

Appendix E

Soil Background Study Report

Soil Background Study Report Iron King Mine – Humboldt Smelter Superfund Site Dewey-Humboldt, Yavapai County, Arizona

Prepared for
United States Environmental Protection Agency
Region 9

75 Hawthorne Street
San Francisco, California 94105

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CH2MHILL®
6 Hutton Centre Drive
Suite 700
Santa Ana, California 92707

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Acronyms and Abbreviations

APSI	area of potential site impact
bgs	below ground surface
COC	contaminant of concern
EPA	U.S. Environmental Protection Agency
mg/kg	milligrams per kilogram
ND	nondetect
UTL	upper tolerance limit
XRF	X-ray fluorescence

Introduction

This report presents the results of the Soil Background Study performed at the Iron King Mine – Humboldt Smelter Superfund Site located in Dewey-Humboldt, Arizona (the site). The site is a combination of sources and releases from two areas: the Iron King Mine and the Humboldt Smelter. A portion of the town of Dewey-Humboldt is situated between the mine and the smelter. Three waterways (Chaparral Gulch, Galena Gulch, and Agua Fria River) transect the site (see Figure 1-1).

The Iron King Mine (the mine) area covers approximately 153 acres. It was periodically active from 1904 until 1968, and was primarily a lead and zinc mine that also produced gold, silver, and copper. Waste rock and tailings were deposited in large piles adjacent to actual mine property boundaries. More recently, the mine tailings from the site have been used to create fertilizer. The Humboldt Smelter (the smelter) occupies approximately 182 acres. It was used primarily as a copper smelter, with most of the ore imported from other parts of the state. In later years, dross was imported for aluminum recovery. This area has substantial surface deposits of tailings, smelter ash, slag, and aluminum dross. The smelter operated from the late 1800s until 1970, with intermittent inactivity. The mine and smelter operations resulted in soil contamination caused by wind- and water-transported tailings and other factors. The contaminants of concern (COCs) detected in soils include arsenic and lead.

The objectives of the study and the report organization are presented in the following sections.

1.1 Objectives of the Soil Background Study

The objectives of the Soil Background Study include the following:

- Develop a defensible approach for differentiating between the distribution of mine- and smelter-related contamination and the distribution of naturally occurring constituents detected in soils surrounding the site.
- Identify the background boundary, which is the boundary of the area that has not been impacted by the mine- and smelter-related contamination (referred to as “background”).
- Estimate background concentration values for COCs (such as arsenic and lead) and other metals detected at the site.
- Identify the area potentially impacted by the mine and smelter operations (referred to as the area of potential site impact [APSI]).

The results of the background study, including delineation of the APSI and estimates of background COC concentrations, are important factors in the remedial decisions pertaining to this site.

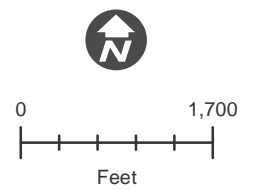
1.2 Report Organization

The report consists of the following sections:

1. Introduction
2. Technical Approach
3. Site Indicator Parameters
4. Identification of Background Boundary
5. Estimates of Background Concentrations
6. Identification of the APSI
7. References



- Streams
- Iron King Mine
- Humboldt Smelter



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Figure 1-1: Iron King Mine Site and Surrounding Region

Iron King Mine - Humboldt Smelter Superfund Site
Dewey-Humboldt, Yavapai County, Arizona

Technical Approach

Arsenic was identified as the primary COC and risk driver for the site. While the distribution of arsenic in soil at and around the site is related to the mine and smelter operations and mine site geology, arsenic also occurs naturally at relatively high concentrations in the surrounding rocks and soils. Therefore, its distribution cannot always be attributed to the site-related operations, and cannot serve as a sole basis for remedial decisions for the site.

The approach developed in this study focuses on identifying specific site-related indicator parameters that could be used to differentiate between site-affected areas and background areas. While these parameters may not necessarily constitute a health risk, they would be used to guide remedial efforts in conjunction with the distribution of COCs and risk drivers such as arsenic and lead. The primary steps of the technical approach used for this background study include the following:

1. Identify site indicator parameters based on the evaluation of available soil data, assessment of the local geologic conditions, and assessment of the potential distribution patterns of chemical constituents associated with the site operations.
2. Identify the background boundary using multiple lines of evidence developed on the basis of the site-specific characteristics, local and regional geology, distribution of soil concentrations, and other factors.
3. Estimate background values of indicator parameters and COCs based on the available soil samples collected in the background area.
4. Identify the APSI based on the estimated background values of the indicator parameters and comparison of these values with available soil concentration data.

These steps are described in detail in Sections 3 through 6.

Site Indicator Parameters

All available soil data obtained from previous studies and incorporated into a site database have been evaluated in order to identify the most appropriate and defensible parameters that could serve as indicators for the site-related impacts. The concentrations of measured soil constituents were examined using mapping techniques, simple statistics, and geologic associations to identify those constituents that would be most clearly associated with the site. The objective of this part of the analysis was to identify a short list of constituents that are not expected to be present at significant concentrations in the area not affected by site-related activities, and to demonstrate a distinct and consistent difference in concentration between site-affected soil and potential background areas.

3.1 Available Soil Data

Data used for this study included all soil data collected as part of the site investigations between 2002 and 2013, including soil data collected at the mine and smelter properties and adjacent areas, residential soil data, and regional soil samples. Locations of soil samples are shown in Figure 3-1. Soil data used for this study include the results of laboratory analysis of soil samples, as well as samples analyzed in the field by x-ray fluorescence (XRF) spectroscopy. Subsets of samples analyzed by XRF in 2008, 2012, and 2013 also were sent for laboratory analyses using analytical method ISM01.3 in order to develop a correlation (using linear regression formulas) between field XRF and laboratory values (see Appendix A). All XRF data used in this study were adjusted using these regression formulas to be comparable with the laboratory data.

As shown in Figure 3-1, the regional soil samples were collected at some distance from the mine and smelter sites. These data were collected with the intent of better representing natural soil chemistry at locations that were not expected to be impacted by the mine- and smelter-related sources. As explained below, the regional data demonstrated some marked differences in trace metal concentrations and some other parameters compared to site- and near-site samples. These differences formed the basis of the approach for identifying background and site-affected areas.

3.2 Geology of the Study Area and Metals

Regional geologic conditions have been evaluated as part of this study to assess natural sources of metals encountered at the site, and determine whether some of these metals are uniquely characteristic of the Iron King Mine and Humboldt Smelter conditions.

3.2.1 Regional Geologic Conditions

The Iron King Mine and Humboldt Smelter are located on the southern edge of Lonesome Valley, the geology of which consists of Precambrian metamorphic rocks overlain by Tertiary volcanic and sedimentary rocks of the Hickey Formation (Figure 3-2).

The Precambrian rocks consist primarily of volcanic breccias, andesitic volcanics, and intrusives (Creasey, 1952). The volcanic breccias are found as two belts, located in the western and eastern portions of the region. The andesitic volcanics are found in the central portion of the region. Intrusive igneous rocks present in the region are composed of diorites, granodiorites, quartz porphyry and gabbro, quartz porphyry, gabbro, rhyolite dikes, and a large quartz diorite. These Precambrian rocks have generally been metamorphosed to a greenschist facies (Creasey, 1952).

The Tertiary Hickey Formation consists of basalt lava flows and sedimentary rocks with fanglomerate, mudflow, and interbedded rhyolitic and basaltic tuffaceous materials (Krieger, 1965).

The Precambrian metamorphic rocks include five local members (Iron King volcanics, Spud Mountain volcanics, Chaparral volcanics, Green Gulch volcanics, and the Texas Gulch Formation). The Iron King Mine is located within the Spud Mountain volcanics unit of the Precambrian metamorphic rocks. The mill area and support areas for the

Iron King Mine are located within the sedimentary rock portion of the Tertiary Hickey Formation. The Humboldt Smelter is located within an area that includes the basalt and sedimentary rocks of the Tertiary Hickey Formation and Iron King volcanics unit of the Precambrian metamorphic rocks (Figure 3-2).

3.2.2 Iron King Mine and Mineralization of Base Metals (Zinc and Cadmium)

Within the Precambrian rock units, there are numerous northwest trending quartz veins, including the Iron King Mine vein. The two primary types of quartz veins present in the area are massive sulfide vein deposits and fissure vein deposits. However, massive sulfide vein deposits are only present in the Iron King Mine, and are not encountered anywhere else in the region (Krieger, 1965). These sulfide deposits include base metal deposits dominated by zinc, lead, and cadmium, sometimes with a component of gold and silver. The Iron King Mine is a zinc-lead mine with the dominant sulfide being pyrite (FeS_2). Besides the main ore minerals such as sphalerite (ZnS) and galena (PbS), other sulfides that are present in Iron King Mine include silver-bearing tennantite $[(\text{Cu},\text{Fe})_{12}\text{As}_4\text{S}_{13}]$, arsenopyrite (FeAsS), chalcopyrite (CuFeS_2), and gold. Note that mineralization associated with the Iron King Mine deposit is relatively narrow, with a maximum width of only 75 feet (Ralph and Chau, 2013; Figure 3-2).

The fissure quartz vein deposits that are present in the region surrounding the Iron King Mine include gold-quartz veins of Precambrian age and gold and silver veins of possibly late Mesozoic or Early Tertiary age with only limited amounts of sulfides (Krieger, 1965). These deposits generally have limited concentrations of base metals such as zinc and cadmium (cadmium is generally associated with zinc). Based on the above, the Iron King Mine is the only base metal massive sulfide deposit in the region, and consequently is expected to have significantly higher concentrations of base metals such as zinc and cadmium in comparison to the rest of the region.

3.2.3 Arsenic and Lead

Arsenic and lead, while associated with the Iron King Mine, are also encountered at elevated concentrations in the surrounding regions. Arsenic is elevated at the Iron King Mine deposit due to the presence of arsenic-bearing sulfide minerals. However, the Iron King Mine deposit is not the only mineral deposit in the region with arsenic-bearing minerals. Naturally occurring arsenic is common for gold-bearing veins (such as the fissure quartz vein deposits described above), because of the presence of arsenopyrite, and is also associated with silicic volcanic materials such as rhyolite, which is widely present within the region. Additionally, arsenic may be found in areas where pesticides have been used.

Lead is also elevated at the Iron King Mine as a result of the mineral deposit. However, other sources of lead, especially in the residential areas, could include lead-based paint and leaded gasoline.

3.2.4 Copper and Aluminum

The Humboldt Smelter, which was primarily a copper smelter, was using ore from at least 50 different mines in the Arizona area (Archaeological Consulting Services, 2008). Two mines that were the primary sources for the smelter included the Blue Bell Mine and the Desoto Mine, located south of Mayer, Arizona (Archaeological Consulting Services, 2008). Both the Blue Bell Mine and the Desoto Mine were base metal deposits that primarily contained pyrite and chalcopyrite with minor amounts of sphalerite, galena, and arsenopyrite (Lindgren and Heikes, 1926). A limited amount of the mineral tetrahedrite $[(\text{Cu},\text{Fe})_{12}\text{Sb}_4\text{S}_{13}]$ was also found at the Desoto Mine. In summary, the two principal sources of ore imported to the Humboldt Smelter were base metal mines that were much richer in copper than the Iron King Mine. While no information is available for other ore sources for the smelter, it is likely that these sources were also from base metal mines.

Another historical site activity that involved imported material was the use of aluminum dross on the Humboldt Smelter property. The remaining dross piles represent a source of enriched aluminum in soil compared to surrounding areas. Aluminum also occurs in enriched concentrations in some volcanic rocks (especially rhyolite) within the region, and the local geology of the Iron King Mine is actually lower in aluminum than regional geologic materials due to the concentration of sulfide deposits. However, the dross is a more concentrated source than any local or regional geologic source of aluminum.

3.3 Identification of Indicator Parameters

The final step in identifying indicator parameters for the site-affected area was evaluating distribution patterns for all metals detected in available soil samples, with an emphasis on metals identified during the assessment of the geologic conditions discussed in Section 3.2.1. The evaluation of metal distribution patterns included the following steps:

1. Statistical analysis of soil samples to include estimates of concentration ranges, means, medians, and standard deviations
2. Plotting distributions in map view of the most promising metals to identify a pattern that would indicate a distinct separation in values between the mine and smelter site/near-site concentrations and regional concentrations of these metals

The statistical distributions of metals that were expected to occur at higher concentrations near the mine and smelter sites, based on the analysis of geologic conditions (i.e., zinc, cadmium, copper, lead, arsenic, and aluminum), were specifically examined to assess the presence of a distinct contrast between the mine and smelter site/near-site and regional concentrations of these metals. The distributions of elements such as antimony and vanadium were also examined because they were expected, on the basis of geology, to occur at higher concentrations in the regional samples collected at significant distance from the mine and smelter sites. The results of this analysis are discussed below.

3.3.1 Zinc and Copper

Based on this concentration mapping analysis, zinc and copper demonstrated a clear and consistent difference between the site/near-site concentrations and regional concentrations. Figures 3-3 and 3-4 show the distribution of zinc and copper concentrations in soil, respectively. The distribution of zinc, including high zinc concentrations at the mine and smelter site, reflects the geology of the mine site (that is, high zinc is associated with Iron King Mine massive sulfide deposits). The distribution of copper (the high copper concentrations at the Humboldt smelter) is characteristic of the historical smelter operations (see Section 3.2). As shown in Figures 3-3 and 3-4, concentrations of both metals drop abruptly with distance from the mine and smelter, in areas north of the Dewey-Humboldt town. These concentration distributions support the conclusion of the geologic analysis presented above regarding limited occurrence of both metals in the regional geology outside immediate proximity to the mine and smelter.

3.3.2 Cadmium and Lead

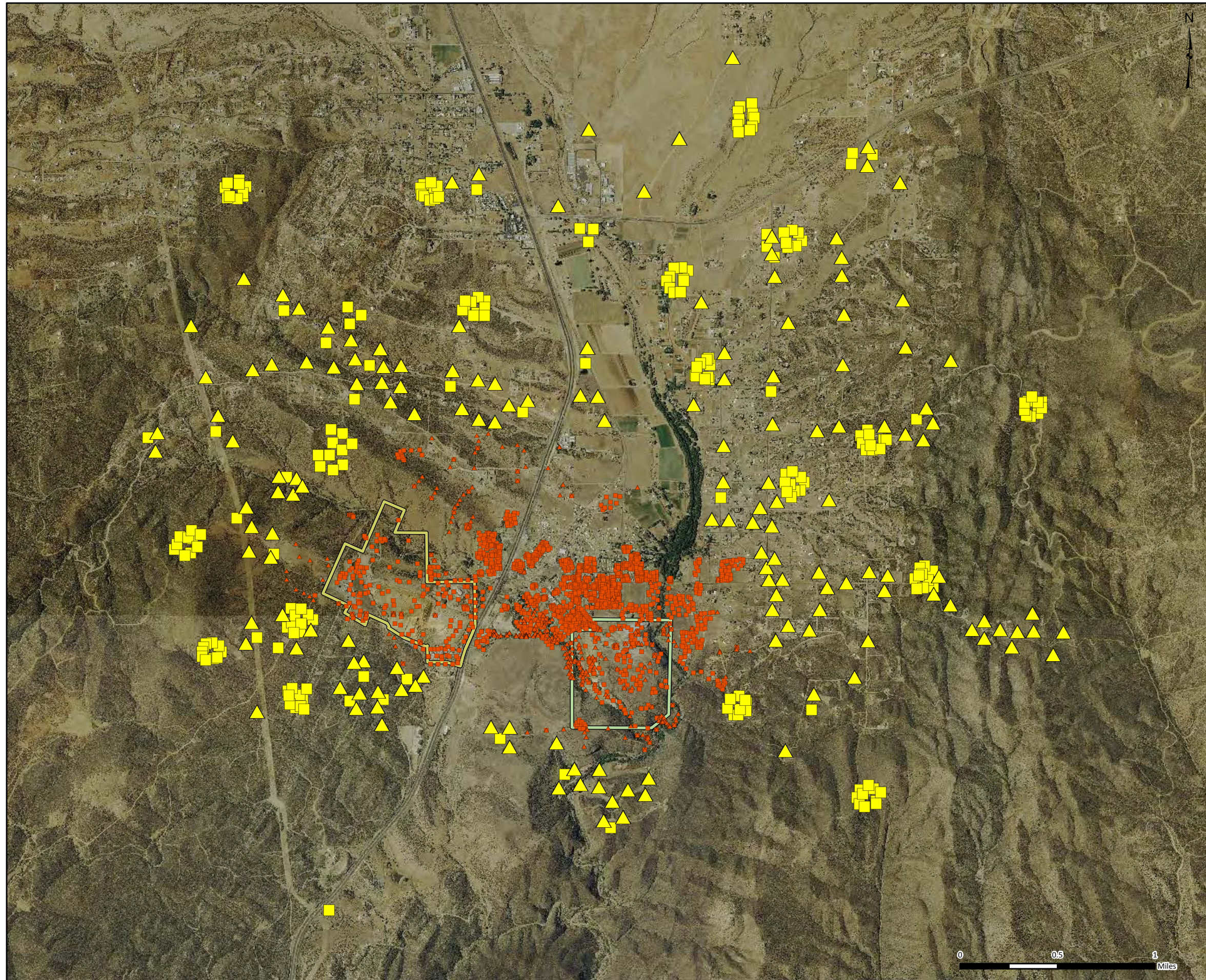
Other base metals such as cadmium and lead also demonstrated a similar distribution pattern of abrupt concentration decrease with distance from the mine and smelter, but the pattern displayed by zinc and copper was more pronounced. The distribution of cadmium was similar to that of zinc, but cadmium was much less abundant in sulfide deposits, and its concentrations dropped below detection limits with distance from the mine. Lead has other potential anthropogenic sources in addition to the mine- and smelter-related operations (for example, lead-based paint and leaded gasoline); therefore, its distribution was less consistent than that of zinc and copper.

3.3.3 Aluminum and Arsenic

Arsenic and aluminum distributions did not exhibit a clear pattern of concentration drop with distance from the mine and smelter. As discussed above, arsenic is present at high concentrations in both the Iron King Mine massive sulfide deposits and in fissure quartz vein deposits, as well as other materials present in the region. Elevated arsenic concentrations in upland soils east of the Aqua Fria River are associated with the presence of arsenopyrite within the numerous quartz veins in this area. Based on the above, arsenic cannot be used for differentiating between the area impacted by the site-related sources and naturally occurring deposits (see Section 3.2). Similar to arsenic, the distribution of aluminum is impacted by enriched concentrations of this metal in volcanic rocks encountered within the region (see Section 3.2).

3.3.4 Indicator Parameters

Based on the above discussion, zinc and copper were identified as the primary indicator parameters for the mine and smelter-affected area. The distribution of zinc is a better indicator for the mine-related impacts, whereas the distribution of copper is more characteristic of the smelter-related impacts. The data for antimony, vanadium, and other elements evaluated as part of this study did not indicate statistically significant separation between the mine- and smelter vicinity and regional data to be usable as indicator parameters



- Samples at and near the Iron King Mine, Humboldt Smelter, and residential areas**
- Laboratory Samples
 - ▲ XRF Samples
- Regional Samples***
- Laboratory Samples
 - ▲ XRF Samples
- ▭ Humboldt Smelter
- ▭ Iron King Mine

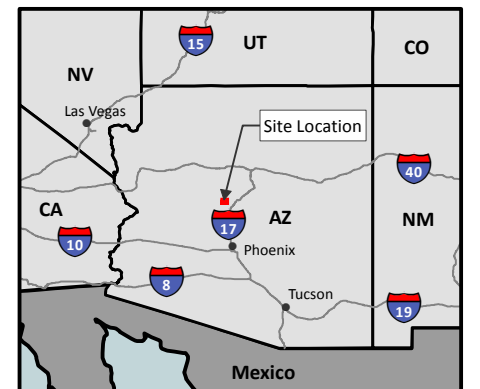
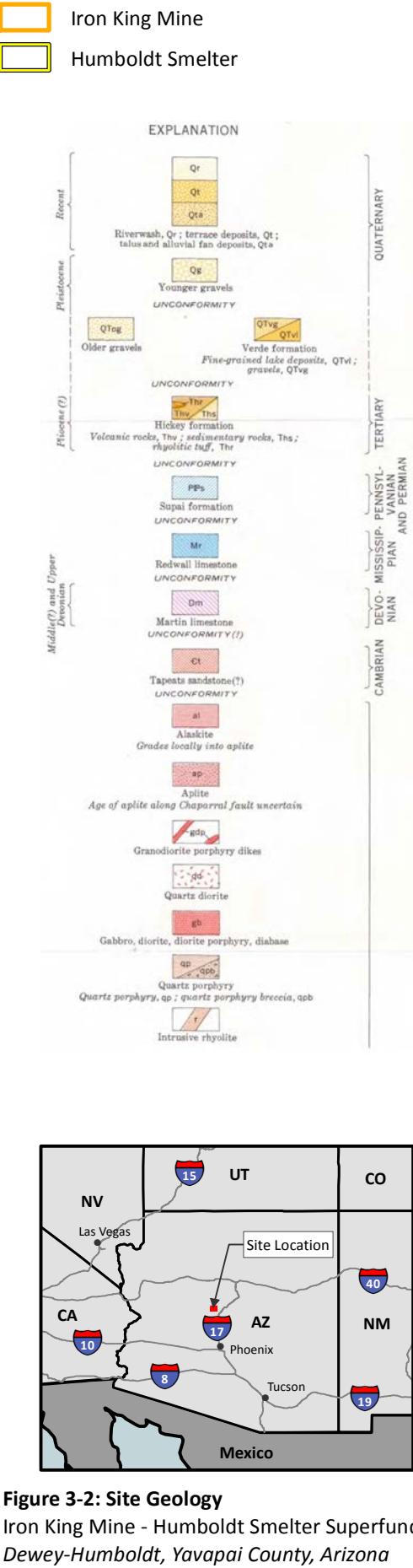
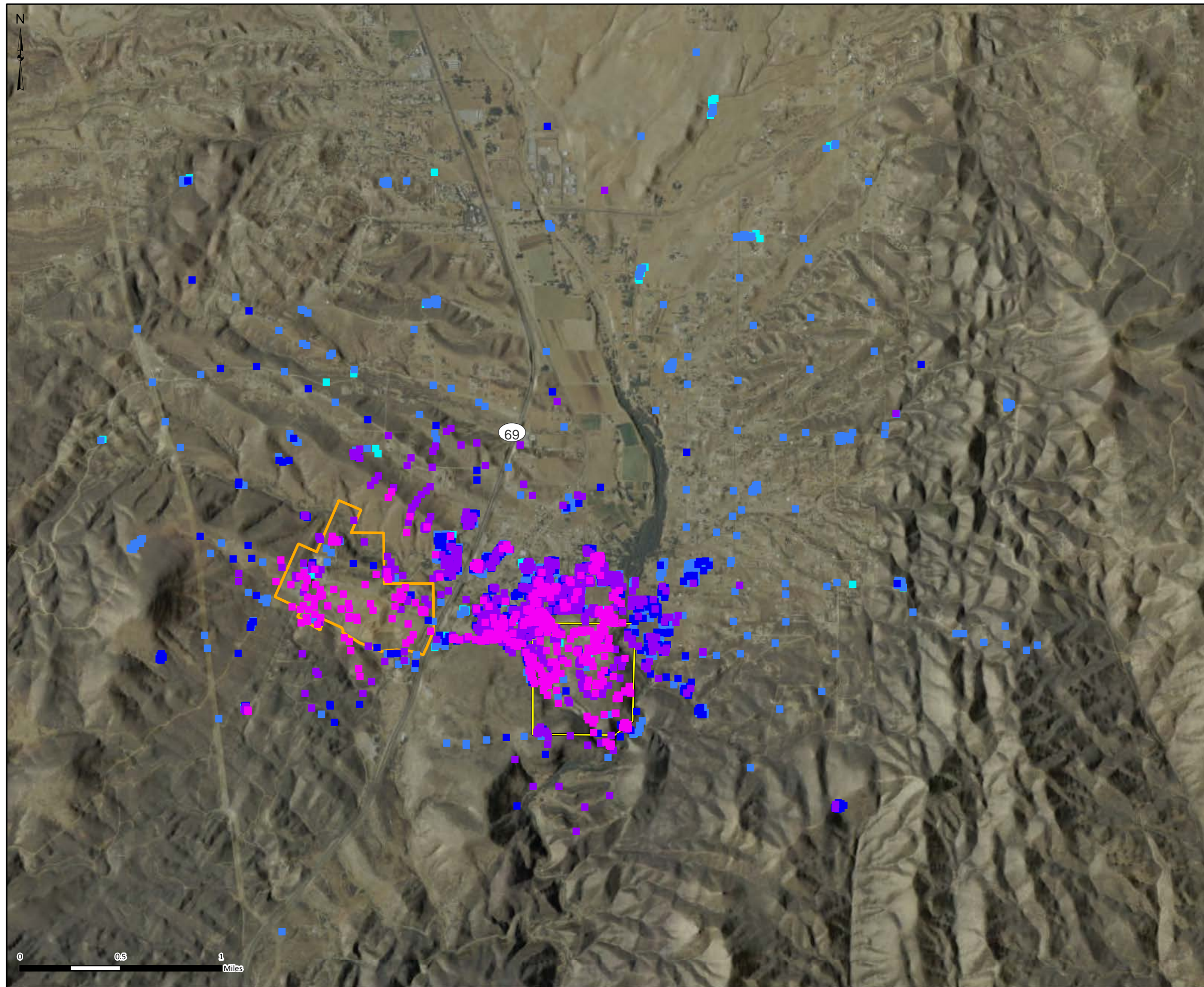


Figure 3-1: EPA Investigation of Naturally-Occurring (Background) Metals in Soils
Iron King Mine - Humboldt Smelter Superfund Site
Dewey-Humboldt, Yavapai County, Arizona





- Iron King Mine
- Humboldt Smelter

Zinc Concentration in Soil

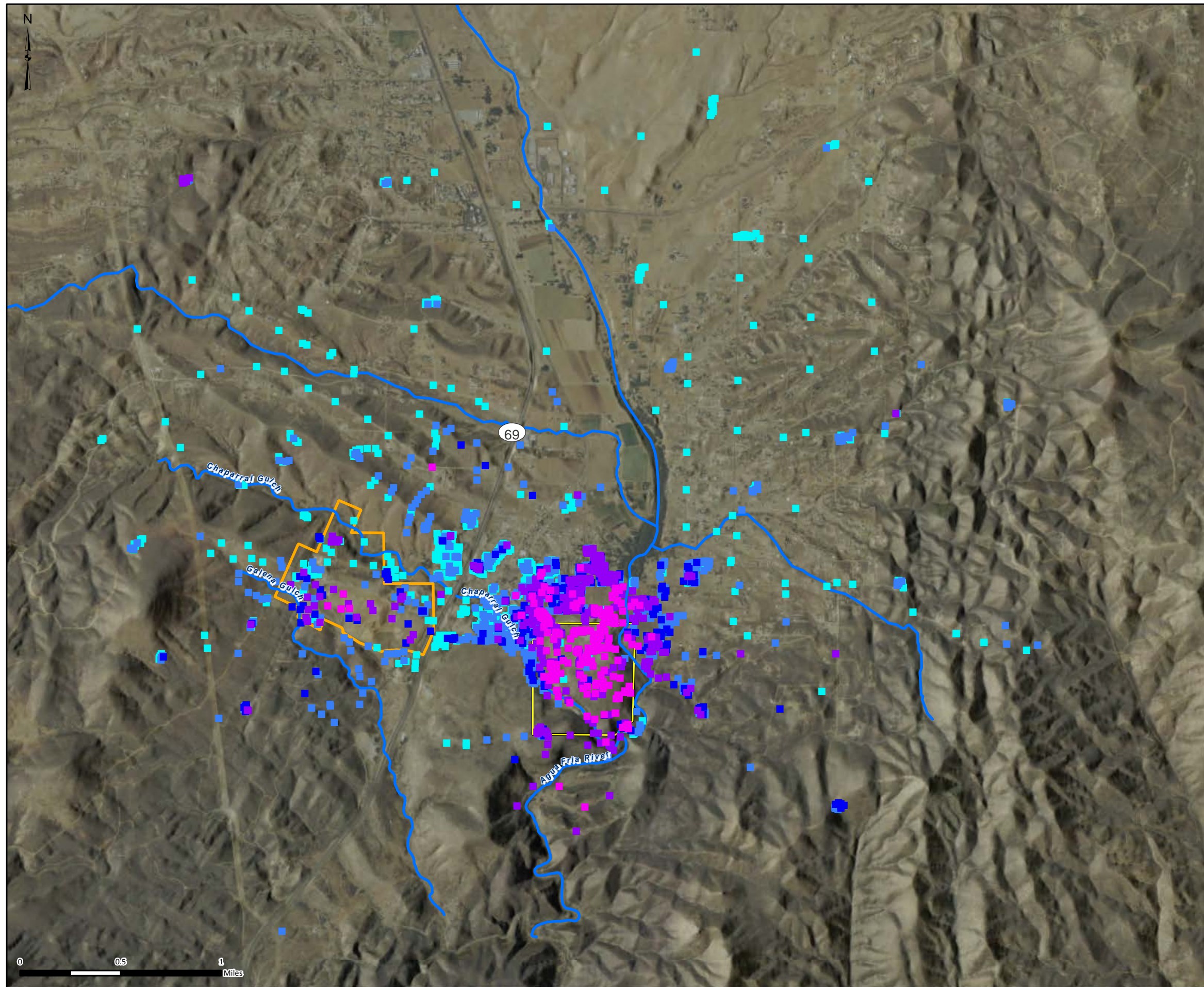
- <50 mg/kg
- ≥50 and ≤100 mg/kg
- >100 and ≤150 mg/kg
- >150 and ≤500 mg/kg
- >500 mg/kg

Notes:
Imagery Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community



Figure 3-3: Zinc Concentrations in Shallow Soil Samples

Iron King Mine - Humboldt Smelter Superfund Site
Dewey-Humboldt, Yavapai County, Arizona



- Streams
- Iron King Mine
- Humboldt Smelter
- Copper Concentrations in Soil**
 - <50 mg/kg
 - ≥50 and ≤100 mg/kg
 - >100 and ≤150 mg/kg
 - >150 and ≤500 mg/kg
 - >500 mg/kg

Notes:
Imagery Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community



Figure 3-4: Copper Concentrations in Shallow Soil Samples
Iron King Mine - Humboldt Smelter Superfund Site
Dewey-Humboldt, Yavapai County, Arizona

Identification of Background Boundary

Selection of the defensible and clearly defined background soil dataset is the next step of the background study approach discussed in this report. The observed rapid decrease in concentrations of the indicator metals with distance from the mine and the smelter described in Section 3 serves as an initial line of evidence that a clear separation exists between naturally occurring soil constituents and those resulting from the mine and smelter operations. This section discusses an additional line of evidence that was used to delineate the boundary between the area potentially impacted by the mine- and smelter-related sources and a background area.

The conceptual model for the background evaluation approach is that soils in the vicinity of the mine and smelter were potentially impacted by a combination of wind-blown dust and stack emissions, along with some fill and roadbed application of mine and smelter soil and/or waste rock/tailings. Based on these potential transport mechanisms for the mine- and smelter-related contaminants, the surface and near-surface soils were likely more impacted by the mine and the smelter than deeper soils. Consequently, the concentrations of mine- and smelter-related contaminants are expected to be higher in surficial soils than those in deeper soils in the areas impacted by the mine and smelter operations. By contrast, natural soils that have not been impacted by the site would not be expected to have shallow soil concentrations of chemical constituents that are significantly elevated compared to deeper soils. Consequently, it is expected that a ratio of shallow to deep soil concentrations would be higher for the mine- and smelter-affected soils than natural soils, for which shallow and deep concentrations are expected to be more comparable. Based on the above, the ratio distribution of shallow to deep concentrations can be used for delineation of the natural unaffected soils that could be considered background.

The ratios of shallow to deep concentrations were calculated for indicator metals and COCs identified in Section 3, including zinc and copper (the selected indicator metals), and arsenic and lead (COCs). All locations for which both shallow and deep samples were available were used for this analysis. Shallow samples were defined as samples with a top depth of zero feet below ground surface (bgs); deep samples were defined as samples with a top depth greater than zero feet bgs.

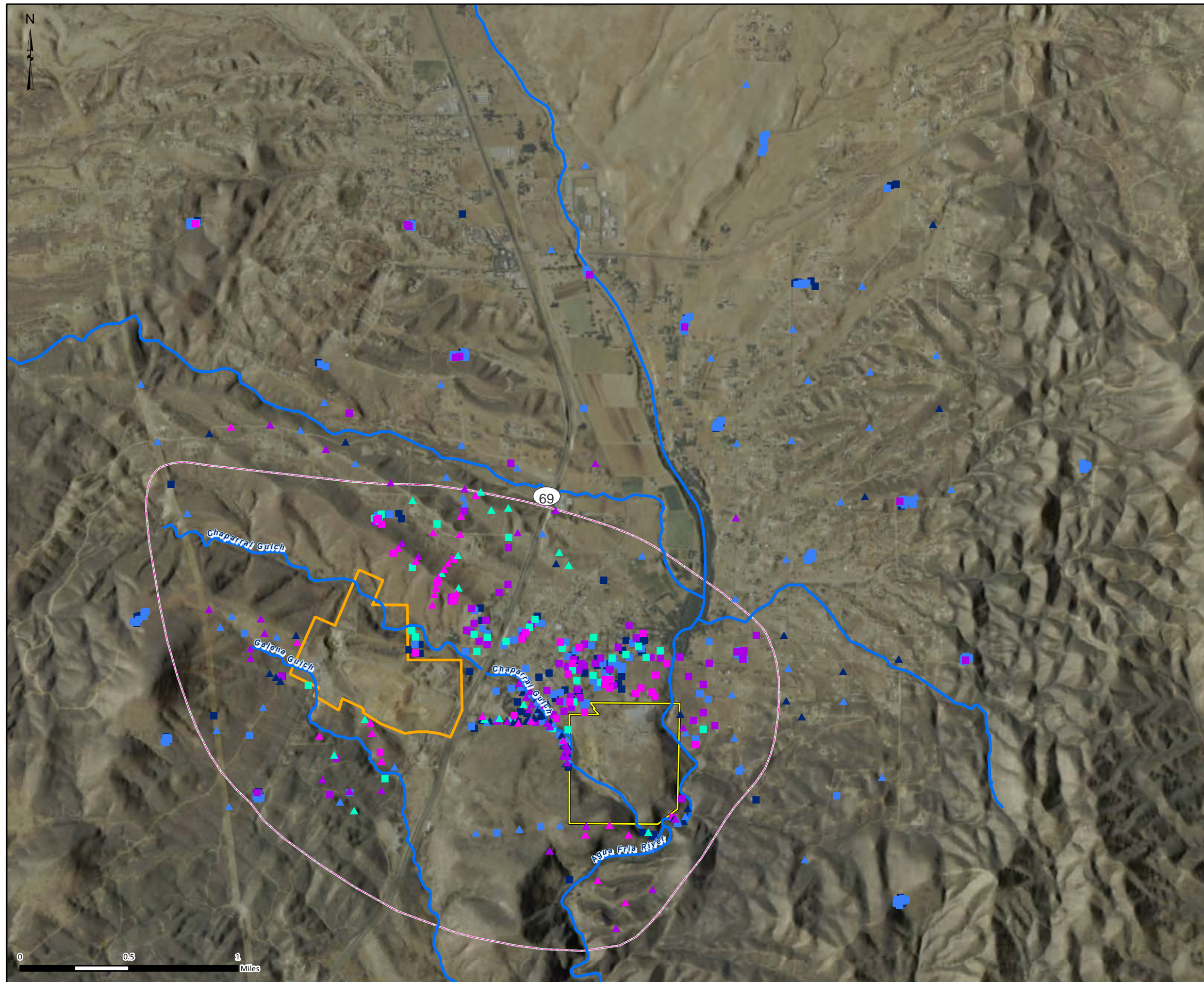
The ratio distribution plots for zinc, copper, arsenic, and lead are shown in Figures 4-1 through 4-4. These distributions consistently indicate that ratios of shallow to deep concentrations above 2.5 for these metals are largely limited to the areas at and near the mine and smelter. Similar to the concentrations of indicator metals, the ratio values for samples collected at a distance were consistently lower than those collected closer to the mine and smelter, and mostly below the value of 2.5. Based on these ratio distribution plots, a ratio of 2.5 appears to be a reasonable threshold value for demarcating the naturally occurring soil representing background for the study area (that is, soils in which ratio values are mostly above 2.5 are considered to be potentially impacted by the mine and the smelter; and soils in which ratio values are mostly below 2.5 are considered to represent background).

An oval shape in Figures 4-1 through 4-4 delineates a frequency of occurrence for the threshold shallow to deep concentration ratio of 2.5 for each of the metals. The frequency for the ratio values above 2.5 is significantly higher inside the oval shape, and lower outside the shape. As shown in these figures, the ratio distribution patterns are relatively similar for all metals considered, and resulted in the same consistent oval shape that demarcates the boundary between the potentially impacted and naturally occurring (background) soils. This consistency in the ratio distribution for all four metals indicates that the shallow to deep concentration ratio of 2.5 is a distinct site-specific characteristic that can be used at this site for distinguishing background soils from potentially impacted soils. Based on this analysis, the soils in the area outside the oval shape are interpreted to represent the background; and soils inside the oval shape may potentially be impacted by the mine and smelter and need to be further evaluated (see Section 6). The oval shape separating the potentially impacted soils from soils representing background is referred to as the “background boundary.”

Figure 4-5 further demonstrates the basis for, and validity of, the ratio analysis described above for the delineation of background. It shows a graph of shallow to deep ratios for the same metals (zinc, copper, arsenic,

and lead) versus the distance from the smelter and the mine in the northern direction. The approximate northern boundaries of the mine and smelter, as well as the northern extent of the background boundary, are also shown on the graph. The graph indicates a distinct drop at the background boundary from a broad range of concentration ratios with many values being above the threshold of 2.5 to a narrow range of ratio values primarily below 2.5 for all metals. Only a few outliers with a ratio above 2.5 exist outside the northern extent of the background boundary, which represents a small percentage of samples collected in this area. The clear break between values of shallow to deep concentration ratios for samples collected inside and outside the background boundary exhibited on the graph for all four metals further confirms the validity of the conceptual model and approach of this ratio analysis for distinguishing background soils.

Please note, however, that while this ratio analysis appears to be sufficient for separating the background soils from the potentially impacted soils (that is, it allows identification of the background data set), it cannot serve as a sole basis for defining the areas impacted by the mine- and smelter-related sources. As mentioned above, the area potentially impacted by the mine and smelter is further evaluated based on the background concentrations of indicator parameters and discussed in Section 6.



- Streams
- Iron King Mine
- Humboldt Smelter
- Background Boundary

XRF Zinc Shallow to Deep Ratio

- ▲ <1
- ▲ ≥1 and ≤1.5
- ▲ >1.5 and ≤2.5
- ▲ >2.5 and ≤4
- ▲ >4

LAB Zinc Shallow to Deep Ratio

- <1
- ≥1 and ≤1.5
- >1.5 and ≤2.5
- >2.5 and ≤4
- >4

Notes:
Imagery Source: Esri, DigitalGlobe, GeoEye, Earthstar Geographics, CNES/Airbus DS, USDA, USGS, AEX, Getmapping, Aerogrid, IGN, IGP, swisstopo, and the GIS User Community

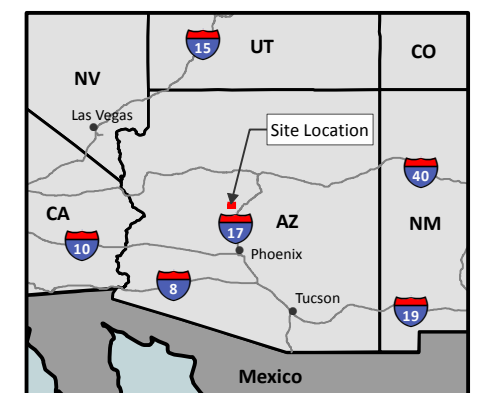
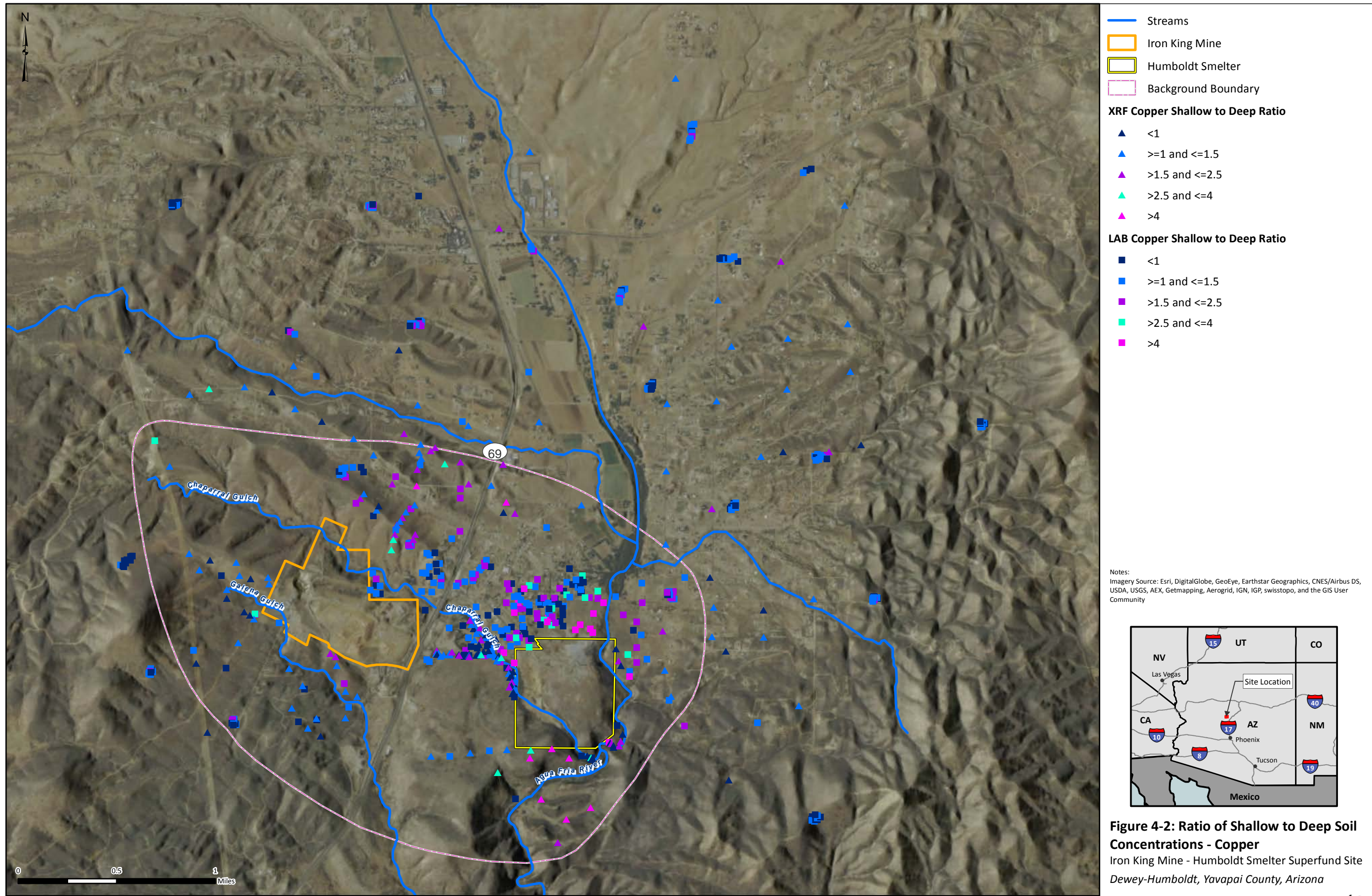
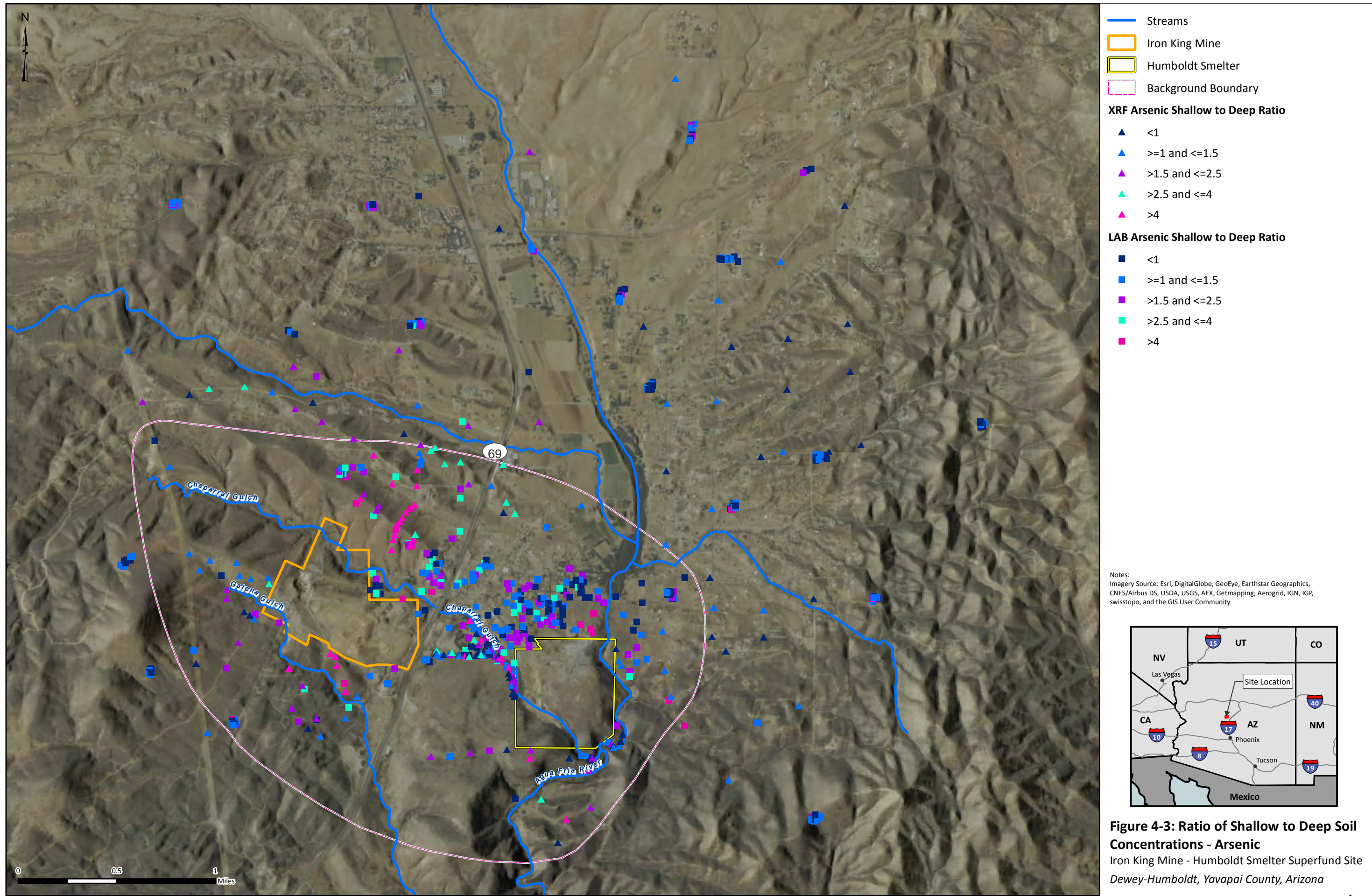
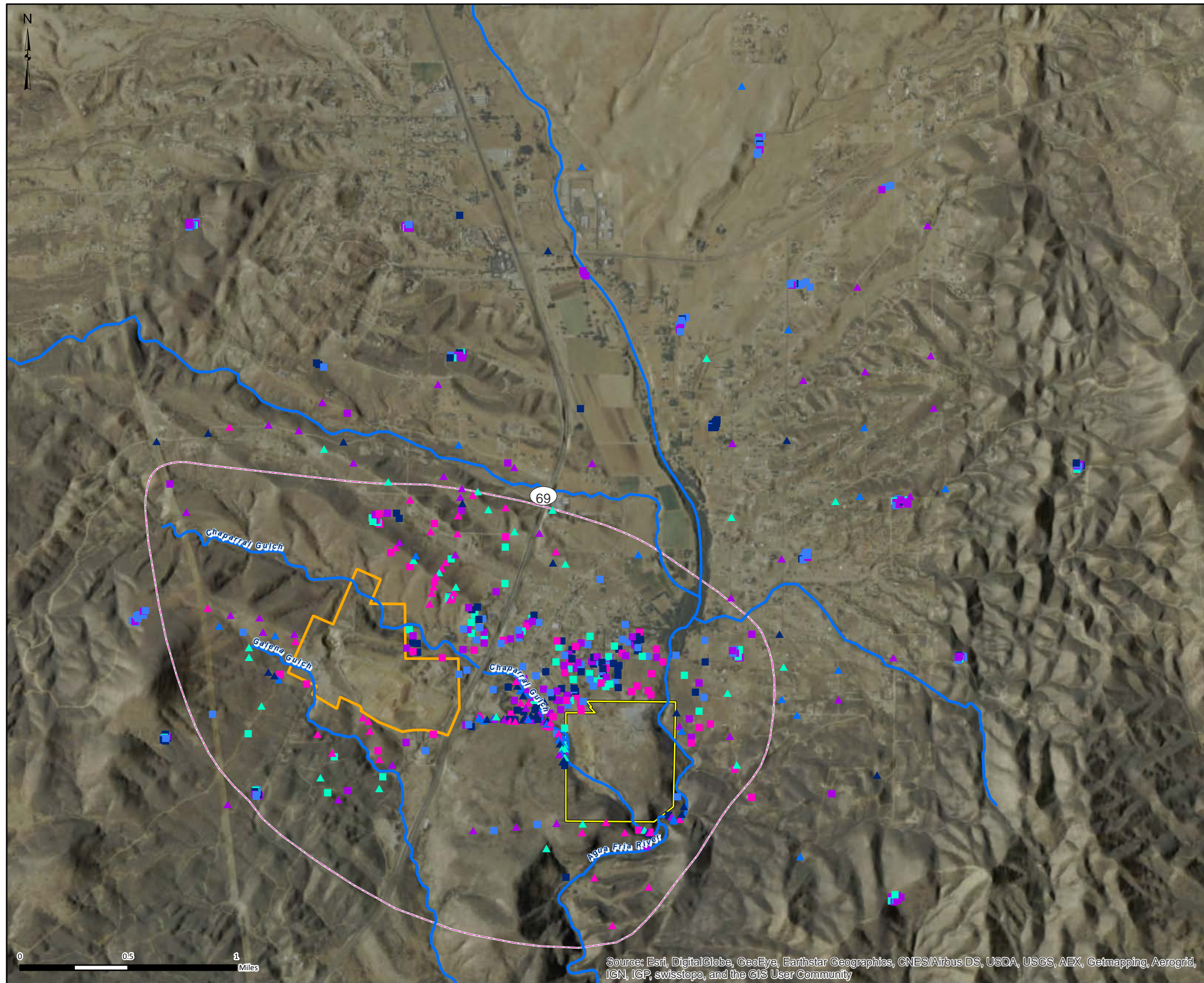


Figure 4-1: Ratio of Shallow to Deep Soil Concentrations - Zinc
Iron King Mine - Humboldt Smelter Superfund Site
Dewey-Humboldt, Yavapai County, Arizona







- Streams
- Iron King Mine
- Humboldt Smelter
- Background Boundary

XRF Lead Shallow to Deep Ratio

- ▲ <1
- ▲ ≥1 and ≤1.5
- ▲ >1.5 and ≤2.5
- ▲ >2.5 and ≤4
- ▲ >4

LAB Lead Shallow to Deep Ratio

- <1
- ≥1 and ≤1.5
- >1.5 and ≤2.5
- >2.5 and ≤4
- >4

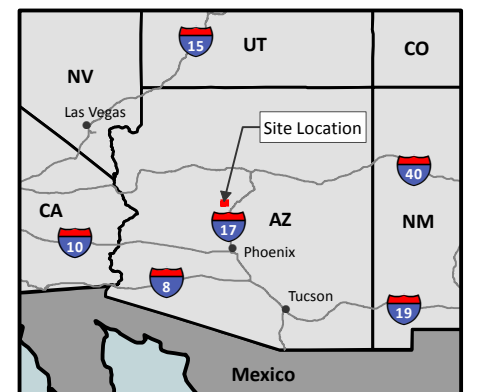


Figure 4-4: Ratio of Shallow to Deep Soil Concentrations - Lead

Iron King Mine - Humboldt Smelter Superfund Site
Dewey-Humboldt, Yavapai County, Arizona

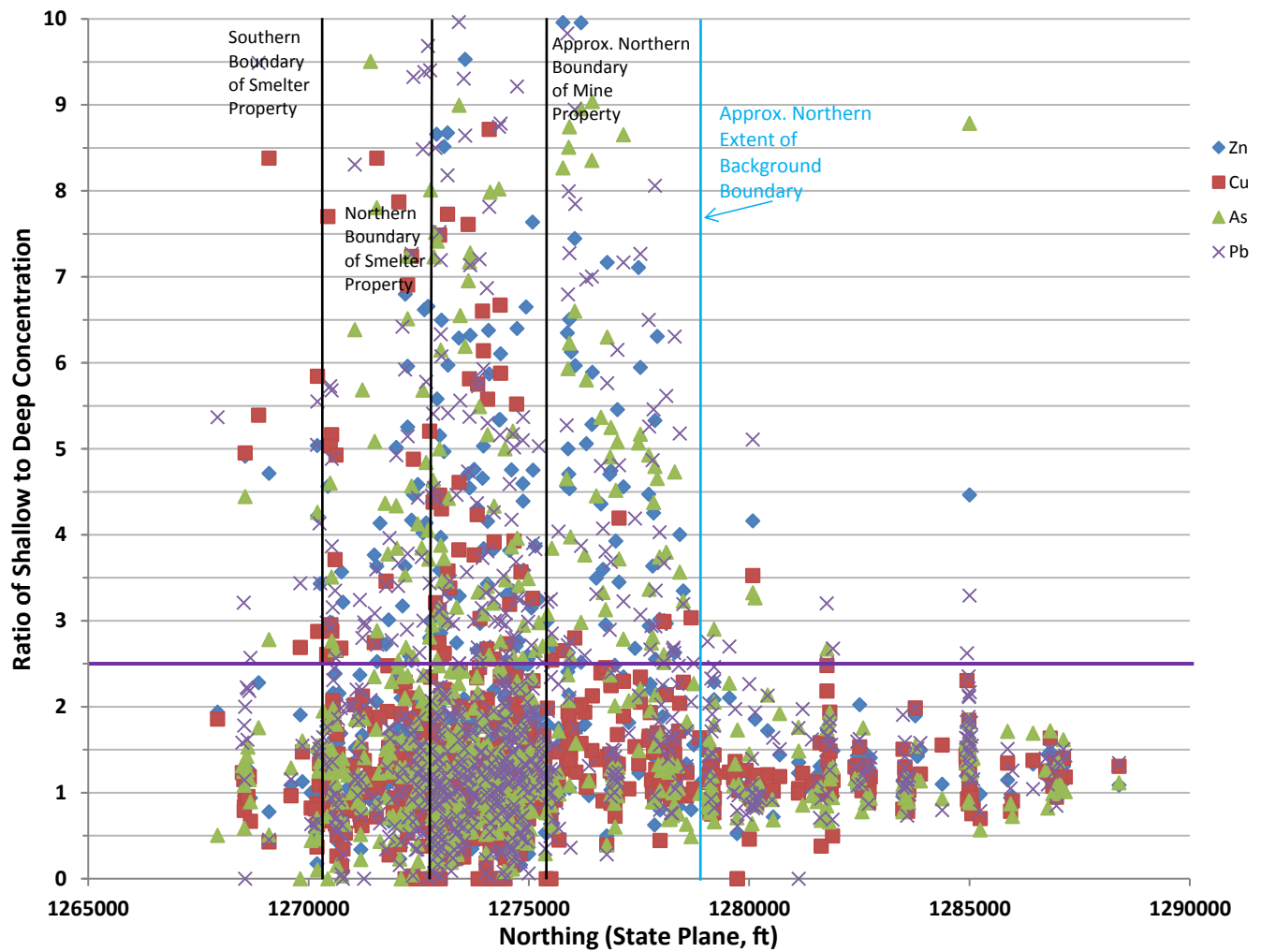


FIGURE 4-5
**Ratios of Shallow to Deep Soil Concentrations
 Versus Northward Distance**
*Iron King Mine – Humboldt Smelter Superfund Site
 Dewey-Humboldt, Yavapai County, Arizona*

Estimates of Background Concentrations

This section presents the statistical methodology and results of the estimation of the background concentrations of the indicator parameters and COCs. The indicator parameters and COCs are discussed in detail in Section 3.

5.1 Statistical Methodology

The statistical analysis of sampling data within the background area identified in Section 4 was performed in order to estimate background values for the indicator metals (zinc and copper) and site COCs (arsenic and lead). The analysis included estimates of the 95th upper tolerance limit (95/95 UTL) for these metals. The 95/95 UTLs are typically used in background investigations as bounding values designed to be greater than 95 percent of the values in the background population with a confidence of 95 percent. This is a conservative approach for defining background concentrations, because it allows up to 5 percent of soil samples with concentrations of target metals equivalent to the upper tail of background values to exceed the UTL and be considered “above background.”

The 95/95 UTLs were calculated using either a distributional assumption (when deemed appropriate for the background data set) or using a nonparametric (no distributional assumption) approach when evidence for a particular distribution was not available. The distributional assumptions for the soil data included the normal, lognormal, and gamma distributions. These distributional assumptions are discussed in the U.S. Environmental Protection Agency (EPA) ProUCL software package (EPA, 2009 and 2010).

The UTLs for arsenic, lead, and zinc were calculated assuming the data adhered to a lognormal distribution. For copper, however, the ProUCL rank-based approach was used to calculate the UTL, because no discernable distribution was available (EPA, 2009 and 2010).

5.2 Screening of Background Data Set

Prior to statistical analysis, the background data set (the soil samples collected in the area identified as background) have been evaluated with regard to spatial differences in samples collected west and east of the Aqua Fria River, as well as differences in samples collected at shallow and deeper depths. The objective of this evaluation was to determine whether background values should be calculated based on the combined sampling data set, or separate data sets of samples collected in different areas and/or different depth intervals. The results of this evaluation are briefly discussed in Sections 5.2.1 and 5.2.2. In addition, the background samples were screened to remove anomalous data. As a result, several samples, which contained significantly elevated concentrations of arsenic and copper, were removed from the background dataset due to their locations near the fault contact with quartz veins.

5.2.1 Spatial Distribution

The background data sets from the areas east and west of the Aqua Fria River were evaluated to assess the potential differences in background concentrations of the indicator metals and COCs. This analysis was performed because concentrations of arsenic are highly variable in soil samples in the background area due to the high variability of rock types and distribution. The higher concentrations of natural arsenic appear to occur in the eastern part of the region (east of the Aqua Fria River), where rhyolitic tuffs are common in the Spud Mountain, Indian Hills, and Texas Gulch Formations (Figure 3-3). These rocks tend to have higher concentrations of arsenic than the other mixed volcanic and sedimentary rocks in the area. As a result, background shallow soil samples collected on the east side of the Aqua Fria River range in arsenic concentration from 5.7 to 421 milligrams per kilogram (mg/kg) (with mean of 49.2 mg/kg), while the background samples collected on the west side of the river range from 3.4 to 92.7 mg/kg (with a mean of 20.9 mg/kg).

However, the mine and smelter sites, and the adjacent areas, including the Dewey-Humboldt town, are generally situated at the convergence of drainages flowing from both the eastern and western parts of the region. These drainages have likely both contributed to the composition of soils in these areas. Therefore, the contribution of metals from the background areas is likely represented by a mixture of higher-arsenic-concentration soils derived

from alluvial washout from the eastern part of the region and a lower-concentration washout from the western part of the region. In addition, these drainages, including the Aqua Fria River, have altered their courses over recent geologic time, which further complicates the variable mixing pattern impacting the soils near the mine and smelter and in the town area. This complex mixing pattern of alluvial washouts from areas with high variability of arsenic sources makes it impossible to differentiate between the impacts of background sources from the areas east and west of the Aqua Fria River. Consequently, the final representative background values for the indicator metals and COCs were estimated based on the combined data set of samples collected in the areas east and west of the Aqua Fria River.

5.2.2 Depth Distribution

Deep and shallow samples from the background data set were also evaluated to assess if one, or a combination, of these data sets is more appropriate for estimating representative background values. While three sets of soil samples (shallow, deep, and a combination of both) were initially considered, the shallow sample data set was ultimately selected for calculating the final representative background values for the following reasons:

1. There are more samples in a shallow data set than in a deep data set, which makes it a more statistically representative.
2. The natural variability of metals, such as arsenic, is higher in the shallow data set than in the deep data set; capturing this variability is important for estimation of the representative background values.
3. People are more likely to be exposed to COCs in the surficial soils than in deeper soils; consequently, understanding background concentrations of COCs in surficial soils is more important.

5.3 Results of Statistical Analysis

The results of statistical analysis are presented in Table 5-1. These results include summary statistics and 95/95 UTL values for the indicator parameters such as zinc and copper, and site COCs such as arsenic and lead. As discussed above, the 95/95 UTL values were calculated based on shallow soil samples from the combined data set of samples collected east and west of the Aqua Fria River. Table 5-1 also shows the basis for the UTL estimates (that is, whether a parametric [lognormal, gamma] or nonparametric basis was used). None of the four metals were below detection limits (that is, there were no nondetects [NDs]) in any background sample, so no assumed values for NDs were necessary.

The estimated UTLs are 136 mg/kg for zinc, 182 mg/kg for copper, 112 mg/kg for arsenic, and 34.8 mg/kg for lead. These estimates indicate that the UTL for arsenic is significantly higher than that for lead. This is expected based on the regional geologic conditions, because arsenic is commonly found in the volcanic rocks of the region, while lead is scarce outside the massive sulfides of the Iron King Mine area.

TABLE 5-1

Summary Statistics and Calculated UTL Values for Selected Metals*Iron King Mine – Humboldt Smelter Superfund Site, Dewey-Humboldt, Arizona*

Grouping	Parameter	Number of Detects	Number of Analyses	Percent Detects	Minimum Detected Value (mg/kg)	Maximum Detected Value (mg/kg)	Arithmetic Mean Value (mg/kg)	Standard Deviation (mg/kg)	95/95 UTL (mg/kg)	UTL Basis
Shallow Background	Arsenic	268	268	100	3.4	421	39.1	36.2	112	Lognormal UTL
Shallow Background	Copper	265	268	99	11	317	57.1	42.4	182	Non- parametric UTL
Shallow Background	Lead	268	268	100	4.05	89.3	15.6	10.5	34.8	Lognormal UTL
Shallow Background	Zinc	268	268	100	27.3	257	79.3	28.7	136	Lognormal UTL

Identification of the Area of Potential Site Impact

As discussed in Section 2, the final step of the technical approach used for this study is to identify the area potentially impacted by the mine and smelter operations (referred to as the APSI). The identification of the APSI was performed based on the analysis discussed in Sections 3 through 5, and additional evaluation of soils inside the background boundary (soils that have not been considered background) described in this section.

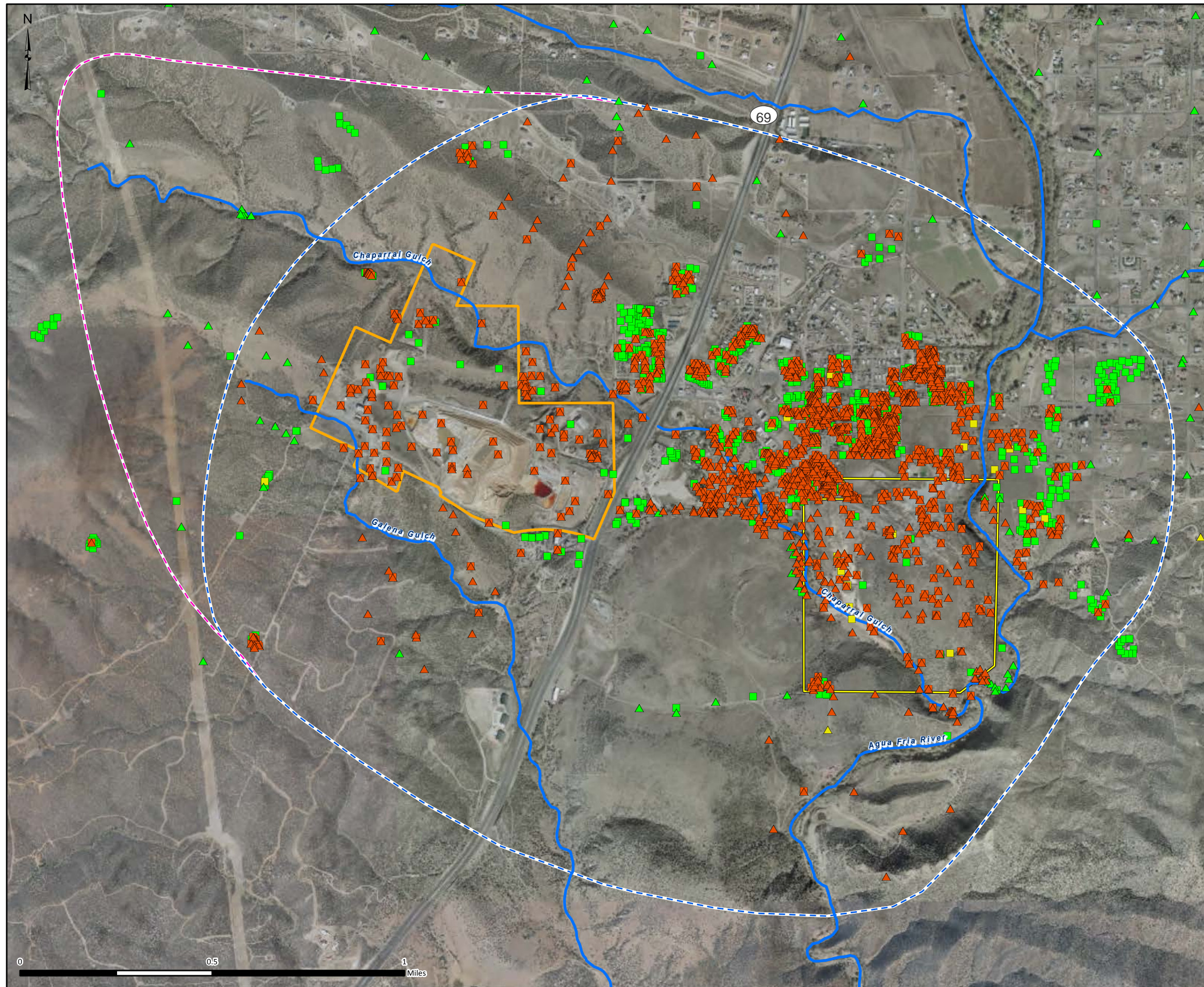
Specifically, Section 3 discusses how the regional geology and historical operations of the mine and smelter have formed a basis for the use of zinc and copper as the indicator metals in identifying soils affected by these operations. Section 4 discusses how the dataset comprising the background samples was defined on the basis of the regional geology, expected range of site influence, and most prominently based on the observed ratios of shallow to deeper soil concentrations of copper, zinc, arsenic, and lead. Section 5 discusses the calculations of statistical UTL values for the indicator metals and COCs using the background dataset to provide an upper bound on the range of background concentrations. This section describes how the estimated background UTLs were used as a statistical basis for identifying the APSI.

As discussed in Section 4, soils in the area outside the oval shape representing the background boundary are designated as background, and soils inside the oval shape could potentially be impacted by the site-related sources. To define the APSI, soils located inside the background boundary (soils that have not been considered background) were further evaluated to determine the extent of potential mine- and smelter-related impacts. For this evaluation, indicator metal concentrations (zinc and copper concentrations) in soil samples collected inside the background boundary (in the area that is not background) were compared to the estimated background values of these metals (the 95/95 UTLs of zinc and copper). Soils with concentrations of zinc and copper exceeding the respective UTLs are likely impacted by the mine and/or smelter operations, because zinc and copper serve as strong indicators for these impacts. Soils that have concentrations of zinc and copper below their respective UTLs are not likely impacted by the mine and smelter operations. The extent of the APSI was defined based on the frequency of shallow sample locations with concentrations of either zinc or copper exceeding their respective UTLs.

Figure 6-1 shows the background boundary as well as the boundary of the area identified as the APSI. Although concentrations of zinc and copper vary within the APSI, most soil samples near the boundary of this area exceed the UTLs for zinc and copper. Therefore, the APSI defines the general lateral extent of soils potentially impacted by the site operations. As shown in Figure 6-1, the extent of the APSI is generally consistent with the background boundary, with the exception of the western side of the area within the background boundary, where concentrations of zinc and copper are generally below their corresponding UTLs. In this area, the extent of the APSI appears to be smaller than the area defined by the background boundary (see Figure 6-1).

Figures 6-2 and 6-3 show UTL exceedances for the site COCs and risk drivers, such as arsenic and lead, within the APSI. Figure 6-2 shows that concentrations of arsenic above the arsenic UTL of 112 mg/kg are found at the mine and smelter sites and in nearby soils, but are less common at greater distances from the site sources. Figure 6-3 shows that lead exceeds the UTL within the APSI more commonly than arsenic. This is likely due to the much lower lead UTL of 34.8 mg/kg.

Please note that arsenic and lead encountered in areas where concentrations of copper and zinc are below their respective UTLs are generally expected to be either naturally occurring or the result of non-site-related activity (for example, pesticide application, lead paint, etc.), even if detected at concentrations above the respective UTLs. This is because this study determined that the mine- and smelter-related impacts, for the most part, are characterized by the above-UTL concentrations of zinc and copper (not arsenic and lead because their concentrations could be elevated due to other non-site-related sources). Please also note that while assessment of potential site impacts and identification of the APSI presented in this report should be considered in the remedial decisions for this site, it is not intended to guide the remedial efforts. Actual areas requiring remediation will be identified after the completion of the risk assessment and feasibility study analysis for this site.



- Streams
- Iron King Mine
- Humboldt Smelter
- Area of Potential Site Impact (APSI)
- Background Boundary

XRF Results

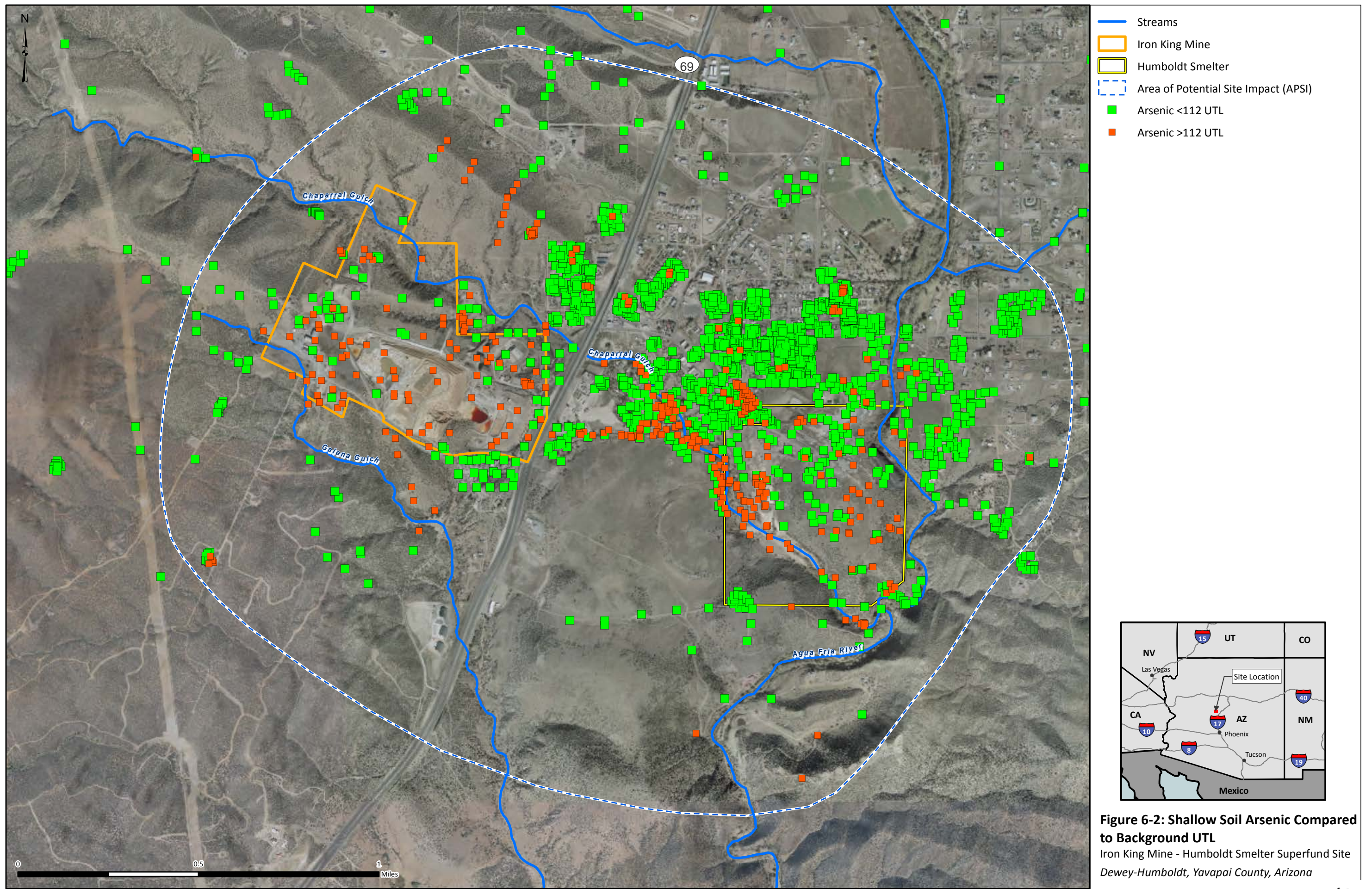
- ▲ Zinc >136
- ▲ Zinc <136 UTL and Copper >182 UTL
- ▲ XRF Zinc <136 UTL and Copper <182 UTL

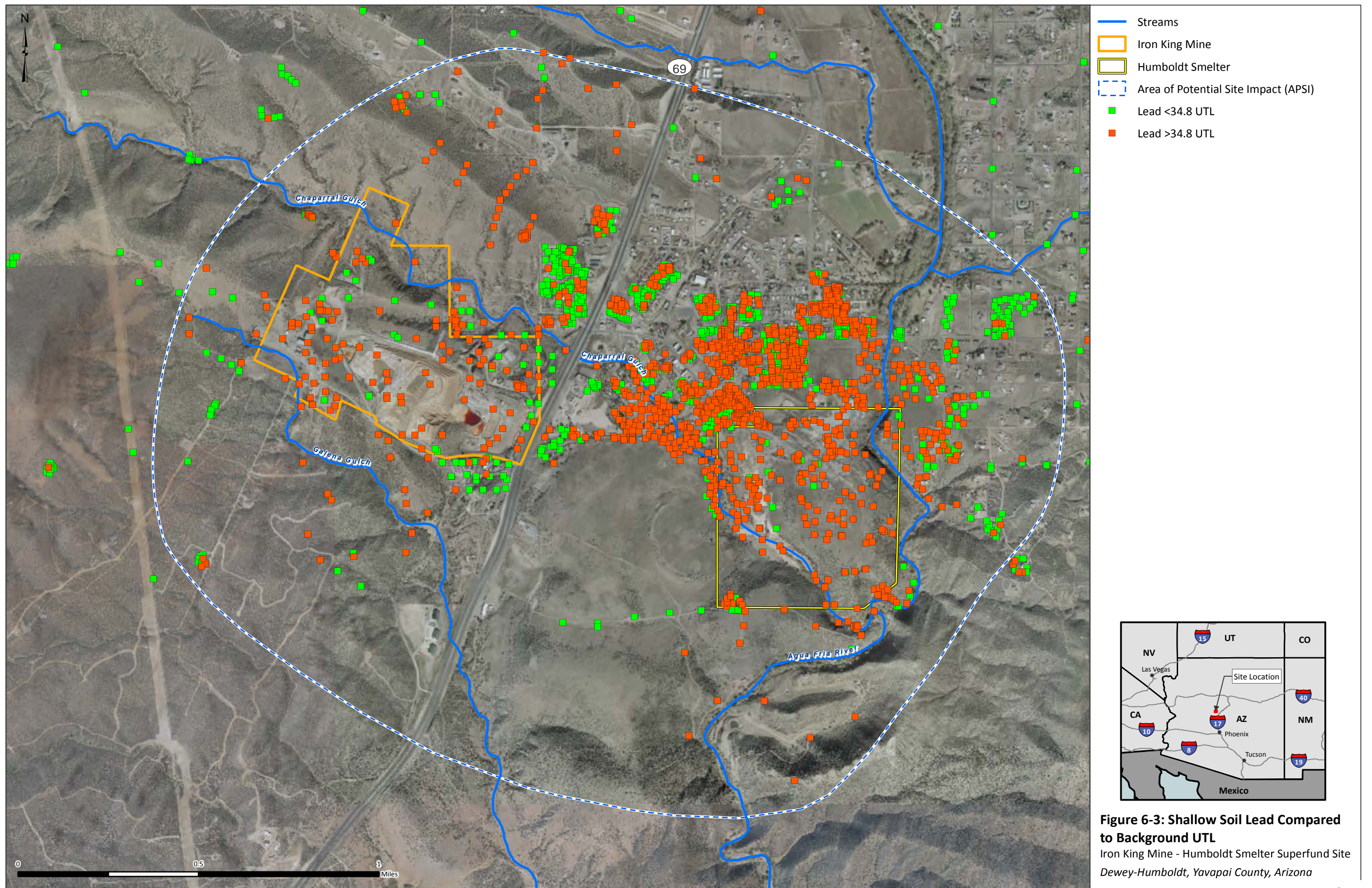
LAB RESULTS

- Zinc >136
- Zinc <136 UTL and Copper >182 UTL
- Zinc <136 UTL and Copper <182 UTL



Figure 6-1: Comparison of Background Zinc and Copper UTL with Soil Concentrations
Iron King Mine - Humboldt Smelter Superfund Site
Dewey-Humboldt, Yavapai County, Arizona





References

Archaeological Consulting Services, Ltd. 2008. *A Cultural Resource and Historic Building Survey for a Remedial Investigation/Feasibility Study at the Iron King Mine-Humboldt Smelter Superfund Site*. Report submitted to EPA.

Creasy, S.C. 1952. "Geology of the Iron King Mine, Yavapai County, Arizona." *Economic Geology*. Vol. 47. pp. 24-56.

Kreiger, M.H. 1965. *Geology of the Prescott and Paulden Quadrangles, Arizona*. U.S. Geological Survey Professional Paper. 467. 127 p.

Lindgren, W. and V.C. Heikes. 1926. *Ore Deposits of the Jerome and Bradshaw Mountains Quadrangles, Arizona*. U.S. Geological Bulletin 782. 192 p.

Ralph, J. and I. Chau. 2013. *Iron King Mine (Lime Rock Patented claim 1714; Copper Platter Patented claim 1714; Patented claims 1714), Humboldt, Big Bug District, Prescott quadrangle, Bradshaw Mts (Bradshaw Range), Yavapai Co., Arizona, USA*. www.mindat.org/loc-50665.html. February.

U.S. Environmental Protection Agency (EPA). 2009. *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities—Unified Guidance*, Office of Resource Conservation and Recovery, March.

U.S. Environmental Protection Agency (EPA). 2010. *ProUCL Version 4.1 Technical Guide (Draft)*, Office of Research and Development.

Appendix A

Laboratory and XRF Data Regression Evaluation

Laboratory and XRF Data Regression Evaluation

Regression analysis was performed on paired samples analyzed for both field X-ray fluorescence (XRF) and laboratory analysis in order to adjust field XRF data to correspond to measured laboratory data. This adjustment was designed to account for inherent differences between the two methods (laboratory analysis and XRF), and should not be viewed as a correction of measured data. Paired laboratory and XRF results for arsenic, copper, lead, and zinc were used to develop regression equations. These equations were used to adjust field XRF data to make them more comparable to laboratory results.

The regression analyses were performed on log 10-transformed data per EPA SW-846 Method 6200 to account for the relatively broad concentration range measured for metals listed above. Although the log transformation typically reduces the impact of outliers on the regression analyses, some “influential” outliers (i.e., several laboratory and XRF data pairs that impact regression analysis more than the majority of data) still remained. To objectively identify these influential outliers, the data were evaluated by calculating studentized residuals (Draper, 1981; Graybill, 1994). Those pairs of XRF and laboratory data that exhibited a studentized residual outside the (+3) to (-3) range were identified as influential observations to be excluded from the regression and correlation statistics. These data pairs are listed in Table A-1.

Regression analysis was then performed for the remaining sets of data (i.e., sets of data that did not include the outliers). Separate regressions were developed for three different field mobilizations, including 2008, 2012, and 2013 data collection efforts. In addition, separate regression analyses were also performed for sieved, unsieved, and in situ samples collected in 2008. The results of these analyses are presented in Table A-2, and include both Pearson and Spearman correlation coefficients (Swan and Sandilands, 1995). Values of these coefficients range from (-1) to 1, with values closer to zero representing random noise and values closer to (-1) or 1 representing greater inverse correlation or positive correlation, respectively. Spearman correlation statistics are rank-based and therefore nonparametric (not influenced by a distributional assumption).

The correlation between the XRF and laboratory data is shown in Figures A-1 through A-20. The outliers that were excluded from the regression equation are shown as red dots; the data used for the regression analysis are shown as blue dots on these figures. The regression lines shown on the figures are represented by the following equation:

$$\text{Estimated Laboratory Value} = 10 ^ { [\text{Log}_{10}(\text{Measured XRF Value}) \times \text{Regression Coefficient} + \text{Intercept}]}$$

The regression coefficients and intercepts for this equation are presented in Table A-2 for each data set. According to EPA SW-846 Method 6200, the XRF data may be further considered:

1. For screening purposes if the laboratory and XRF data correlation coefficient is 0.7 or greater; and
2. For valid determinative analysis if the correlation coefficient is 0.9 or greater.

All of the correlation coefficients estimated based on the XRF and laboratory data pairs for this site were at least 0.9 or greater. This consistently strong correlation for all groups of data (i.e., 2008, 2012, and 2013 mobilizations and sieved, unsieved, and in situ samples) provides a good support for the use of the XRF data in combination with the laboratory data. Based on the above, XRF data measured in the field were adjusted using these correlation equations and used in combination with the available laboratory data for the soil background study described in this report.

References

- Draper, N.R. and H. Smith. 1998. *Applied Regression Analysis*. New York: John Wiley & Sons. 736 pp.
- Graybill, F.A. and H.K. Iyer. 1994. *Regression Analysis: Concepts and Applications*, Duxbury Press. 650 pp.
- Swan, A.R.H. and M. Sandilands. 1995. *Introduction to Geological Data Analysis*. Cambridge, MA: Blackwell Science. 446 pp.

Tables

Table A-1**Influential Observation Pairs Excluded from Adjustment Equation Calculations****Based Upon Studentized Residual Values**

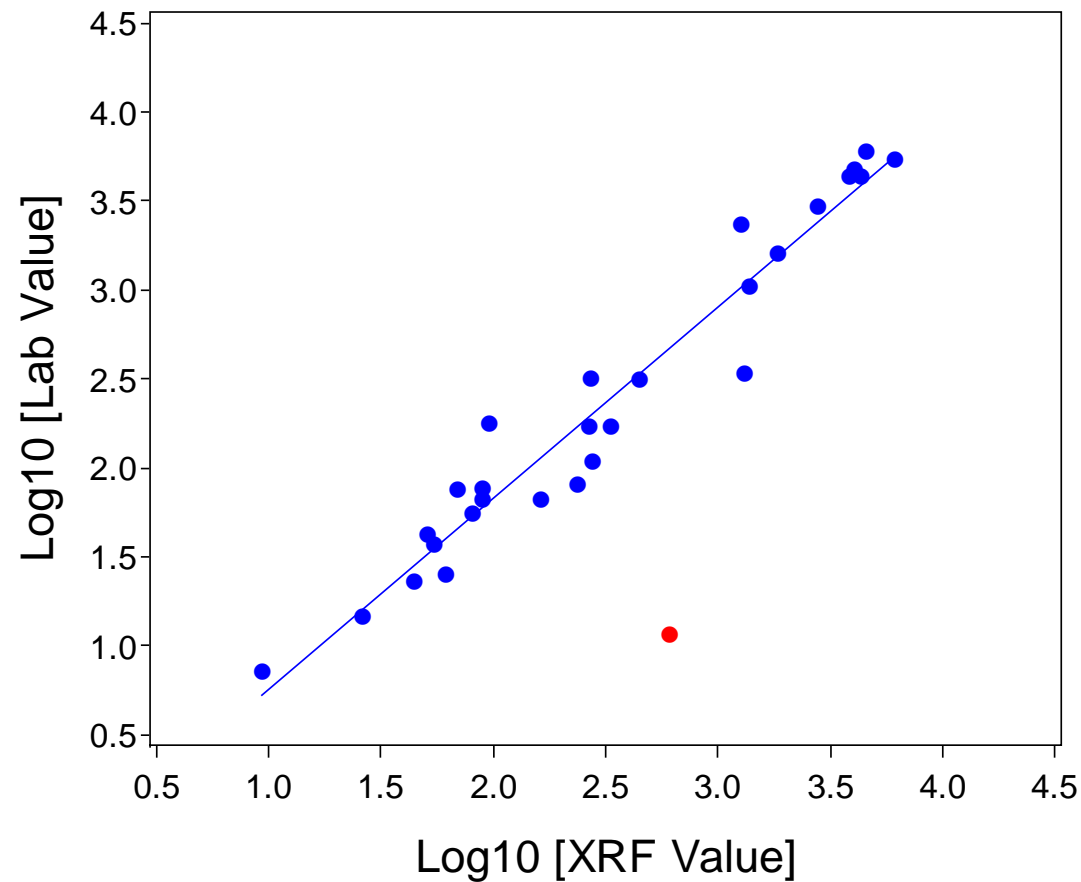
Grouping	Year	Constituent	Sample ID	Log10 (XRF)	Log10 (Lab)	XRF	Lab
Sieved	2008	Arsenic	HSJ-514-0-2	2.78	1.06	605.4	11.4
Unsieved	2008	Arsenic	HSJ-514-0-2	2.69	1.06	494.52	11.4
	2012	Arsenic	265	1.47	1.26	29.59804	18
Unsieved	2008	Copper	HSJ-514-0-2	3.90	4.36	8012.66	22900
In-Situ	2008	Copper	IKJ-555-0-6	2.27	2.44	185.7	273
	2012	Copper	46	0.74	1.04	5.5	11
	2012	Copper	339	0.74	1.04	5.5	11
	2013	Copper	648	2.81	3.03	651.11	1070
Sieved	2008	Lead	HSJ-514-0-2	2.98	1.96	946.12	92.2
Unsieved	2008	Lead	HSJ-514-0-2	2.81	1.96	641.33	92.2
	2012	Lead	215	1.64	1.18	43.81523	15
	2013	Lead	811	2.13	2.95	134.88	882
Sieved	2008	Zinc	HSJ-514-0-2	3.99	2.65	9845.37	449
Unsieved	2008	Zinc	HSJ-514-0-2	4.11	2.65	12746.36	449
	2012	Zinc	291	2.89	2.34	777.7662	220

Table A-2
Adjustment Equation Statistics

					Correlation Coefficients	
Year	Grouping	Constituent	Intercept	Regression Coefficient	Pearson	Spearman
2008	Sieved	Arsenic	-0.328	1.079	0.974	0.974
2008	Unsieved	Arsenic	-0.206	1.094	0.969	0.968
2008	In-Situ	Arsenic	-0.353	1.136	0.997	1.000
2012		Arsenic	-0.108	1.070	0.990	0.982
2013		Arsenic	-0.196	1.039	0.993	0.988
2008	Sieved	Copper	-0.472	1.095	0.984	0.979
2008	Unsieved	Copper	-0.232	1.046	0.981	0.976
2008	In-Situ	Copper	-0.145	1.029	0.999	1.000
2012		Copper	-0.210	0.990	0.984	0.966
2013		Copper	-0.334	1.089	0.971	0.956
2008	Sieved	Lead	-0.496	1.111	0.966	0.952
2008	Unsieved	Lead	-0.085	1.019	0.978	0.959
2008	In-Situ	Lead	-0.253	1.104	0.993	1.000
2012		Lead	-0.480	1.142	0.992	0.980
2013		Lead	-0.200	1.055	0.990	0.987
2008	Sieved	Zinc	-0.231	1.005	0.974	0.973
2008	Unsieved	Zinc	-0.108	1.014	0.959	0.939
2008	In-Situ	Zinc	-0.335	1.089	0.991	0.900
2012		Zinc	0.186	0.853	0.988	0.942
2013		Zinc	-0.240	1.049	0.987	0.987

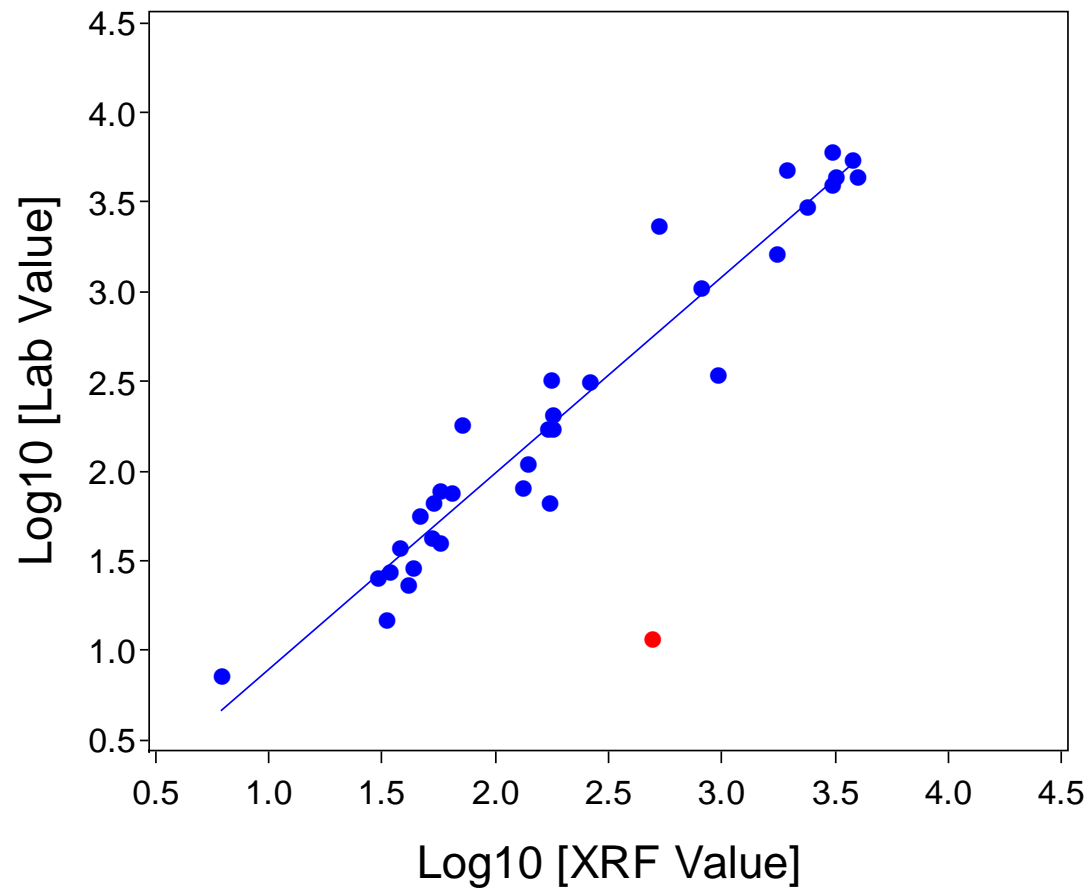
Figures

Figure A-1
Arsenic - Lab vs XRF
2008 Sieved



Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

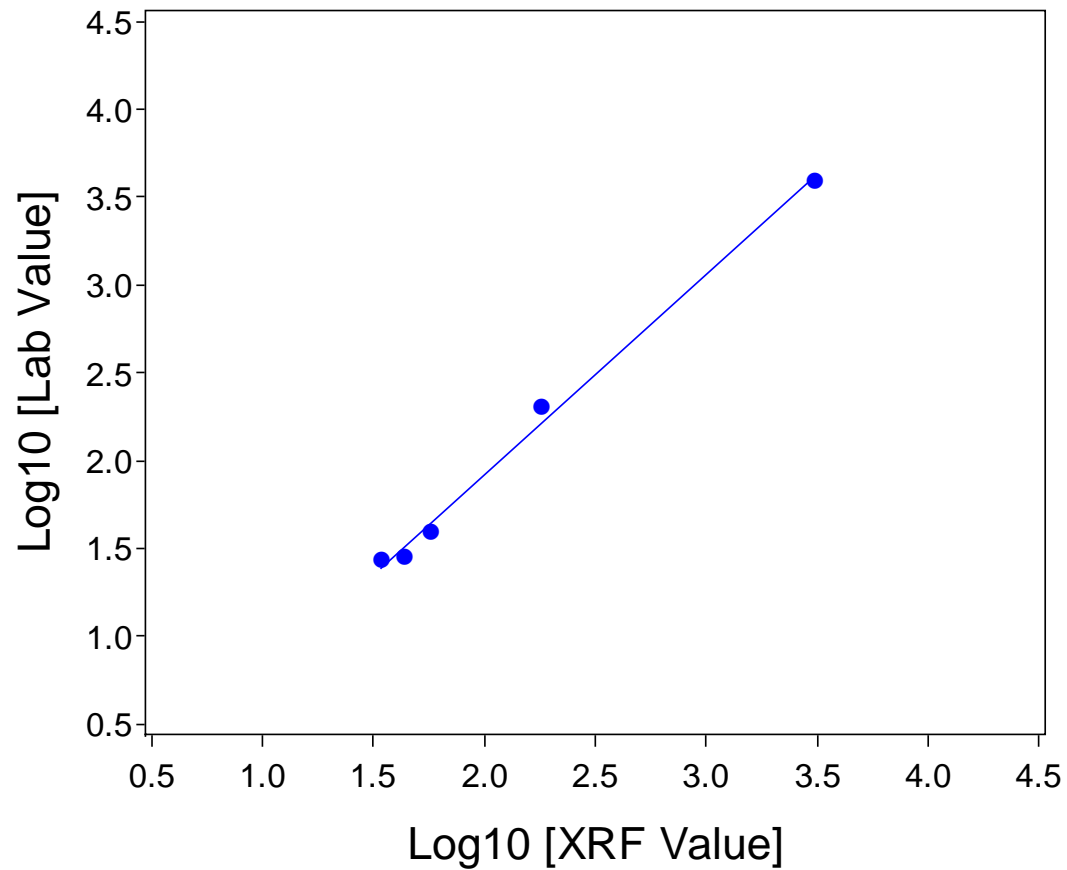
Figure A-2
Arsenic - Lab vs XRF
2008 Unsieved



Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

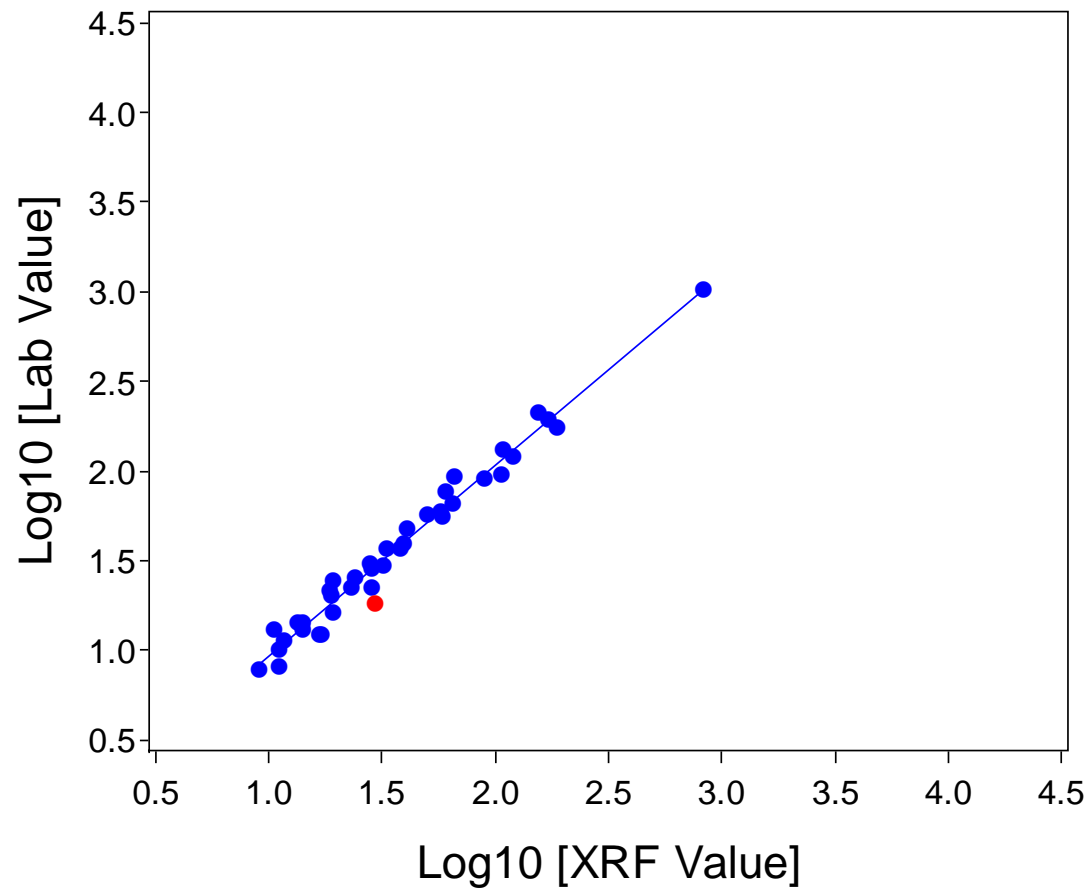
Figure A-3

Arsenic - Lab vs XRF 2008 In-Situ



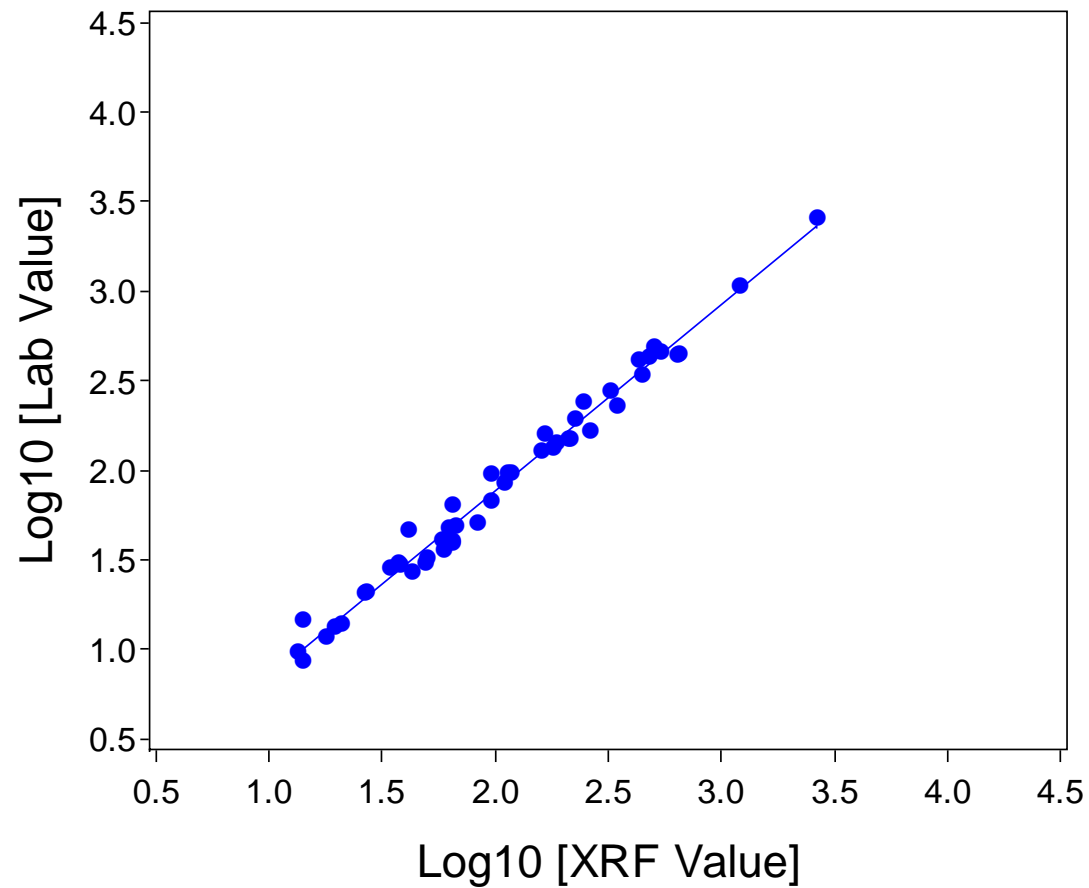
Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-4
Arsenic - Lab vs XRF
2012



Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-5
Arsenic - Lab vs XRF
2013

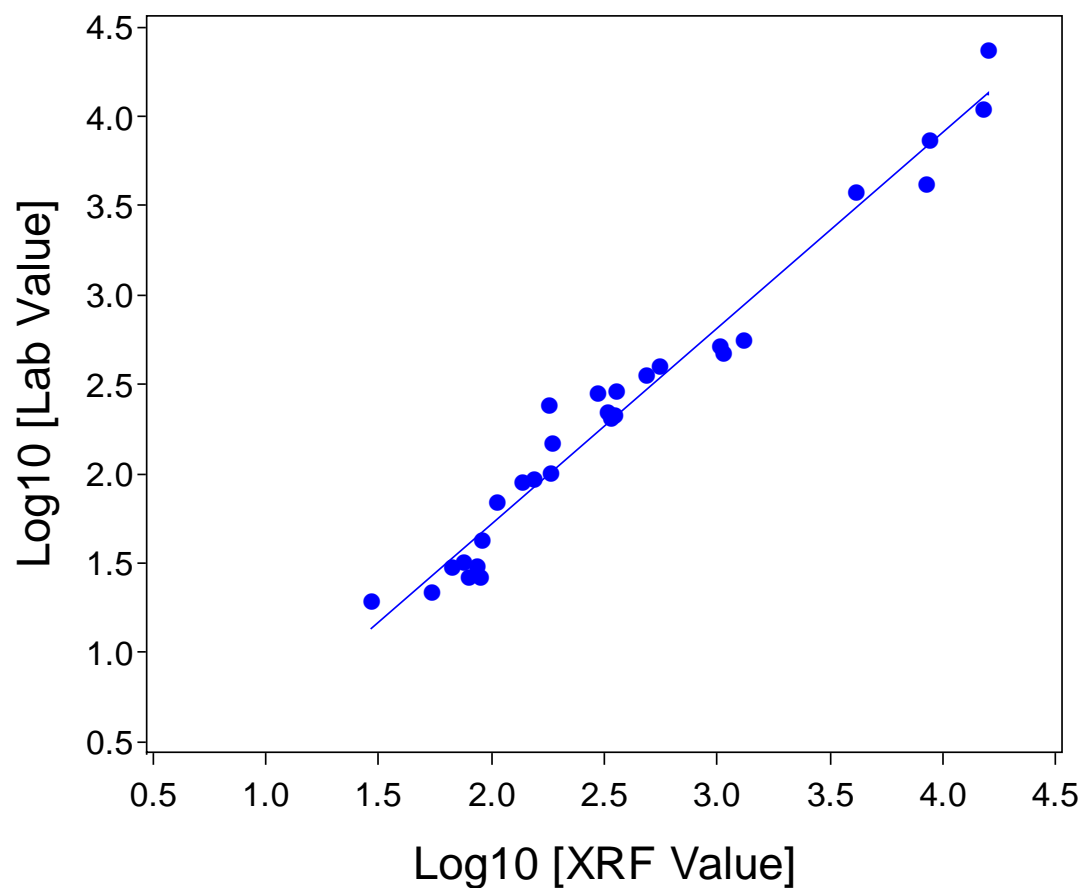


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-6

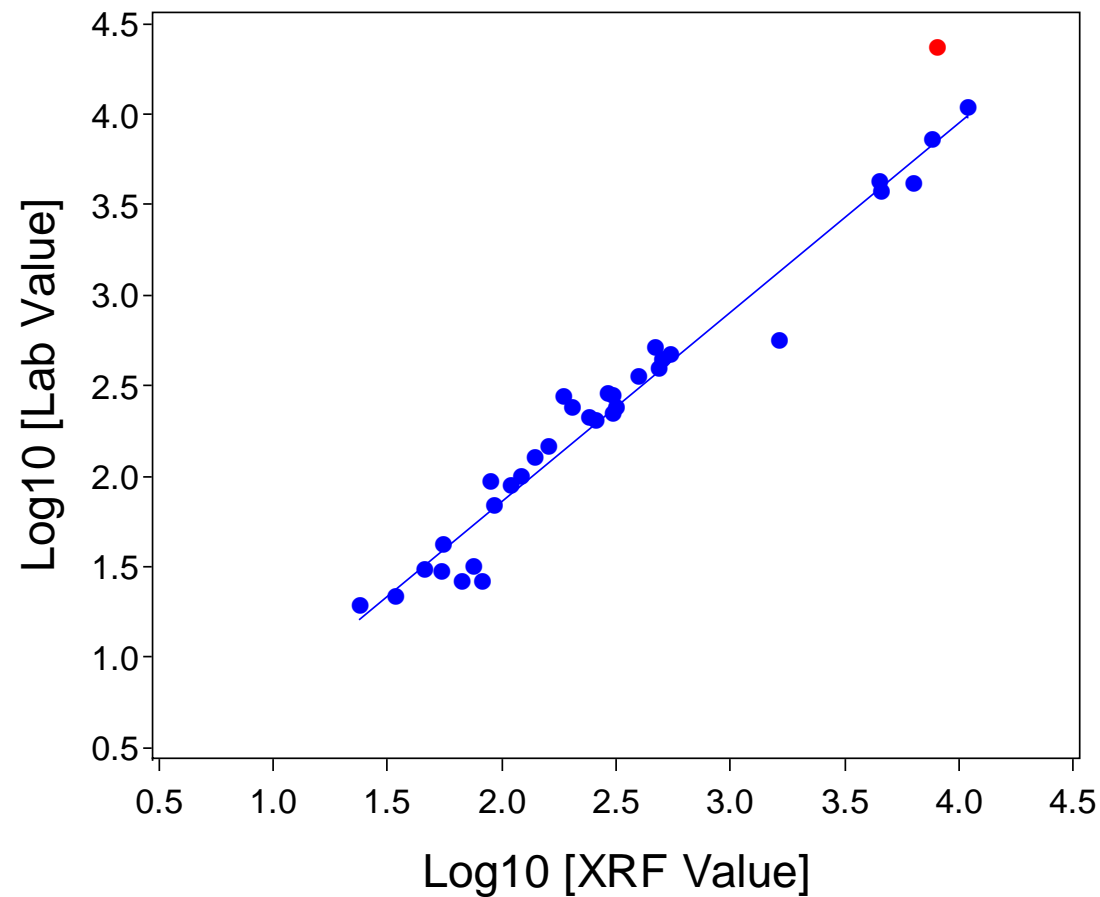
Copper - Lab vs XRF

2008 Sieved



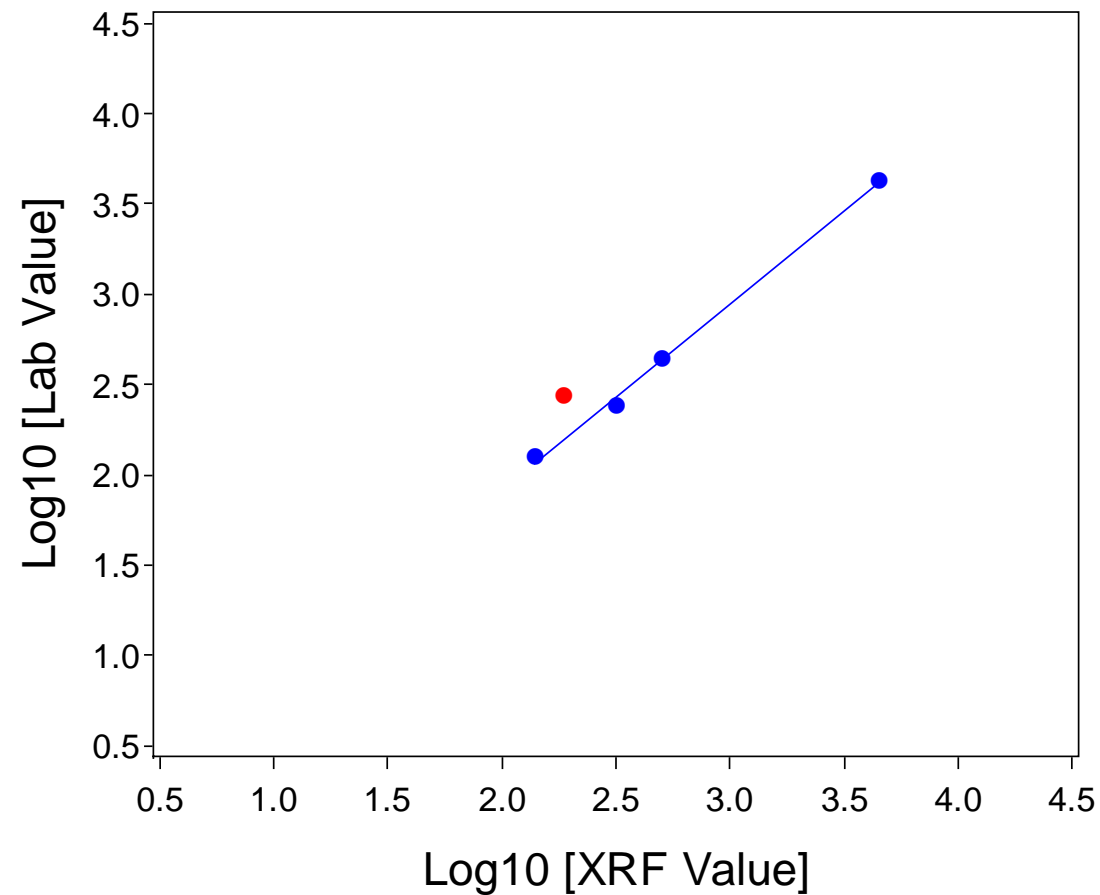
Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-7
Copper - Lab vs XRF
2008 Unsieved



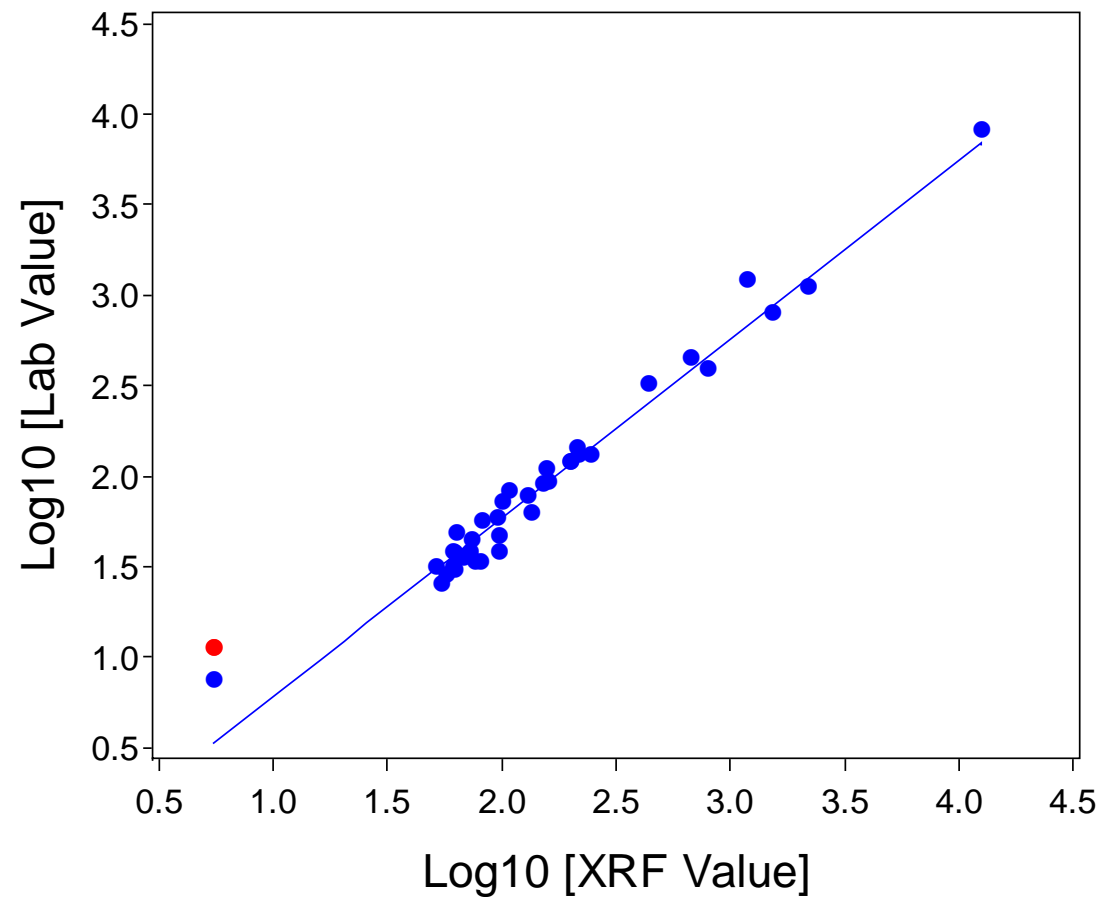
Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-8
Copper - Lab vs XRF
2008 In-Situ



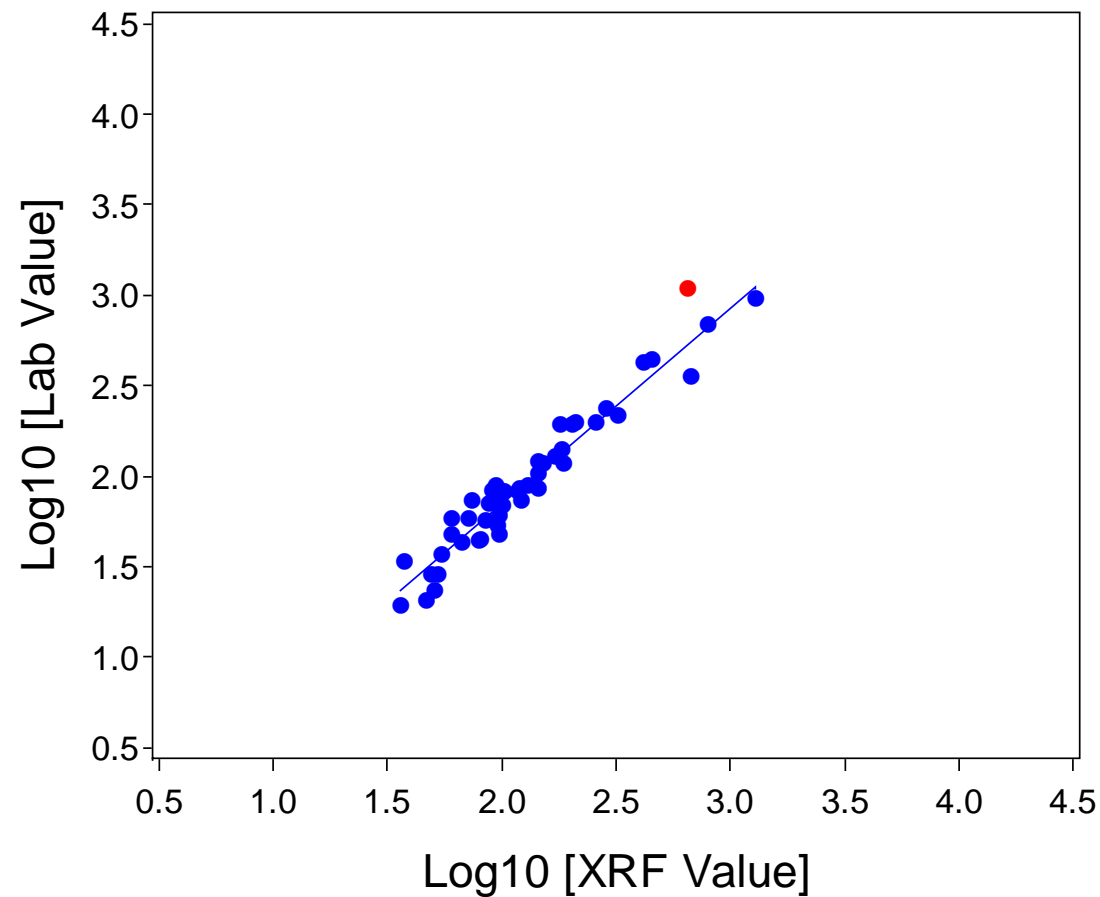
Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-9
Copper - Lab vs XRF
2012



Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-10
Copper - Lab vs XRF
2013

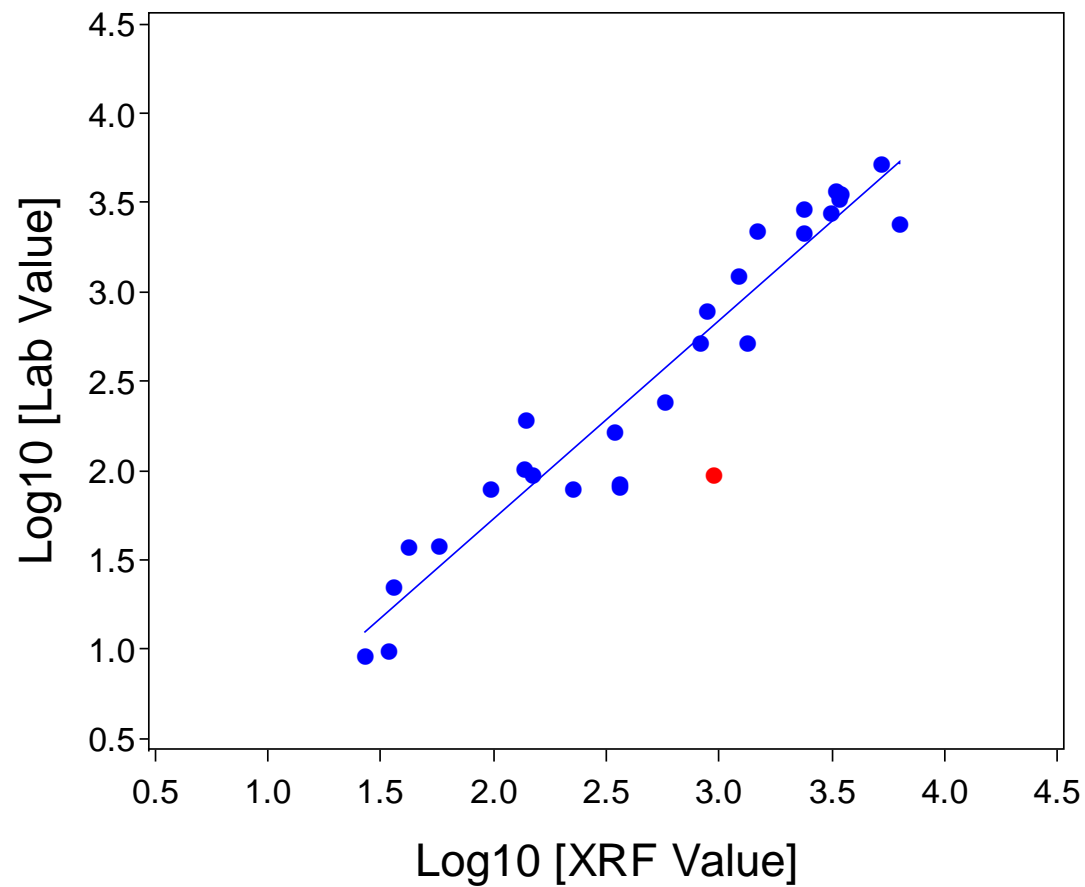


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-11

Lead - Lab vs XRF

2008 Sieved

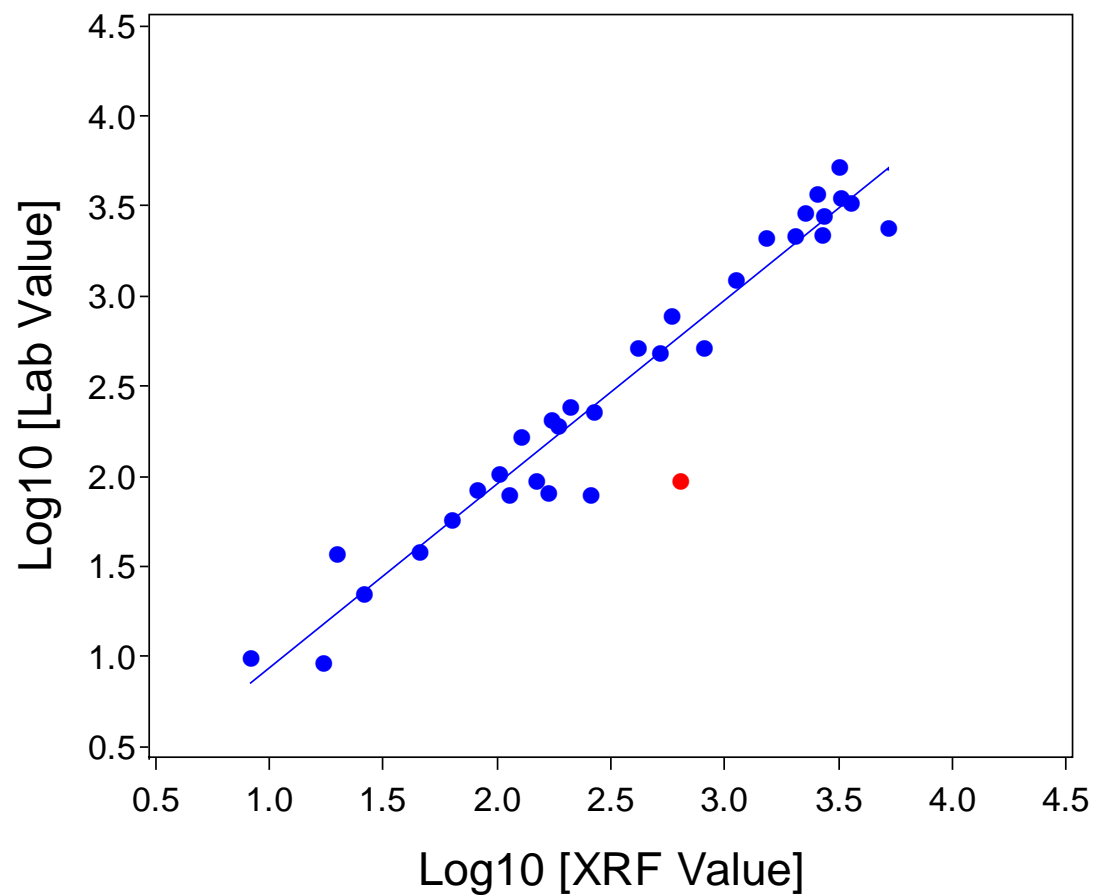


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-12

Lead - Lab vs XRF

2008 Unsieved

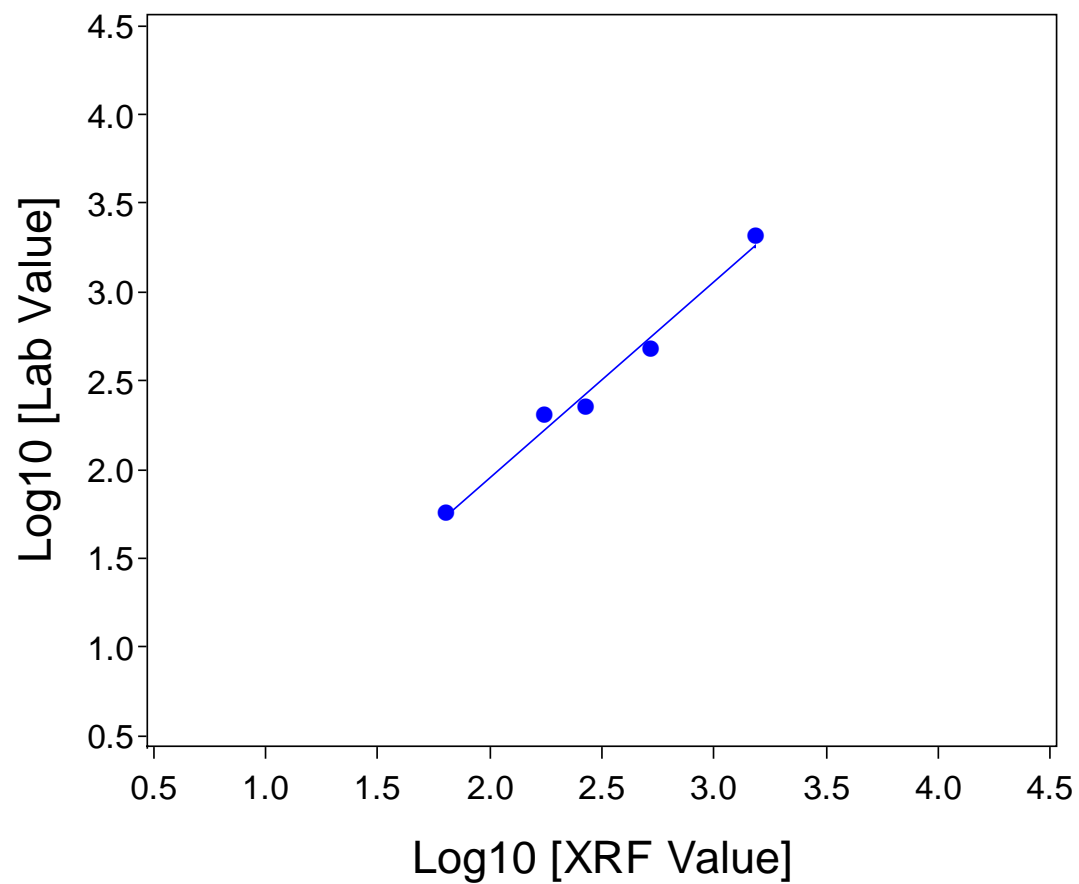


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-13

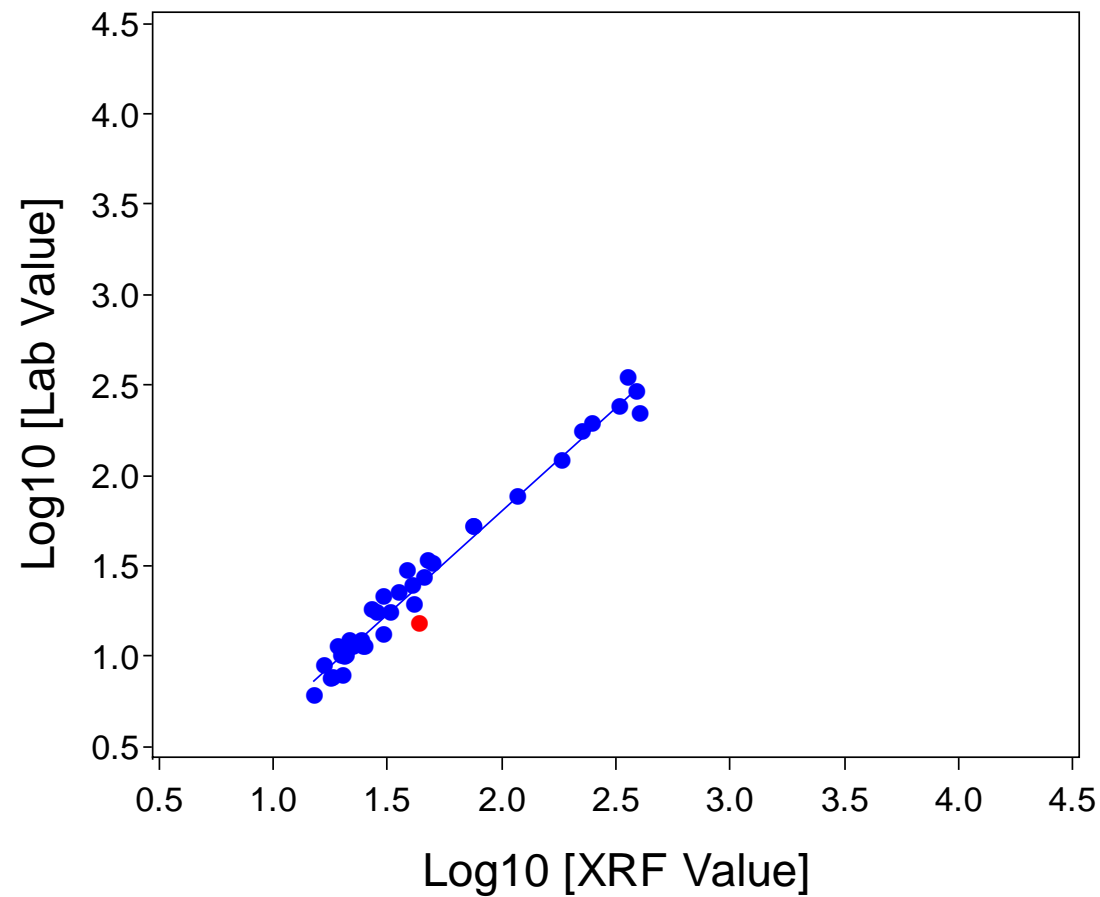
Lead - Lab vs XRF

2008 In-Situ



Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-14
Lead - Lab vs XRF
2012

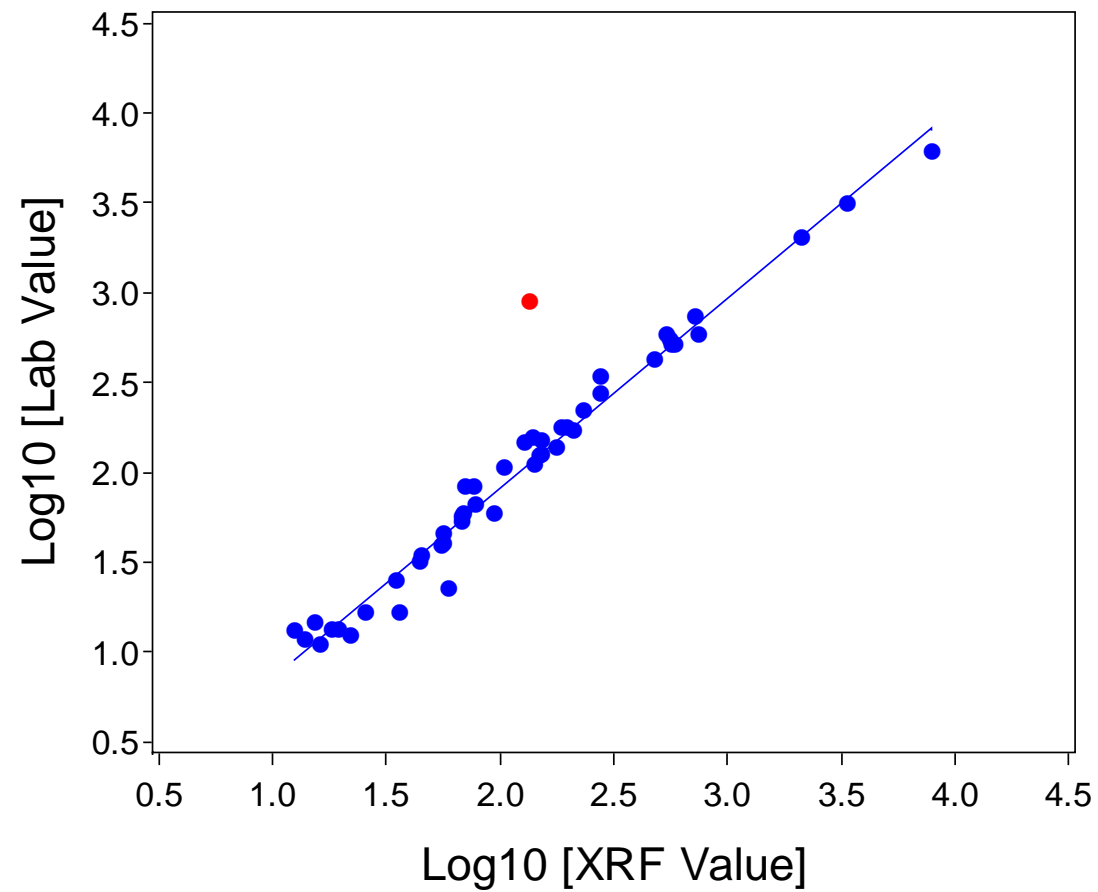


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-15

Lead - Lab vs XRF

2013

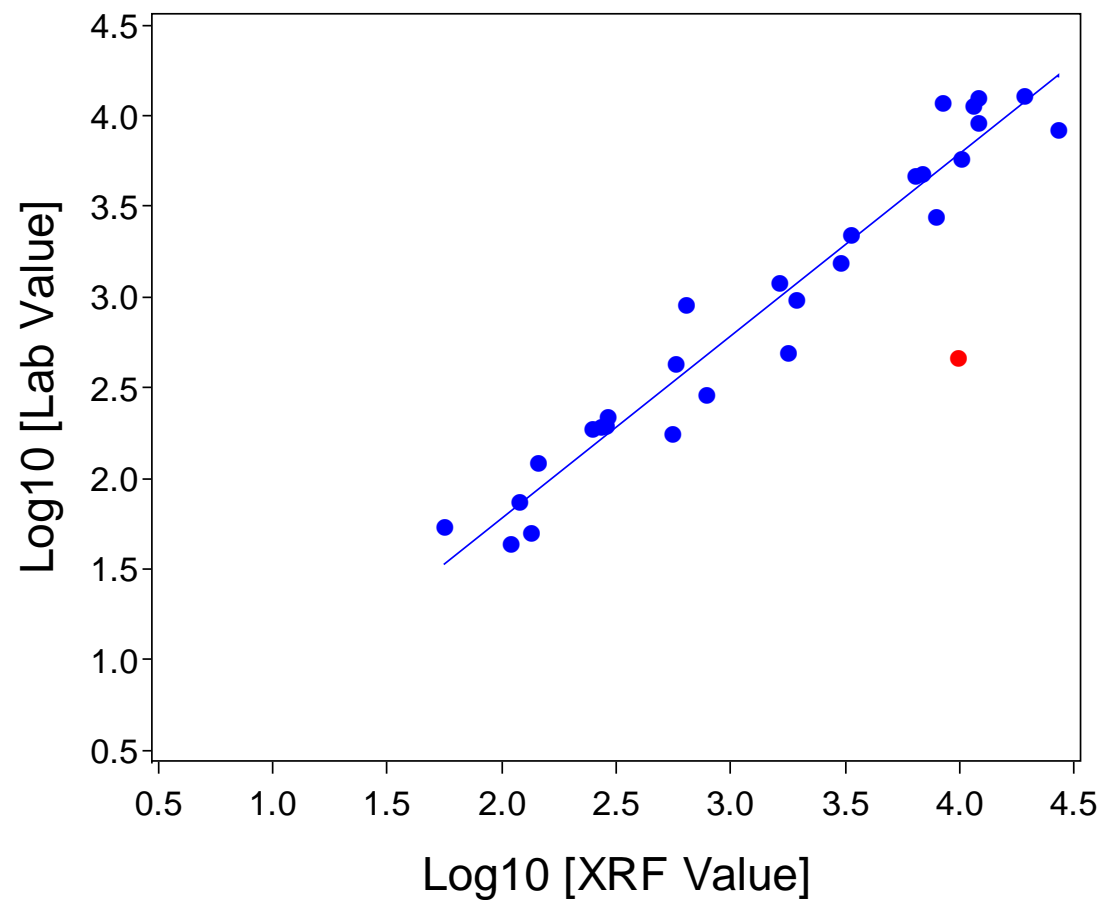


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-16

Zinc - Lab vs XRF

2008 Sieved

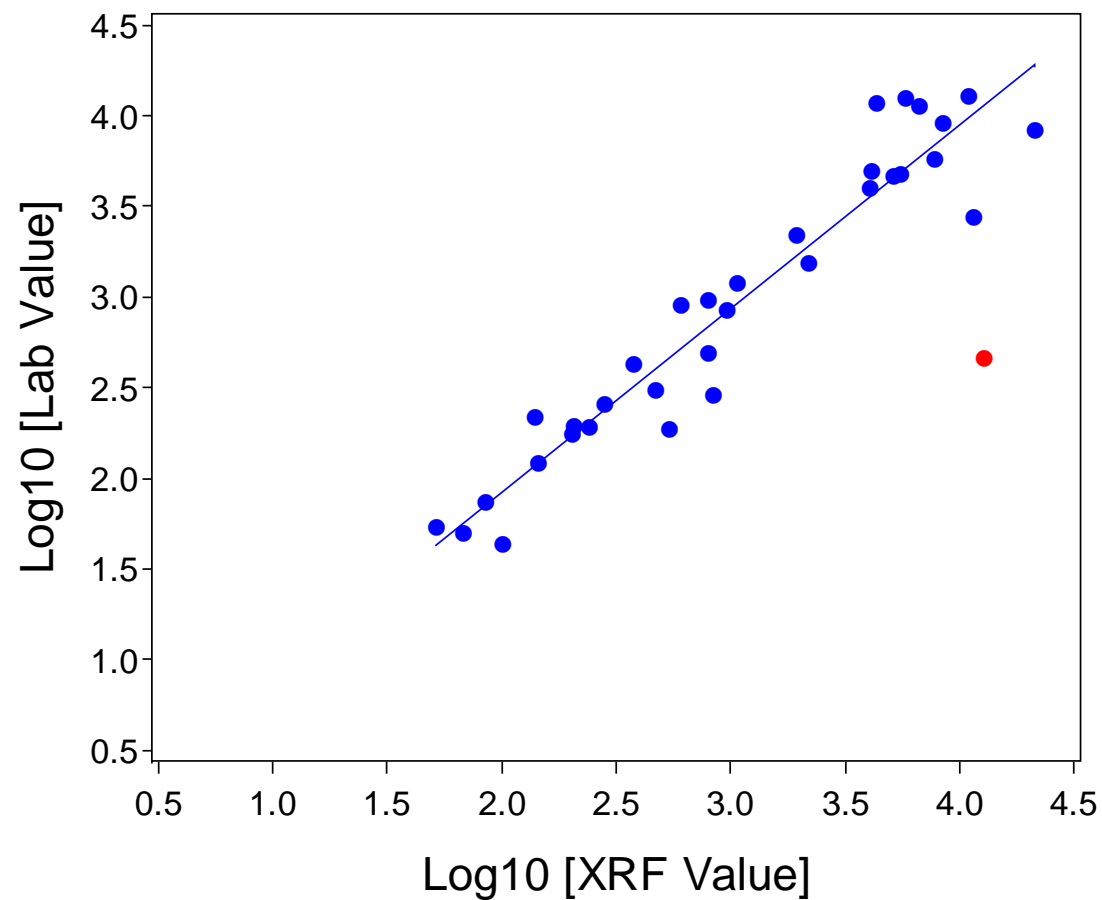


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-17

Zinc - Lab vs XRF

2008 Unsieved

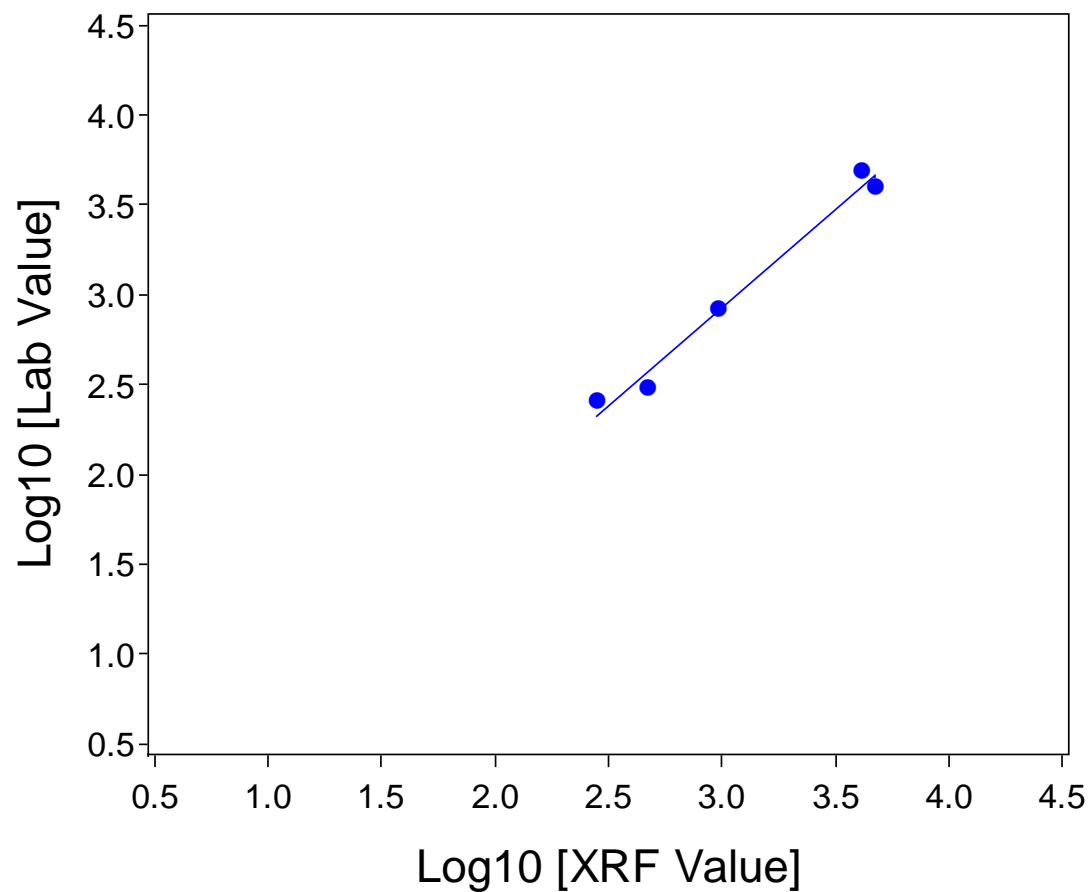


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-18

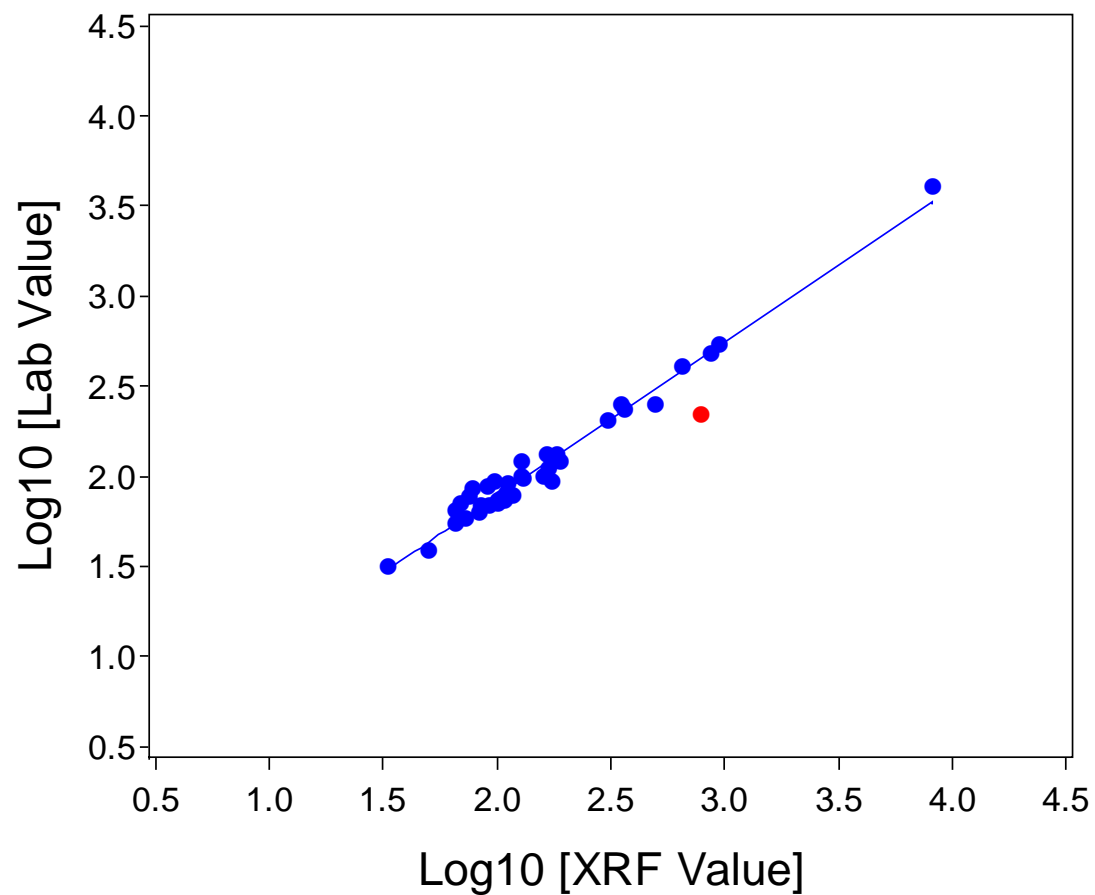
Zinc - Lab vs XRF

2008 In-Situ



Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-19
Zinc - Lab vs XRF
2012

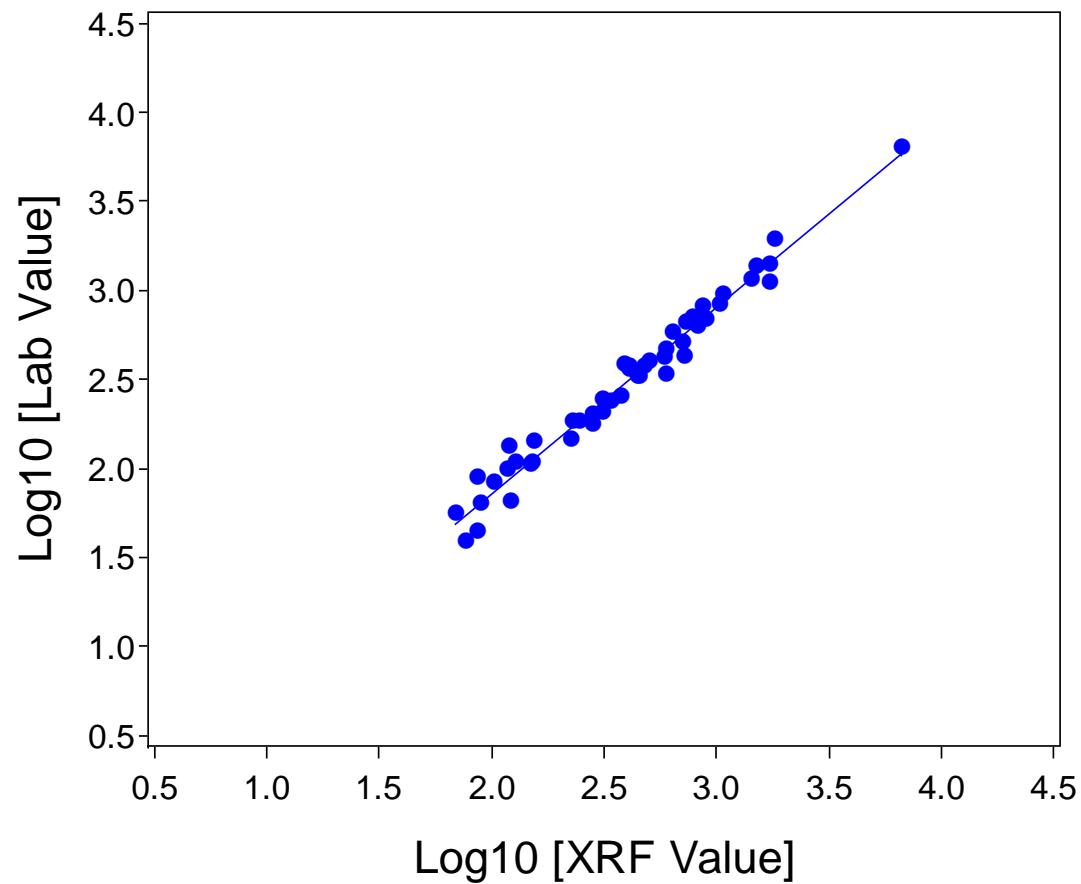


Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.

Figure A-20

Zinc - Lab vs XRF

2013



Note: Regression equation parameters and correlation coefficients are provided in Table A-2. Data excluded from the regression are shown as red dots and listed in Table A-1.