 0.00 | -13.00 | 24.00 | 230.00 | -90.00 | -40.00 | -30.00 | -3.00 | -80.00 | -7.00 | -20.00 | -10.00 | -3.25 |
| Beryllium | 0.20 | -0.02 | -0.07 | -0.32 | -0.32 | -0.16 | 0.00 | -0.12 | -0.25 | 0.00 | -0.09 | -0.16 | -0.11 |
| Cadmium | -0.62 | N/A | N/A | N/A | -0.14 | -0.08 | -0.24 | N/A | -0.39 | N/A | N/A | -2.20 | -0.61 |
| Chromium | 57.00 | 110.00 | -100.00 | -50.00 | 98.00 | 26.30 | 57.00 | -8.00 | -10.00 | -10.00 | -20.00 | 10.00 | 13.36 |
| Cobalt | 4.00 | -7.00 | 10.80 | 3.00 | -6.00 | -1.00 | 0.00 | 0.00 | -9.00 | 2.00 | 0.00 | 2.00 | -0.10 |
| Copper | 0.00 | 24.00 | 42.00 | 5.00 | -11.00 | -8.00 | -4.00 | -8.00 | -7.00 | -10.00 | -40.00 | 240.00 | 18.58 |
| Lead | -1.00 | -0.10 | 341.00 | -1.20 | -2.60 | -8.00 | -1.00 | -2.20 | -8.00 | -0.70 | -0.50 | 7.00 | 26.89 |
| Molybdenum | 0.53 | N/A | -0.80 | -0.11 | 0.07 | -0.10 | -0.20 | 0.04 | -0.37 | N/A | N/A | N/A | -0.12 |
| Nickel | 11.00 | -10.00 | 33.00 | 10.00 | -2.00 | 2.10 | -2.00 | -9.00 | -50.00 | -40.00 | -100.00 | -17.00 | -14.49 |
| Selenium | 0.10 | -0.05 | 2.30 | 1.20 | -0.04 | -0.47 | -0.02 | 1.30 | -0.40 | 0.11 | 0.01 | -0.20 | 0.32 |
| Silver | -0.60 | N/A | N/A | N/A | N/A | N/A | N/A | -0.95 | N/A | N/A | N/A | N/A | -0.78 |
| Tin | -3.50 | N/A | -0.50 | N/A | N/A | -1.20 | N/A | N/A | N/A | N/A | N/A | 8.90 | 0.93 |
| Vanadium | 13.00 | 10.00 | -70.00 | -70.00 | -40.00 | -5.00 | 0.00 | -70.00 | -18.00 | -30.00 | -53.00 | 0.00 | -27.75 |
| Zinc | 20.00 | 10.00 | 30.00 | 6.00 | -23.00 | -210.00 | 3.00 | -15.00 | -17.00 | 7.00 | -15.00 | -10.00 | -17.83 |

Table A3-2. Concentrations of elements digested by EPA methods 3051A and 3050B

Attachment A3

Appendix B Data (on CD-ROM)