Analysis of Spatial Correlations of Metals at the Former Harshaw Chemical Company FUSRAP Site - 9341

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ABSTRACT

Analysis of the spatial distribution of a number of hazardous metals in soil in relation to that of uranium from historical government-sponsored operations at the Former Harshaw Chemical Site is being used as part of weight-of-evidence approach to identify metal contamination that is potentially eligible for cleanup under FUSRAP. The concentrations of uranium and other metals in soils across the site were determined using field X-ray Fluorescence (XRF) and laboratory methods during the site remedial investigation. Spatial correlations were evaluated using site maps of metals concentrations and regression analysis using scatter-plots of paired metal concentrations in soil sampling locations. The analysis did not identify any additional metals should be addressed under FURSAP, while the wide distribution of molybdenum, originally included on the basis of site records, could be associated with both government and commercial operations.

INTRODUCTION

The Remedial Investigation (RI) at the Former Harshaw Chemical Company (Harshaw site) performed under the FUSRAP authority by the USACE-Buffalo District included an X-ray fluorescence (XRF) analysis conducted in the field for multiple metals in site soils. Soil samples were prepared and analyzed with an Innov-X Alpha-6500R detector that utilized a Moxtek tantalum X-ray tube (Innov-X Systems, Inc.). Each bagged soil sample was shot four times for 30 seconds each, which produced a combined concentration result and uncertainty estimate.

The resulting XRF dataset provided a screening tool to support site decisions, in accordance with a weight of evidence approach, regarding metal concentrations at the industrial Harshaw site. The metals analyzed for this exercise included the following:

- **Arsenic** (As)
- **Cadmium** (Cd)
- **Chromium** (Cr)
- **Cobalt** (Co)
- **Copper** (Cu)
- **Iron** (Fe)
- **Lead** (Pb)
- **Manganese** (Mn)
- **Molybdenum** (Mo)
- **Nickel** (Ni)
- **Strontium** (Sr)
- **Thallium** (Tl)
- **Uranium** (U)
- **Zinc** (Zn)

In general, field XRF performance for site metals produced acceptable detection limits and data usability. In some cases XRF detection limits were below background (Zn and Mn). In other cases the detection limits were above background, but well below risk screening levels (U, Cu,

Pb, Ni, and Mo). Finally, in the case of Cd and Cr, the XRF detection limits were concurrent with screening values.

A sample-specific comparison of XRF-derived data against XRF- and/or laboratory-derived total uranium (or uranium-238) data was performed to achieve two goals:

1. Determine whether potentially hazardous metals correlate spatially with uranium and thus are potential FUSRAP responsibility, and
2. Determine if other inter-metal correlations exist to evaluate their potential use for classifying FUSRAP-related contaminated soil shipments and implementing disposal facility waste acceptance criteria.

The FUSRAP cleanup at Harshaw is addressing areas impacted by uranium processing carried out from about 1942 to 1953 under the Manhattan Engineering District and Atomic Energy Commission (MED/AEC). Molybdenum is the only hazardous metal that has been identified from site records as being associated with these programs. Molybdenum was controlled in feed materials to minimize its presence in produced uranium hexafluoride. While molybdenum is cited in records, tight controls on its concentration in feeds suggest that any site contamination would be of low concern. Several other metals, including arsenic, barium, manganese, nickel, vanadium, and zinc, are known to be present as impurities in ore concentrate feed materials at other sites, but are not mentioned in Harshaw records. Metal contamination from this source, which is discussed further, below, is similarly not thought to present a significant contamination concern. The inclusion of several of these metals in the XRF data set allows this assumption to be tested. The main purpose for the analysis of the metals listed above was for hazardous waste characterization of soils potentially contaminated by both uranium and hazardous metals from commercial operations at the former Harshaw Chemical Company.

Metals Spatial Distribution Maps

An initial spatial analysis indicated the collocation in soil of several metals with uranium contamination, which would be expected since commercial and governmental operations utilized the same operational corridors. Figure 1 is an example of such an analysis for uranium and lead, which shows the concentrations of these metals acoss the site as determined via the XRF. The concentration levels shown are keyed to roughly similar levels of concern. MED/AEC activities were conducted mainly in Building G-1, shown in Figure 1.

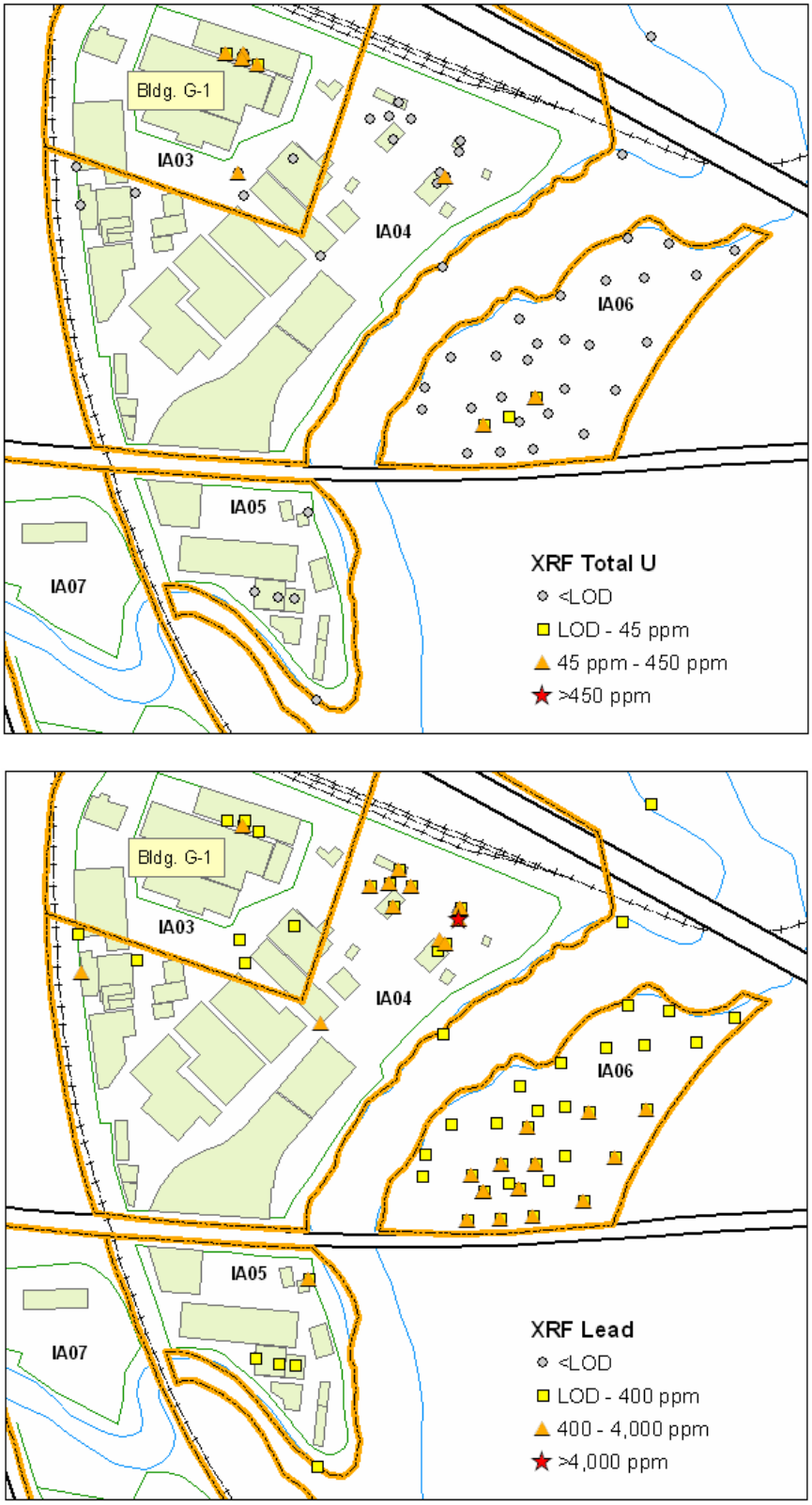

Fig. 1. Comparison of Spatial Distributions of Uranium (top) and Lead (bottom).

Project-area background values were used when available; otherwise generic soil background levels quoted elsewhere for the U.S. or EPA health risk screening criteria were applied.

Non-radiological metals commonly found in uranium ore concentrates, such as those processed at the site, and/or raffinate waste streams from the processing of such MED/AEC-related materials include As, Ba, Mn, Mo, Ni, V, and Zn [1]. Ba and V data are absent in the current data set since the XRF did not provide results for these elements. Additionally, XRF-based arsenic results are subject to interference from lead, which is prevalent at the site, and thus the arsenic data may be biased high. Other potential MED metals may include Cd, Cr, Cu, Fe, Pb and zirconium (Zr) from gangue minerals in western-U.S. uranium ore that also may show presence in site process raffinate. Of these, only Fe, which is non-hazardous, was reported in Weldon Spring raffinate sludges [1]. Weldon Spring processed similar uranium feeds at about the same time as Harshaw MED/AEC operations. Other metals present in uranium ore were normally removed at milling sites in the preparation of the ore concentrates processed at Harshaw.

Regression Analysis of Paired Metal Concentrations

To further assess the spatial correlation of metals and uranium soils data, scatter plots of total uranium concentrations (or U-238 in a few cases) were plotted against field XRF metals concentrations for sample locations and depths that appear in both datasets. Additional metal-to-metal comparisons were made using laboratory only data (e.g., Ni and Mo have both lab- and XRF-based datasets).

Correlations of concentrations of uranium with other metals or among other metals in the current analysis provide an additional indicator of spatial correlation for geographically dispersed metals. When the concentrations of the metals generally rise and fall together across the sampled geographic space it can be inferred that the metals are similarly distributed, and quite possibly borne of similar processes; for example, from dumping of materials from different sources in the same locations, or that the correlated metals were constituents of the same source material; for example, metals in ore concentrates.

The current analysis uses concentration correlations determined from scatter plots of paired metals to support the initial spatial analysis based on metals distribution maps. The results of the scatter plots are exemplified by Figures 2 and 3, which provide a subset of site-wide comparisons to show several levels of correlation that were observed.

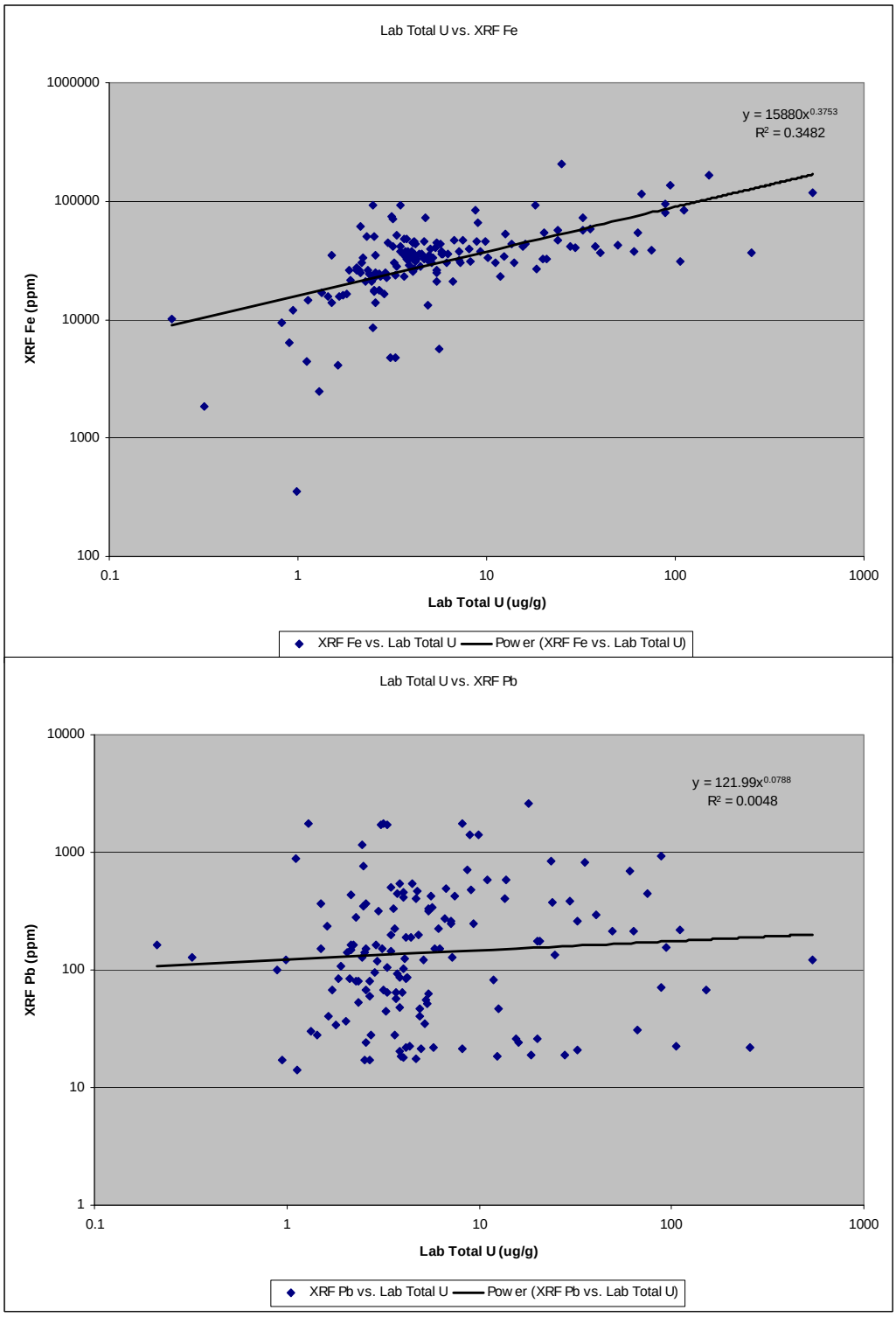

Fig. 2. Uranium Versus Fe (top) and Pb (bottom) Sitewide Scatterplot.

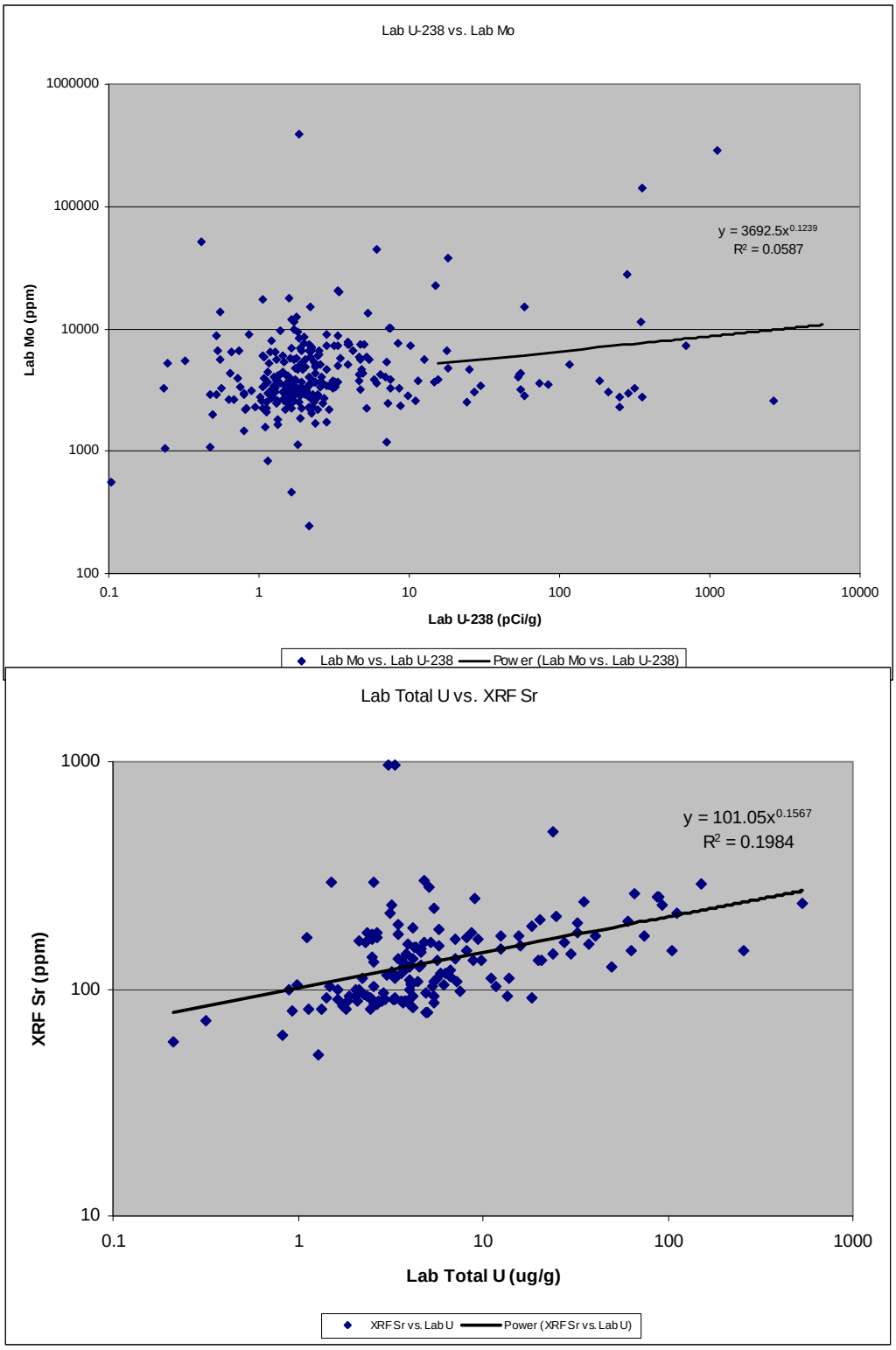

Fig
. 3. Uranium Versus Mo (top) and Sr (bottom) Sitewide Scatterplot.

The use of logarithmic plots appears most applicable to these data sets due to nominal log-normal data distributions, although the metal datasets were not formally screened to confirm that data were so distributed.

The scatter plots were fit with power-function trend lines that produced regression coefficients that were used to qualitatively designate the weakness or strength of metal correlations. These qualitative designators are bracketed using the following regression coefficient (r-squared) ranges:

- Uncorrelated analytes are highly scattered with r-squared values <0.20
- Weakly Correlated analytes have r-squared values between 0.20 and 0.50
- Moderately Correlated analytes have r-squared values between 0.50 and 0.70
- Strongly Correlated analytes have r-squared values between 0.70 and 1.00

Table I provides the regression coefficients for uranium versus several other metals using both site-wide and smaller investigation area (IA)-specific data sets; note that some metals were not treated equally due to data density constraints. The site is divided into five main soil IAs, IA03-IA7 (Figure 1).

Table I. Correlation Coefficients for the Regression of Concentrations of Various Metals against Uranium on a Sitewide and Investigation Area Basis

Metal	**Sitewide**	**IA03**	**IA04**	**IA05**	**IA06**	**IA07**
Arsenic (As)	0.04	0.13	0.23	0.003[b]	0.25	NA[a]
Cadmium (Cd)	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]	NA[a]
Chromium (Cr)	0.0002	NA[a]	0.012	NA[a]	0.15	NA[a]
Cobalt (Co)	0.31	0.45	0.17	0.26[b]	0.32	NA[a]
Copper (Cu)	0.04	0.06	0.14	0.003[b]	0.12	NA[a]
Iron (Fe)	0.35	**0.62**	0.38	0.002[b]	0.19	NA[a]
Lead (Pb)	0.005	0.21	0.06	0.29[b]	0.18	NA[a]
Manganese (Mn)	0.08	0.01	0.03[b]	0.16[b]	0.04	NA[a]
Molybdenum (Mo)	0.06 to **0.84**[c]	0.02	**0.52**	0.26	0.25	0.01[b]
Nickel (Ni)	0.16	0.00005	0.0003	0.009	**0.51**	NA[a]
Strontium (Sr)	0.20	**0.70**	0.07	0.02	0.30	NA[a]
Thallium (Tl)	0.12	0.14	0.0009	0.04	0.14	NA[a]
Zinc (Zn)	0.001	0.23	0.22	0.21[b]	0.02[b]	NA[a]

[a]Not analyzed due to scarcity or lack of laboratory or XRF data pairs.
[b]Negative correlation.
[c]The regression coefficient of 0.84 for Mo/U is limited to the XRF dataset; laboratory data adds variability to the analyses, as shown in the IA-specific results.

RESULTS AND DISCUSSION

The graphical evaluations of site-wide and available IA-specific observations support a weight of evidence approach to site metals contamination, which is summarized below.

- **Arsenic** is found at elevated levels on site and ranges from very weakly to uncorrelated with uranium concentrations. Since arsenic occurs as a common sulfide mineral in metallic ores, it likely was imported commercially at Harshaw. Arsenic was present at 3-1,100 ppm in Weldon Spring raffinate sludge. However, its lack of correlation with uranium residuals indicates that Arsenic is not MED/AEC-related and thus will not be addressed under FUSRAP.
- **Cadmium** data are limited but indicate somewhat elevated levels. The small dataset does not show a correlation with uranium and thusly considered a commercial-process contaminant at Harshaw that will not be addressed under FUSRAP.
- **Chromium** data also are limited and do not show correlation with uranium. Elevated chromium appears limited to IA04 and IA06, where commercial processes and apparent surface disposal occurred, respectively. Chromium shows a weak correlation with nickel and will not be addressed under FUSRAP.
- **Cobalt** is weakly (to moderately) correlated with uranium and can be a gangue element in western-U.S. uranium ore; Co is moderately elevated at Harshaw. Cobalt correlates well with iron, moderately to well with lead, and weakly with nickel. Although a possible uranium-ore related metal, it ranged only as high as 44 ppm in Weldon Spring raffinate sludges. Due to stronger correlations with non-MED/AEC metals at Harshaw, cobalt will not be addressed under FUSRAP.
- **Copper** concentrations are well scattered throughout the range of uranium and appear very weakly to uncorrelated with uranium. Copper shows a moderate correlation with lead and weak correlation with nickel, all of which indicates it will not be addressed under FUSRAP.
- **Iron** concentrations correlate weakly (to moderately) with site-wide uranium, moderately well with lead and cobalt, and weakly with copper and molybdenum. Iron at Harshaw may be from hydrothermal iron and/or ore-body gossan (as gangue) that commonly occurs with many metal ore bodies. In addition, eastern U.S. coal (Pennsylvanian age) that likely was used on site can contain up to 10% of iron sulfide (pyrite), which would have contributed to site iron concentrations. Iron also may be attributed to acid handling and storage, as well as industrial fill activities. Although the Weldon Springs results for iron in raffinate sludges indicate iron can be an MED-related metal, the collocation assessment indicates that iron should not be addressed under FUSRAP, nor is it generally of health concern.
- **Lead** concentrations appear uncorrelated with site-wide uranium and weakly correlated to uranium in IA03. Lead appears variably correlated with cobalt, copper, and iron, as previously discussed. Molybdenum ore may contain lead-bearing wulfenite (Pb [MoO4]); however, Mo and Pb do not correlate at Harshaw. Apparently, lead concentrations appear correlated with commercial operations that included copper and iron processing. Lead will not be addressed under FUSRAP, although it is commonly found in similar process areas and thus may pose a remedial-action waste disposal issue and potential worker risk during future FUSRAP actions.
- **Manganese** concentrations are uncorrelated with site uranium. Manganese is most prevalent in IA06, where commercial wastes apparently were landfilled as indicated by the presence of several metals. Manganese will not be addressed under FUSRAP.
- **Molybdenum** is spatially collocated with uranium on an IA basis (i.e., well present in MED/AEC-related processing areas), although site-wide concentrations appear uncorrelated. IA-specific data show that Mo is wide-spread and best correlates with low

levels of uranium in IA04, which might reflect that both MED/AEC and commercial sources existed for Mo at Harshaw, which is consistent with the original site conceptual model. Mo can be a by-product or co-product from copper ore processing, although it does not correlate well with Cu, Fe, Pb, or Ni. It was present at 16-1600 ppm in Weldon Spring raffinate sludges. Molybdenum will be retained as a MED-related constituent under FUSRAP in accordance the existing site model, although it appears well distributed throughout the range of uranium and not fully attributable only to MED processes due to presence in commercial-use areas.

- **Nickel** appears throughout the site and is elevated in IA07, where landfilling activities occurred from 1951 to 1972, as seen on aerial photographs. Nickel manufacturing processes dominated site shipments prior to MED/AEC activities. Nickel is uncorrelated with uranium, specifically in IA03, where commercial nickel products overlapped uranium process areas; nickel-contaminated fill apparently was spread and graded in IA04 as was uranium- and thorium- contaminated materials. The limited footprint of uranium in IA06 correlates with nickel due to collocated waste placement. Spatial analyses indicate that uranium contamination falls within a larger nickel footprint. While nickel was present at up to 8,800 ppm in Weldon Spring raffinate sludges, the vast majority of elevated nickel samples at Harshaw coincide with only low levels of uranium, further indicating separate providence. Nickel will not be addressed under FUSRAP.
- **Strontium** concentrations are weakly correlated with site-wide uranium and strongly correlated with uranium in IA03, where elevated uranium data govern the correlation within a narrow range of strontium results. Strontium may be a gangue element in uranium ore and appears to be found at the highest levels in IA04 then IA03. Strontium will not be addressed under FUSRAP but appears to fall within a potential uranium remediation footprint.
- **Thallium** concentrations are generally uncorrelated with uranium. Thallium is a common element found in western-U.S. Uranium ores. However, the vast majority of thallium corresponds to uranium concentrations commonly below the risk-based cleanup levels. Thallium will not be addressed under FUSRAP.
- **Uranium** data exhibit a wide range of concentrations in areas affected by MED/AEC processes, as well as areas that apparently received residue spoils (dumping), including: IA03 next to Building G-1, select IA-04 locations, a small hot spot in IA06, and demolition debris in IA07 (Figure 1). The XRF-detected metals that weakly to moderately correlate with uranium are cobalt, iron, molybdenum, strontium, and possibly thallium. Weaker correlations are seen with nickel and zinc due to closely located process areas and fairly widespread disposition of uranium process residues throughout the site. Future remediation of uranium-contaminated areas could include areas exhibiting non-MED/AEC metals, which could affect waste manifests and possibly disposal costs. However, FUSRAP authority will be limited to remediating MED/AEC-impacted areas only and not non-MED/AEC metal areas.
- **Zinc** concentrations are weakly to uncorrelated with uranium. A large majority of elevated Zn locations are in IA06, where commercial metal processing wastes were apparently placed. While zinc ranged from 24-2,100 ppm in Weldon Spring raffinate sludges, it is not correlated with uranium and will not be addressed under FUSRAP.

The sitewide log-log scatter plots indicate that the vast majority of metals contamination at the Former Harshaw Chemical Site is not well correlated with site-wide uranium concentrations. A significant amount of scatter in the XRF and/or laboratory metals data throughout the range of uranium concentrations, even when tempered by logarithmic analyses, shows that most site metal contamination is not attributable to MED/AEC-related processes.

The IA-specific scatter plots used in conjunction with spatial data plots and site history indicate that, while some commercial processes overlapped with MED/AEC-related processes in certain areas, these lines of evidence do not indicate that any additional metals are clearly MED/AEC - related as defined by association with uranium residues, while molybdenum might be of both commercial and government origin.

Several IAs show stronger uranium correlations between certain metals due to the close proximity of associated use processes and likely on-site residue disposal activities. Figure 4 shows stronger correlations between copper and lead than between copper and iron in IA-specific plots. As noted in the Introduction, one of the purposes of inter-metal correlations will be to evaluate their potential use for classifying FUSRAP-related contaminated soil shipments and implementing disposal facility waste acceptance criteria.

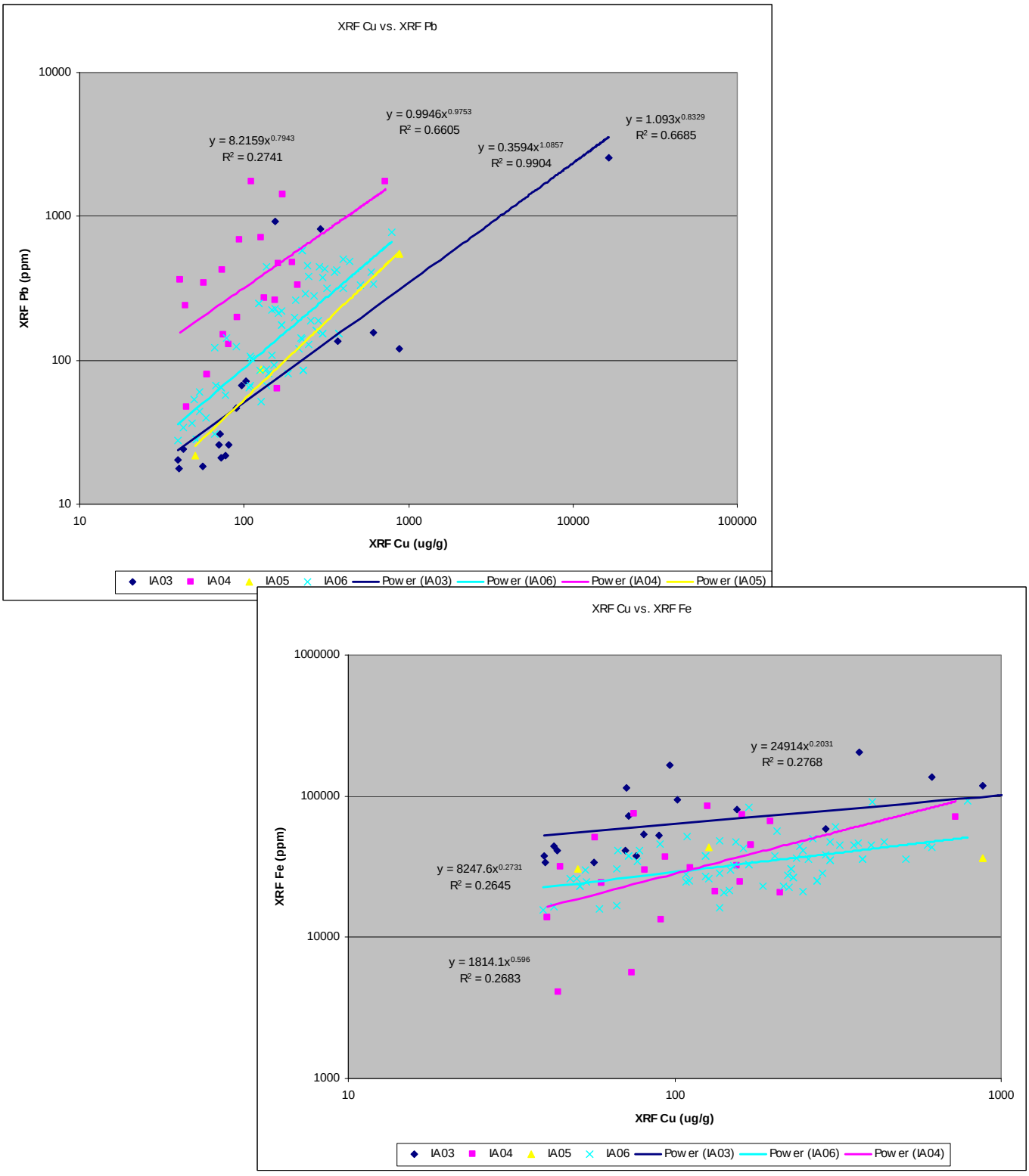

Fig. 4. Cu Vs. Pb (top) and Cu vs. Fe (bottom) IA-Specific Scatterplots.

The following bullets indicate that non-MED/AEC metals in several IAs will have a high potential for co-removal with MED/AEC contaminants due to proximity with uranium-contaminated areas. Some metal pairs show significant IA-specific correlations that are discussed below (regression coefficients are in parantheses):

- IA03:
  - Uranium is generally correlated with Co, Fe, Pb, Sr, possibly Tl, and Zn.
  - Metal that show variable correlations include Cu/Fe (0.28), Pb/Fe (0.29), Pb/Sr (0.30), Co/Pb (0.56), Cu/Pb (0.67), Co/Fe (0.70), Sr/Fe (0.72), and Mo/Ni (0.95 using XRF-only data), as exemplified by Figure 4, which shows correlations for Cu versus Pb and Fe.

- IA04:
  - Uranium is moderately to strongly correlated with Fe, Mo and Zn.
  - Metal pairs that show various levels of correlation include Cu/Fe (0.27), Cu/Pb (0.27), Co/Pb (0.45), Co/Fe (0.78), and Mo/Ni (0.86 using XRF-only data).

- IA05:
  - Uranium is weakly correlated with Mo
  - Metals that shows moderate correlation are Ni/Mo (0.33 using lab-only data), Co/Pb (0.89), and Cu/Pb (0.99)
  - The paucity of XRF data from IA05 may show good correlations although these may be driven by limited data points.

- IA06:
  - Uranium is weakly to moderately correlated with Co, Mo, Ni and, and Sr due to the disposal of wastes in IA06
  - Metal pairs that show various degrees of correlation include Co/Fe (0.23), Cu/Fe (0.26), Ni/Mo (0.33 with lab-only data and 0.99 with XRF-only data), Pb/Sr (0.34), Fe/Sr (0.42), Co/Pb (0.43), Co/Ni (0.60), and Cu/Pb (0.66).

This exploratory data analysis, although not fully cross correlated with all analytes, shows that several metals are more correlated with uranium (Co, Fe, Mo, Sr, and to a lesser degree Ni) than many XRF identified metals, especially when evaluated on an IA basis (i.e., evaluated on a commercial processing area basis). Several significantly elevated and weakly correlated, non-MED/AEC metals at the site also indicate where site areas received commercial residues or wastes. Historic disposal activities on the Harshaw property (e.g., in IA04, IA06 and IA07) apparent on aerial photos and evident via this study indicate that cobalt, copper, iron, lead, nickel, and zinc (as a partial list assessed herein) may impact FUSRAP remediation but will unlikely govern FUSRAP actions.

The presence of elevated concentrations of Co, Fe, Pb, Mo, Ni, and Tl (relative to health-risk screening levels) may pose risks to remediation workers and residents, thereby indicating the need for administrative and engineering controls to protect workers from non-MED constituents during future FUSRAP-related cleanup activities.

The previously identified MED/AEC-related metal, molybdenum, is the only non-radiological metal retained under FUSRAP. Molybdenum is also found throughout the site and is weakly (to moderately in IA04) correlated with uranium. The inclusion of molybdenum under FUSRAP

may require remedial actions outside the uranium footprint, which may require the use of field screening techniques for Mo, such as XRF.

In summary, the analysis of the spatial distributions, concentration scatter plots, aerial orthophotos, and operational records generally confirms that the large array of industrial metals found on the Harshaw site fall outside the FUSRAP purview. The USACE will further assess site conditions in subsequent CERCLA documents to ensure that molybdenum is addressed along with MED-related radiological contaminants of concern under the FUSRAP authority. Collocated metals outside the authority will be co-remediated and but will not define the extent of remediation.

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