Appendix D
National Exposure Research Laboratory (NERL)
And University of Colorado Laboratory for
Environmental and Geological Studies (LEGS)
Lead and Arsenic Reports

Arsenic and Lead Contamination in Soils – Omaha Nebraska

Evan Englund
May, 2004

Introduction

An exploratory data analysis was conducted to investigate the relationship between lead and arsenic contamination in Omaha residential soils. The data used were from two files. "Big Table-Pb-As-CORRECTED 20040430.xls" contains routine XRF analyses from quadrant and zone samples in residential yards. "All lab data for kriging 20040504.xls" contains laboratory analyses for a subset of the residential samples. The data collection was not designed for the purpose of evaluating the lead-arsenic relationship, so formal statistical tests and procedures were not used. Data analysis was largely graphical. Numerous plots were used to look at the relationship between lead and arsenic and at their relationships to other metals. Also examined was the relationship between lead and arsenic and distance from the refinery. The data were also plotted in sequential order to look for changes in sampling or analytical methods that might confound the data analysis.

Conclusions

- High levels of arsenic contamination (>25 ppm) are not related to the widespread lead contamination from the refinery site. The sources of this contamination are unknown.
- Most samples appear to have traces of arsenic contamination correlated with the lead. The source of this low-level contamination is probably the refinery.
- At the lowest lead concentrations (<50 ppm) the associated arsenic concentrations generally fall below 15 ppm. These are consistent with typical "background" levels across the U.S.
- At lead levels in the range of 400 to 1000 ppm, the upper range of arsenic increases to about 20 ppm.

Discussion

Laboratory data for arsenic are not representative of the entire sample population. Arsenic was measured only in the first 28% of the laboratory samples. Spatially, these are biased closer to the refinery. This limits the usefulness of laboratory arsenic data for detailed spatial analysis with variogram modeling and kriging.

The relationship between arsenic and lead in laboratory samples is shown Figure 1, with the logarithmic axes. For comparison, Figure 2 shows arsenic and lead for a nationwide sample of "undisturbed" (presumably uncontaminated) soils collected by the USGS. The scale is the same as Figure 1. As a first approximation, arsenic concentrations less than 15 or 20 ppm and lead concentrations less than 50 or 60 ppm can be considered not significantly contaminated. The Omaha samples are consistent with the USGS samples at the lower concentrations, but most lie on a trend that shows high levels of lead contamination associated with low levels of arsenic contamination. The lead contamination has already been demonstrated to be spatially consistent with the assumption that the refinery is the source. It is reasonable to assume that the associated increases in arsenic are from the same source.

The only significant departures from the general trend are samples with high (>20 ppm) levels of arsenic contamination. These are not correlated with lead and thus are from some other source.

Figure 3 shows a scatterplot matrix with a number of other metals of interest in addition to arsenic and lead. Note the very strong relationship between lead and zinc. This is what we would expect to see (and do see at other sites) when the only source of zinc contamination is the same as the lead. It is likewise the pattern we would expect to see for arsenic and lead if both were from a single source. Any departure from this ideal pattern is an indicator of multiple sources.

High values of arsenic do not appear to be correlated with high values of any of the other metals shown. In particular, the lack of association with copper and chromium suggests that wood treated with copper chromium and arsenic (CCA) is not a major source of arsenic.

Figures 4–7 show XRF and laboratory measurements for lead and arsenic plotted against the sequential ID number. This shows roughly how the samples varied through time over the course of the investigation. The gaps in the sequence appear to be gaps in the numbering, not missing data. For lead, the XRF and lab data have the same basic pattern, which presumably reflects the locus of sampling activity moving through the plume. The arsenic XRF data do not show the same pattern as lead (most arsenic XRF measurements are non-detects and not shown). The early arsenic XRF measurements appear to have used an instrument or procedure with a lower detection limit. Laboratory arsenic measurements represent only the early phase of investigation.

Figures 8-11 show XRF and laboratory measurements for lead and arsenic, this time plotted against distance from the refinery source. Both XRF and laboratory data sets show the same pattern for lead – a strong decrease with distance from the refinery. The laboratory data include drip zone samples, which accounts for the higher frequency of high lead concentrations. Arsenic XRF data show no trend with distance. The laboratory data do show a decreasing trend with distance, but only at the low levels that are usually non-detects with XRF. This supports the interpretation from Figure 1, that arsenic contamination from the refinery does not raise total arsenic above 20 ppm in residential areas. The higher arsenic laboratory measurements, like the XRF measurements, are not related to distance from the refinery.

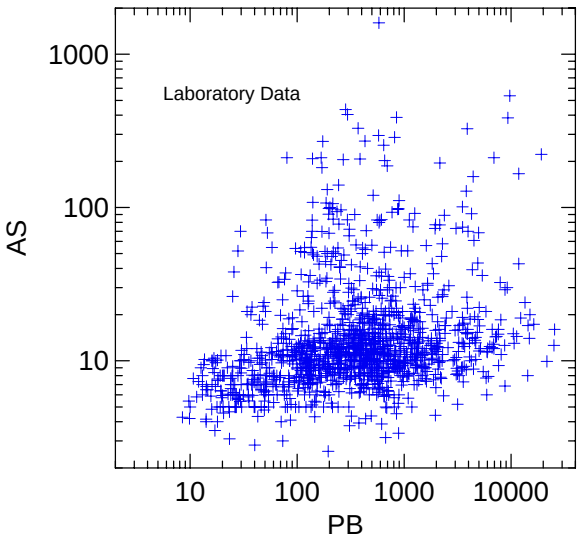


Figure 1 Laboratory analyses of lead and arsenic in Omaha residential soils.

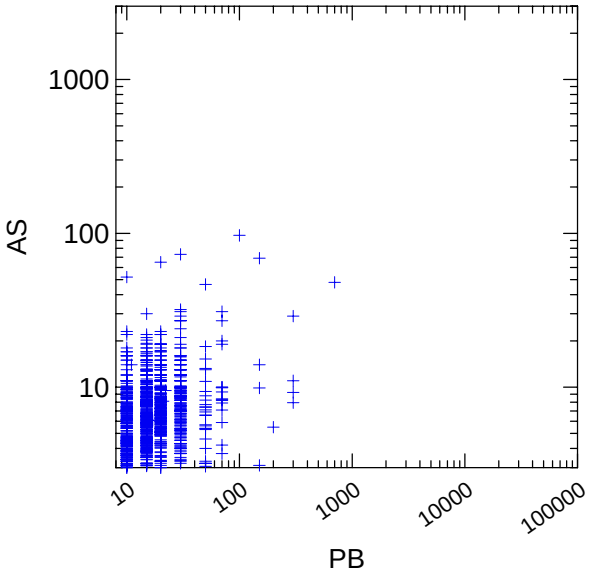


Figure 2 Lead and arsenic in a national sample of U.S. soils. (from USGS Professional Paper 1270)

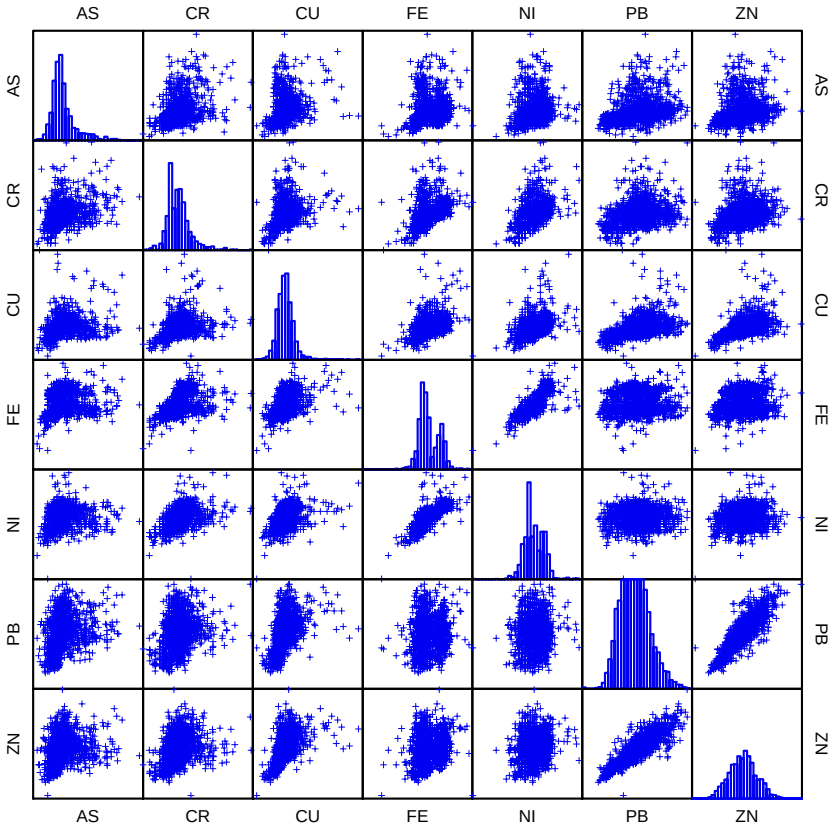


Figure 3 Scatterplot matrix of laboratory analyses of metals in Omaha residential soils.

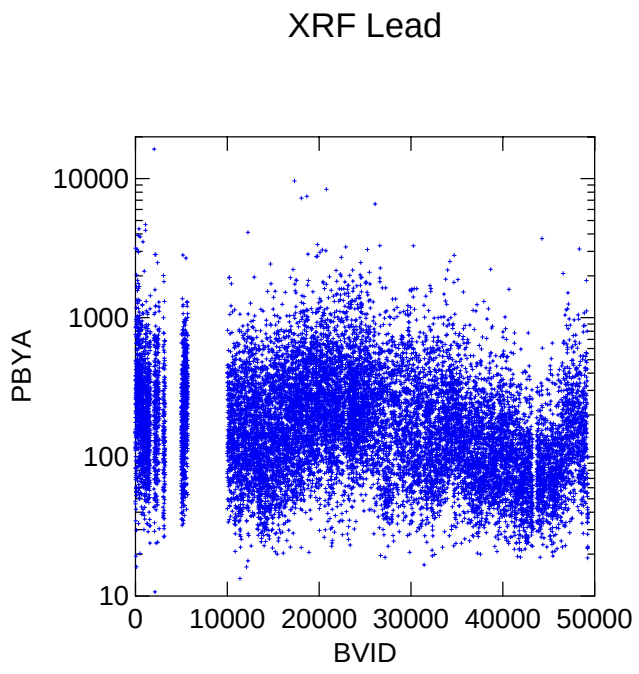


Figure 4 XRF lead (yard quadrant YA) versus sequential ID number

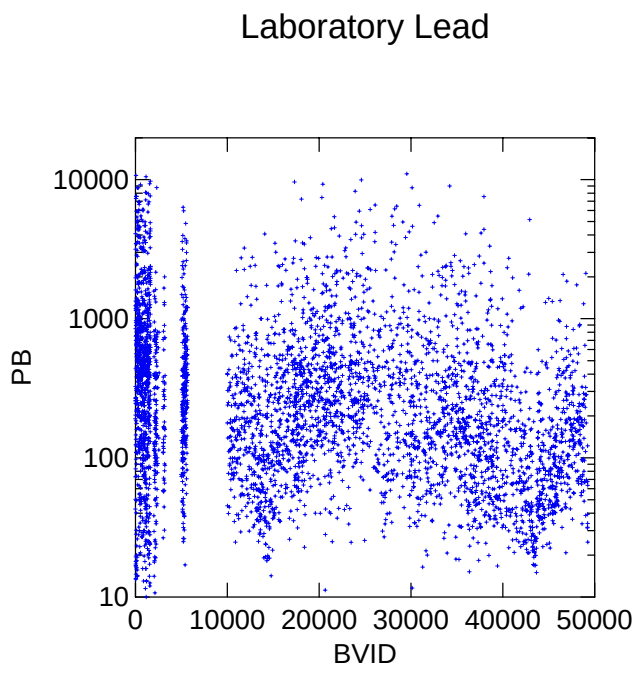


Figure 5 Laboratory lead (including drip zone samples) versus sequential ID number.

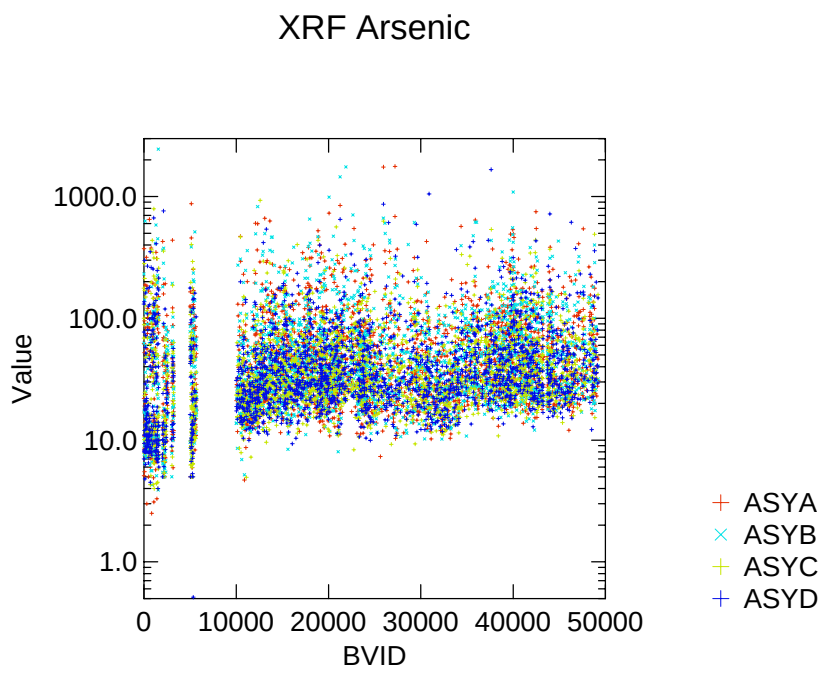


Figure 6 XRF arsenic (all yard quadrants) versus sequential ID number.

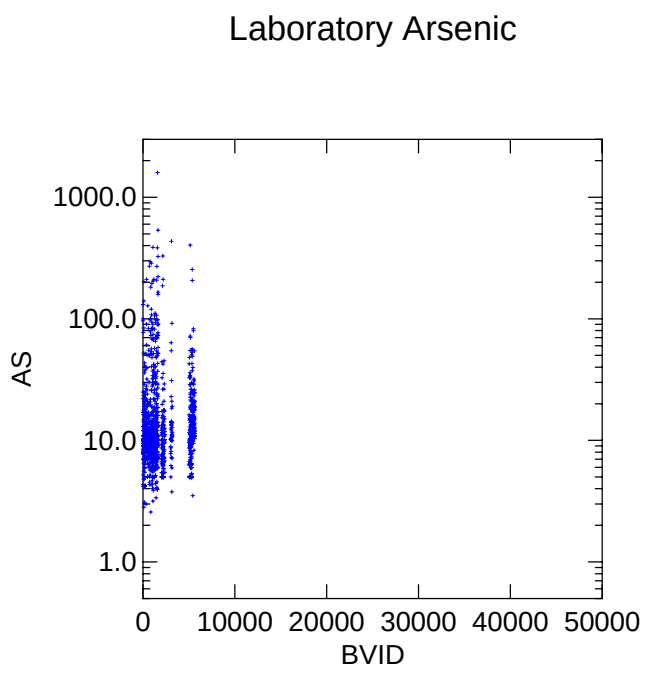


Figure 7 Laboratory arsenic versus sequential ID number.

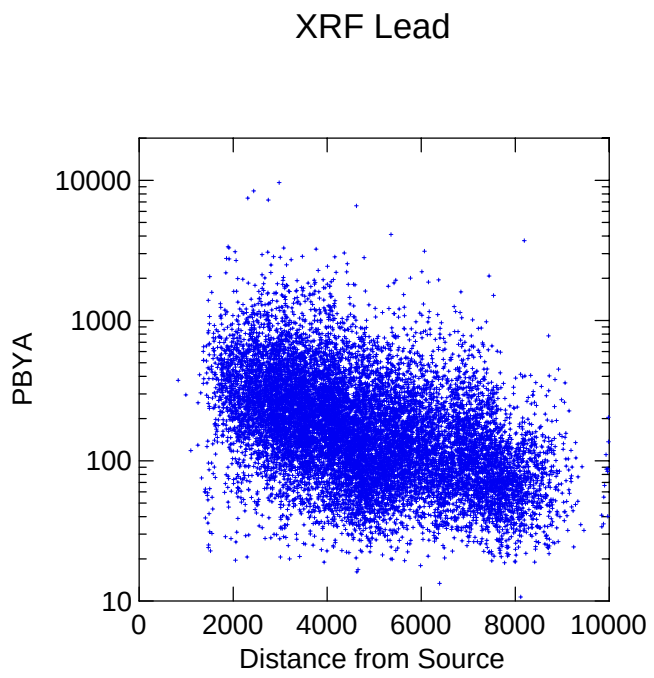


Figure 8 XRF lead (yard quadrant YA) versus distance from refinery.

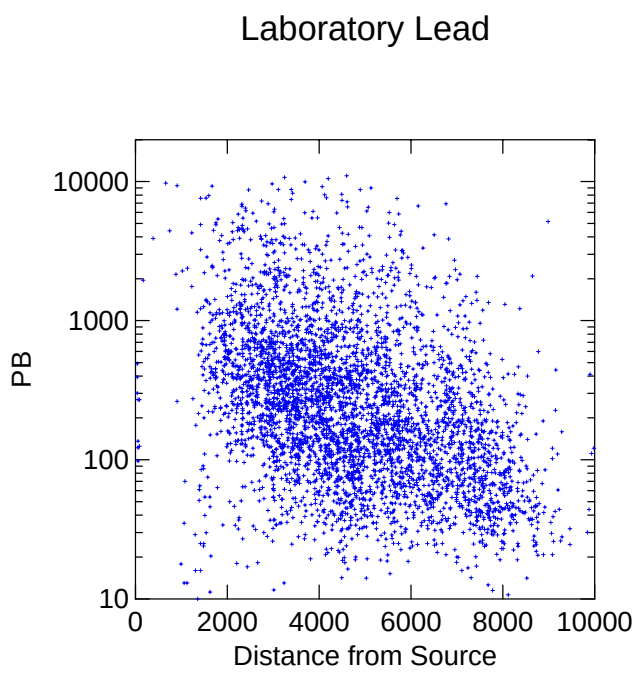


Figure 9 Laboratory lead (including drip zone samples) versus distance from refinery.

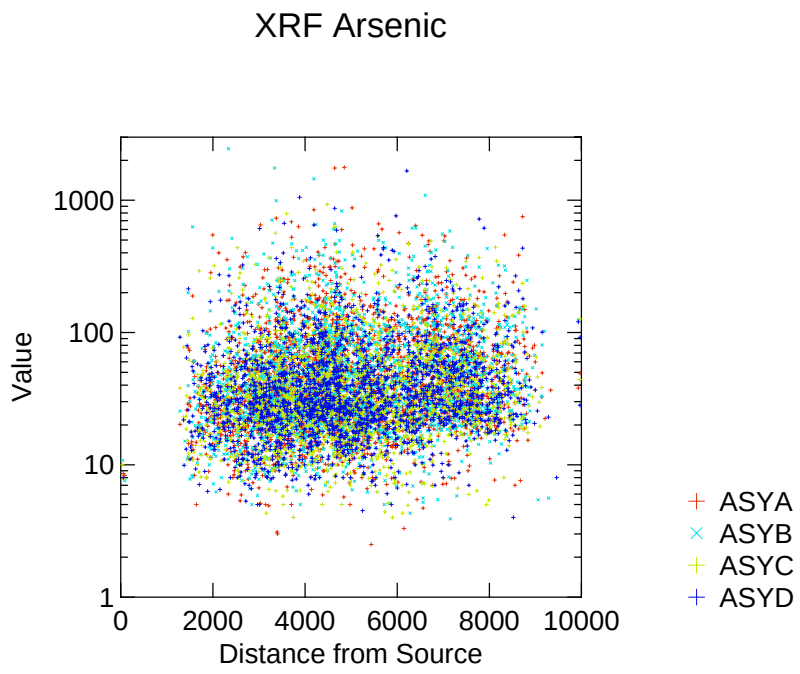


Figure 10 XRF arsenic (all yard quadrants) versus distance from refinery.

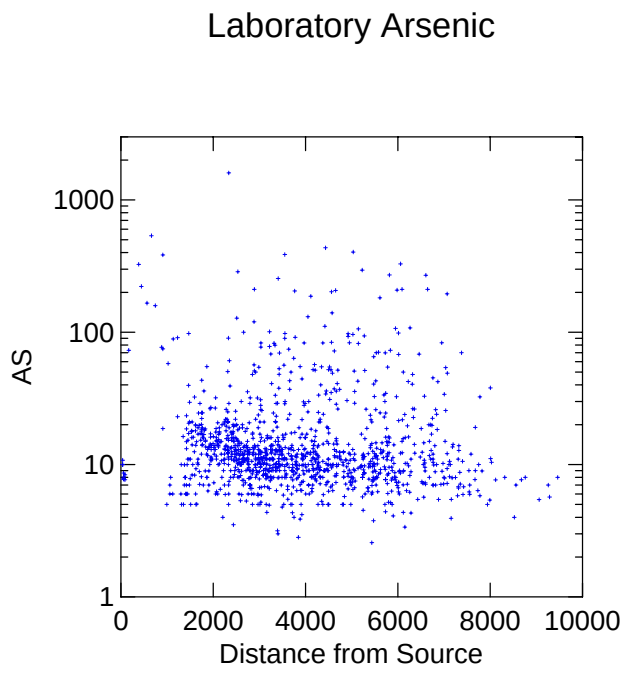


Figure 11 Laboratory arsenic versus distance from refinery.

Spatial Distribution of Lead and Arsenic Contamination
Omaha, Nebraska

Evan Englund
May, 2004

Conclusions

- Lead contamination is concentrated in the vicinity of the refinery source, and decreases with distance from the source. This is the expected pattern from a single primary point source of contamination.
- Arsenic does not show the same pattern as lead. In spite of problems with arsenic data, three different methods show spatial patterns that are roughly consistent with each other, and not consistent with lead. In particular, the arsenic data show high values at the western boundary of the heavily sampled area, where the lead concentrations are lowest.

Procedure

This report examines the spatial distributions of lead and arsenic contamination in soils in Omaha Nebraska. The purpose is to map broad spatial trends or patterns in the contamination in order to make a visual test of the hypothesis that lead and arsenic contamination are closely related to each other and are derived primarily from a single refinery source. The maps shown here use data transforms to reduce variability in order to distinguish between areas of relatively high and low contamination. They should not be used to estimate actual contaminant concentrations or to identify areas requiring remediation or further sampling.

The maps are contour maps of un-weighted moving averages of log-transformed or indicator-transformed concentration. Un-weighted moving averages were used instead of kriging for simplicity. Kriging is a *weighted* moving average, where the sample weights are calculated to minimize estimation variance, given a model of the spatial variance among samples (i.e., the variogram). Variograms of both arsenic and lead (not shown) have high "nugget effects". Nugget effects combine measurement error variance and short-distance spatial variability. In kriging, high nugget effects reduce the importance of sample proximity, which tends to make sample weights more equal. When the variogram model is composed entirely of nugget effect, all sample weights are equal, and kriging is identical to an un-weighted moving average.

The practical significance of using un-weighted moving averages for the maps is that they are over-smoothed. This is not a problem here, where the estimates are not being used for decision-making, but simply to look at the broad spatial patterns and trends.

The data used were from two files. "Big Table-Pb-As-CORRECTED 20040430.xls" contains routine XRF analyses from quadrant and zone samples in residential yards. "All lab data for kriging 20040504.xls" contains laboratory analyses for a subset of the residential samples.

Figure 1 shows the distribution of lead. The mean of the XRF measurements of the four quadrants in each yard was log-transformed, then un-weighted moving averages of the log values were calculated for points on a 100-meter square grid, and the results were contoured. This would be difficult to back-transform into estimates of lead concentration, but the pattern of high and low concentrations is clearly shown. The highest values occur near the refinery source, and decrease with distance from the source.

Figures 2, 3, and 4 show the spatial distribution of arsenic calculated by different methods. Different approaches are used because of problems with arsenic data. XRF measurements are mostly non-detects, while laboratory data are sparse and do not represent the entire sampled area.

Figure 2 is an indicator map based on XRF analysis. The indicator transform of a set of data simply assigns a value of one or zero to a sample depending on whether its measured value is above or below a threshold concentration. In this case all samples with arsenic measurements were assigned values of one, while samples with non-detects were assigned values of zero. In effect, the detection limit is the indicator threshold. Although "detection" is not exactly the same as "above a constant threshold", it is assumed to be a reasonable approximation. The un-weighted moving average of these indicator values is equal to the fraction of detects in the moving window. A value of 0.3 on the map, for example, indicates that 30% of the samples in that vicinity are detects, and 70% are non-detects. This can be interpreted as an estimate of the probability that a new sample taken nearby would have an arsenic concentration detectable by the current XRF method.

Figure 3 shows the distribution of arsenic based on XRF data. Analysis in this case was limited to one quadrant (YA). Arsenic non-detect flags were not available in the data set used in this analysis. Samples with no arsenic value were assumed to be non-detects if a lead measurement was present for the same quadrant. If no lead measurement was present, the sample was assumed not analyzed. Non-detects were assigned estimated background concentrations of 7.4 ppm (ln As = 2.0) Data were log-transformed, and moving window averages were computed and contoured as in Figure 1. Figures 2 and 3 show very similar patterns. This suggests that the areas of highest average arsenic concentrations are related to an increase in the overall number of contaminated samples, not to isolated extreme outliers. The pattern of high arsenic is distinctly different from that of lead, and shows no obvious relationship with the location of the refinery.

Figure 4 shows the distribution of arsenic based on laboratory data. Most residences with laboratory measurements did not have more than one. If more than one was available, only one was used. A sample in this case could represent any quadrant or non-drip zone at a residence. Only 1% of the laboratory arsenic measurements were reported as non-detects at a detection limit of 5 ppm. For these, the detection limit was substituted. Data were log-transformed, and moving window averages were computed and contoured as in Figures 1 and 3. The pattern is generally similar to Figures 2 and 3 in the western half of the map, but shows some additional high arsenic areas in the east. The laboratory data set includes some samples from a transect extending eastward from the refinery site. These samples were not included in the XRF data set. This difference in data accounts for some of the differences between the XRF and laboratory maps. The spatial pattern of laboratory arsenic, like the pattern of XRF arsenic, appears unrelated to lead.

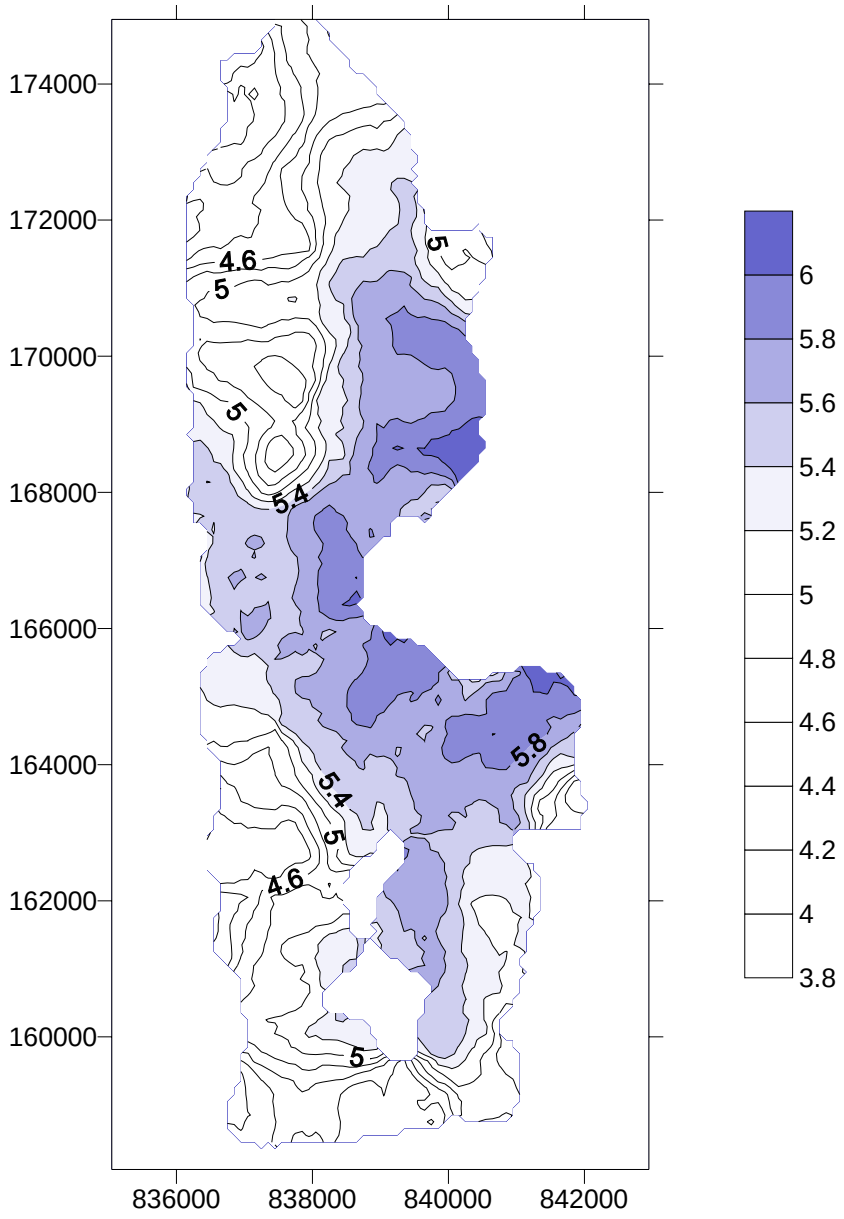


Figure 1 Moving average of XRF ln Pb

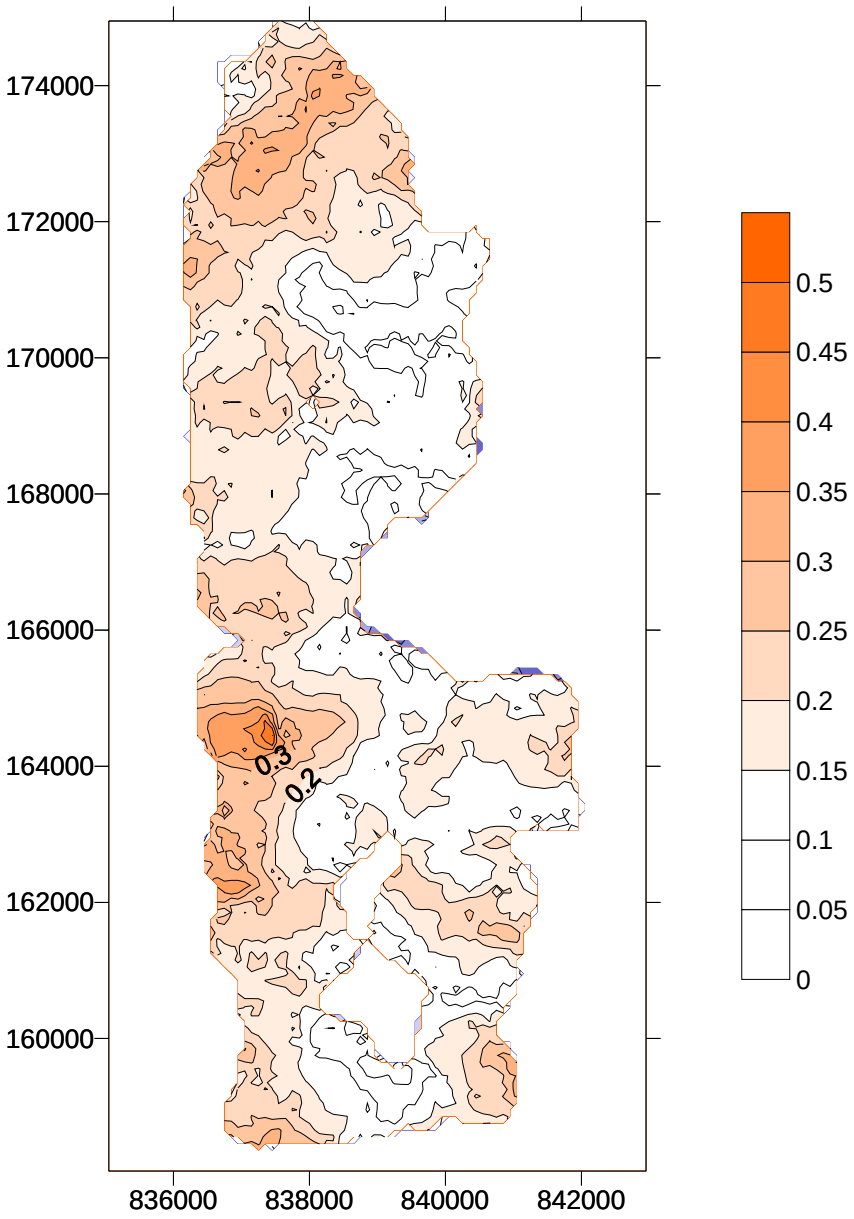


Figure 2 Moving average of XRF Arsenic indicator (probability of detect)

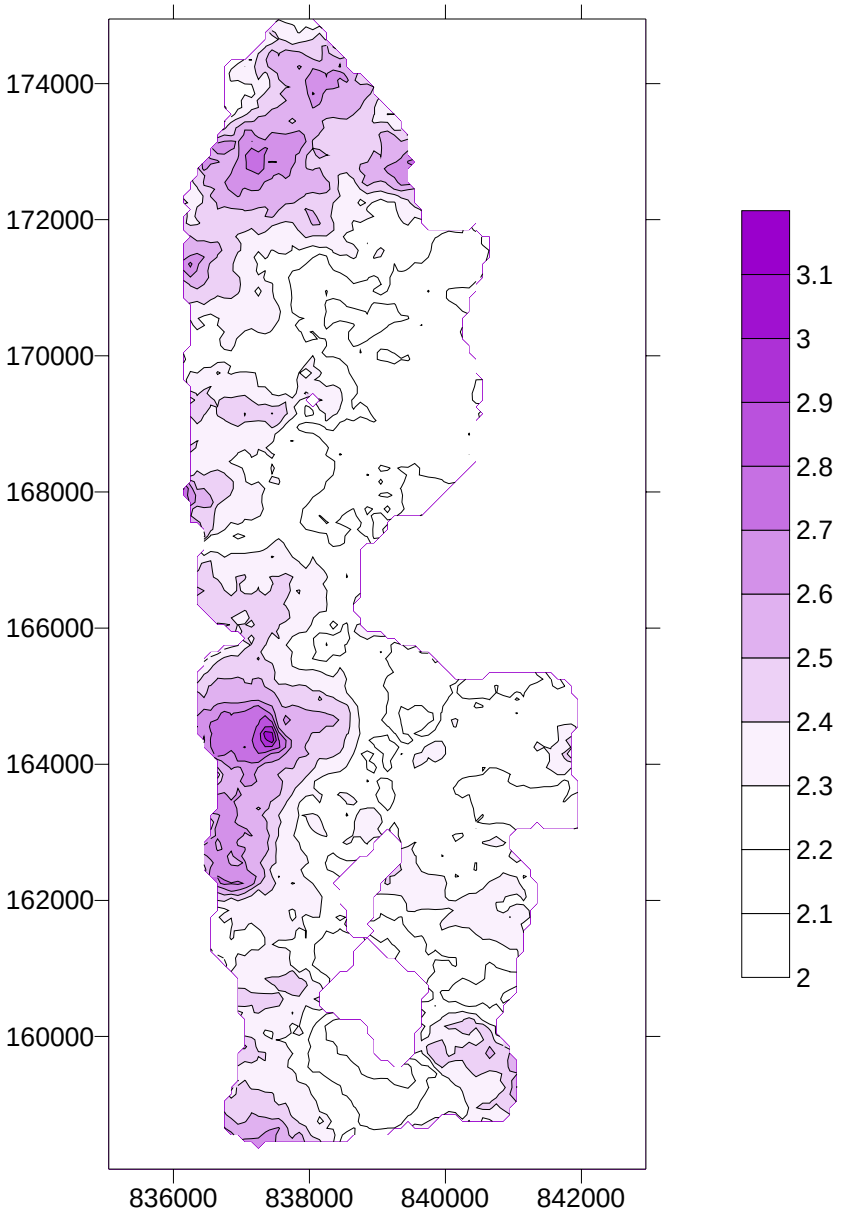


Figure 3 Moving average of XRF ln As (non-detects = 2)

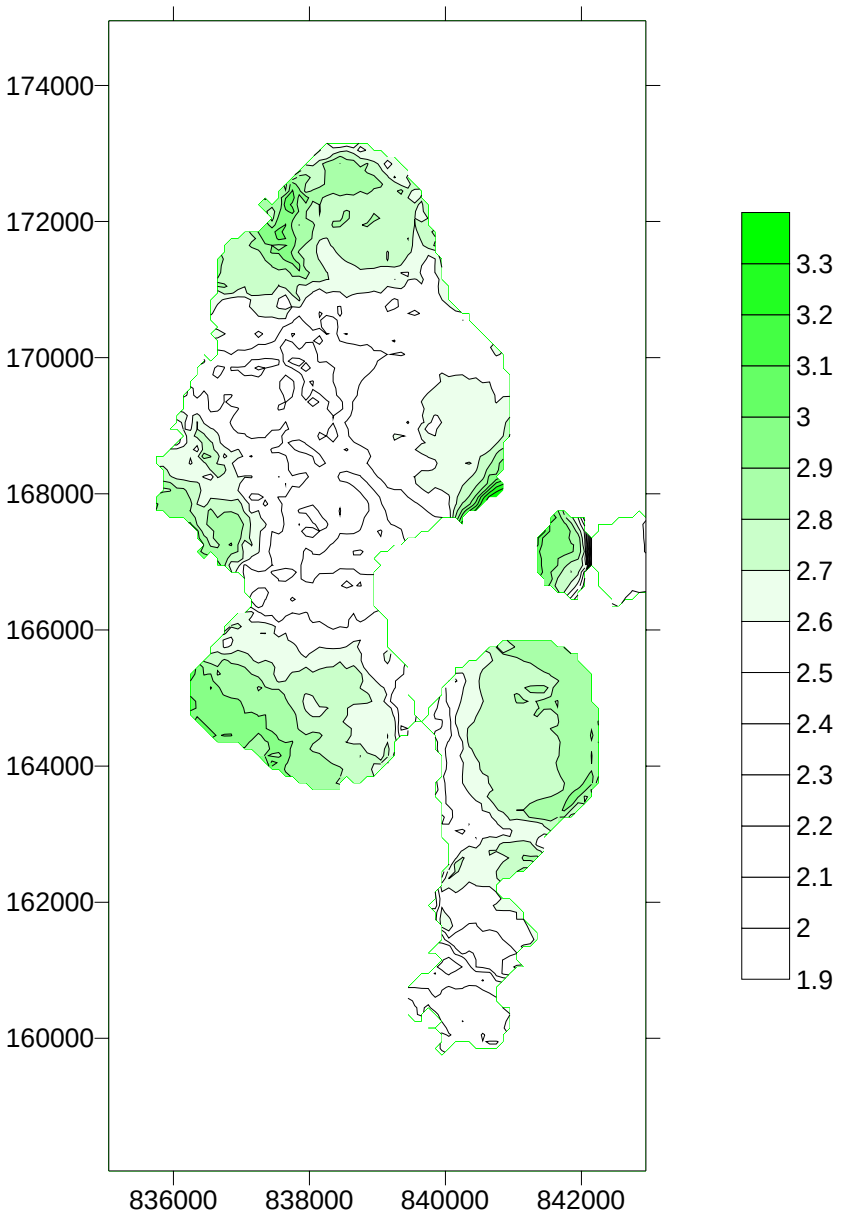


Figure 4 Moving average of laboratory ln As.

Omaha Lead Site

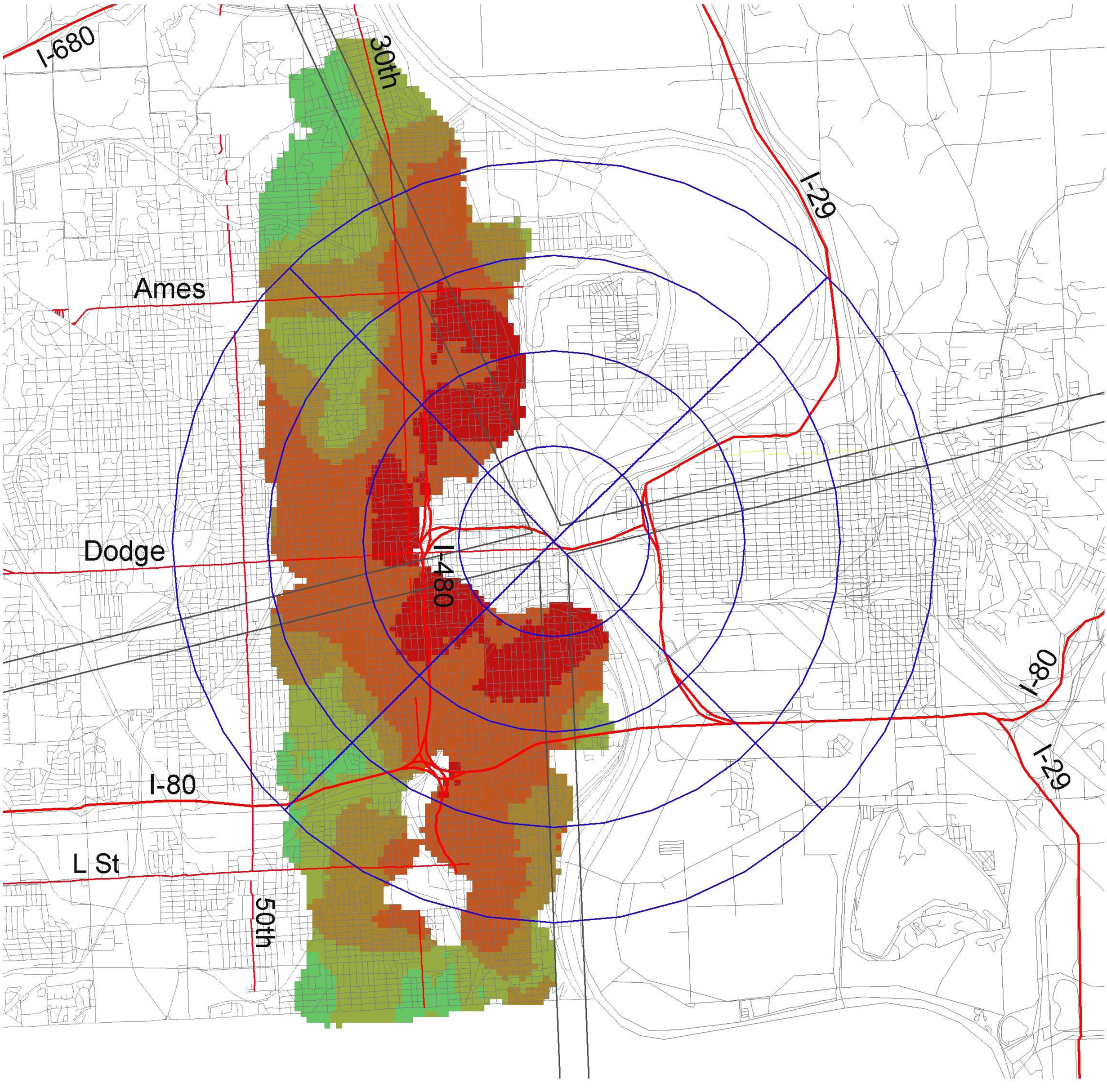
Unweighted Moving Average of Log Values for Lead Means by XRF

3.9 - 4.3
4.3 - 4.8
4.8 - 5.2
5.2 - 5.7
5.7 - 6.2

6,326 distinct 100-sq-m cell locations used in analysis;
Data file: ejefigure1g; Maximum value represented = 6.16

1 0 1 Miles

N W E S



Omaha Lead Site

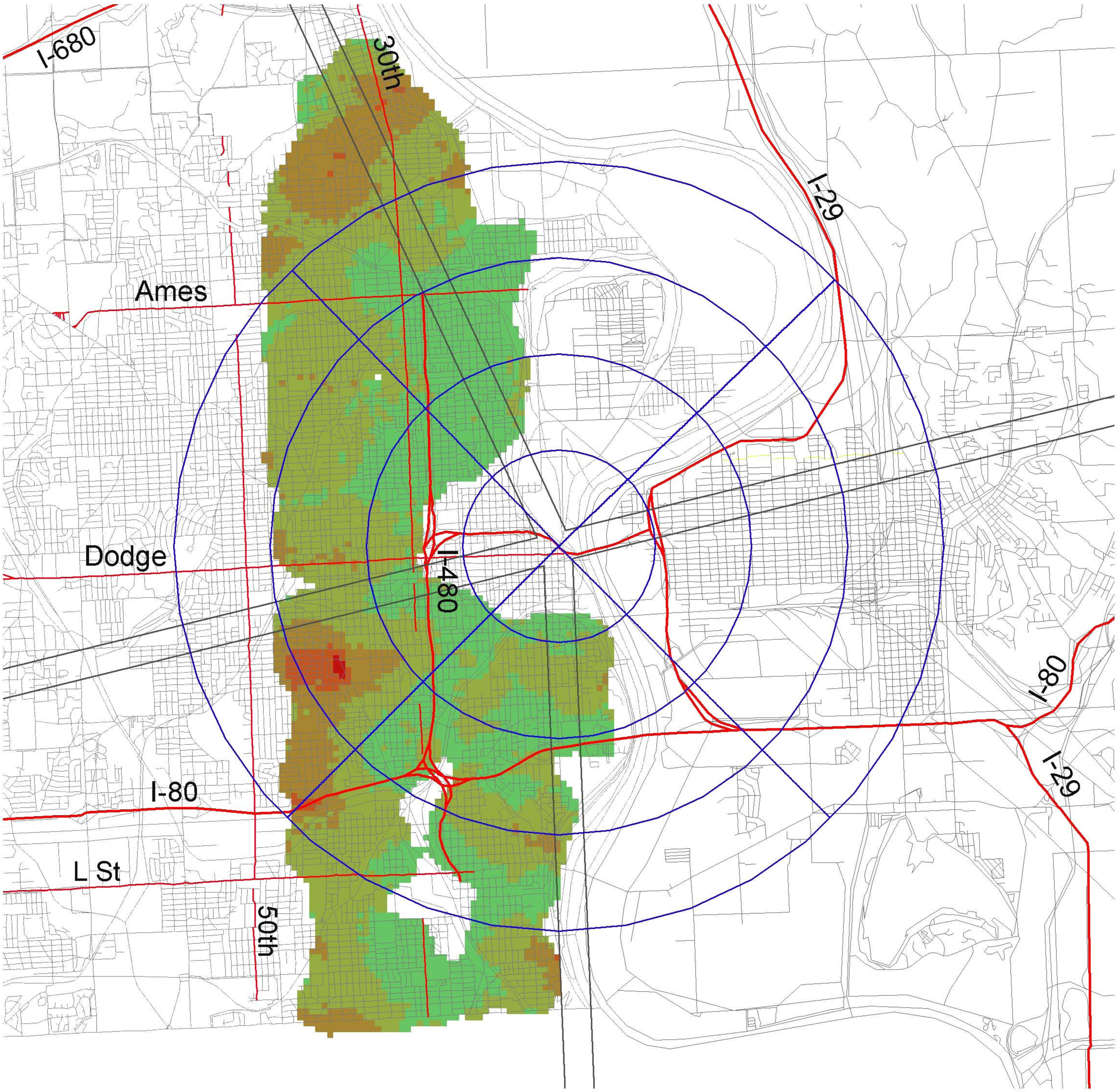
Probability that Arsenic Levels are Detectable by XRF Method

0.0 - 0.1
0.1 - 0.2
0.2 - 0.3
0.3 - 0.4
0.4 - 0.5

6,254 distinct 100-sq-m cell locations used in analysis;
Data file: ejefigure2g; Maximum probability represented = 0.50

1 0 1 Miles

N W E S



Omaha Lead Site

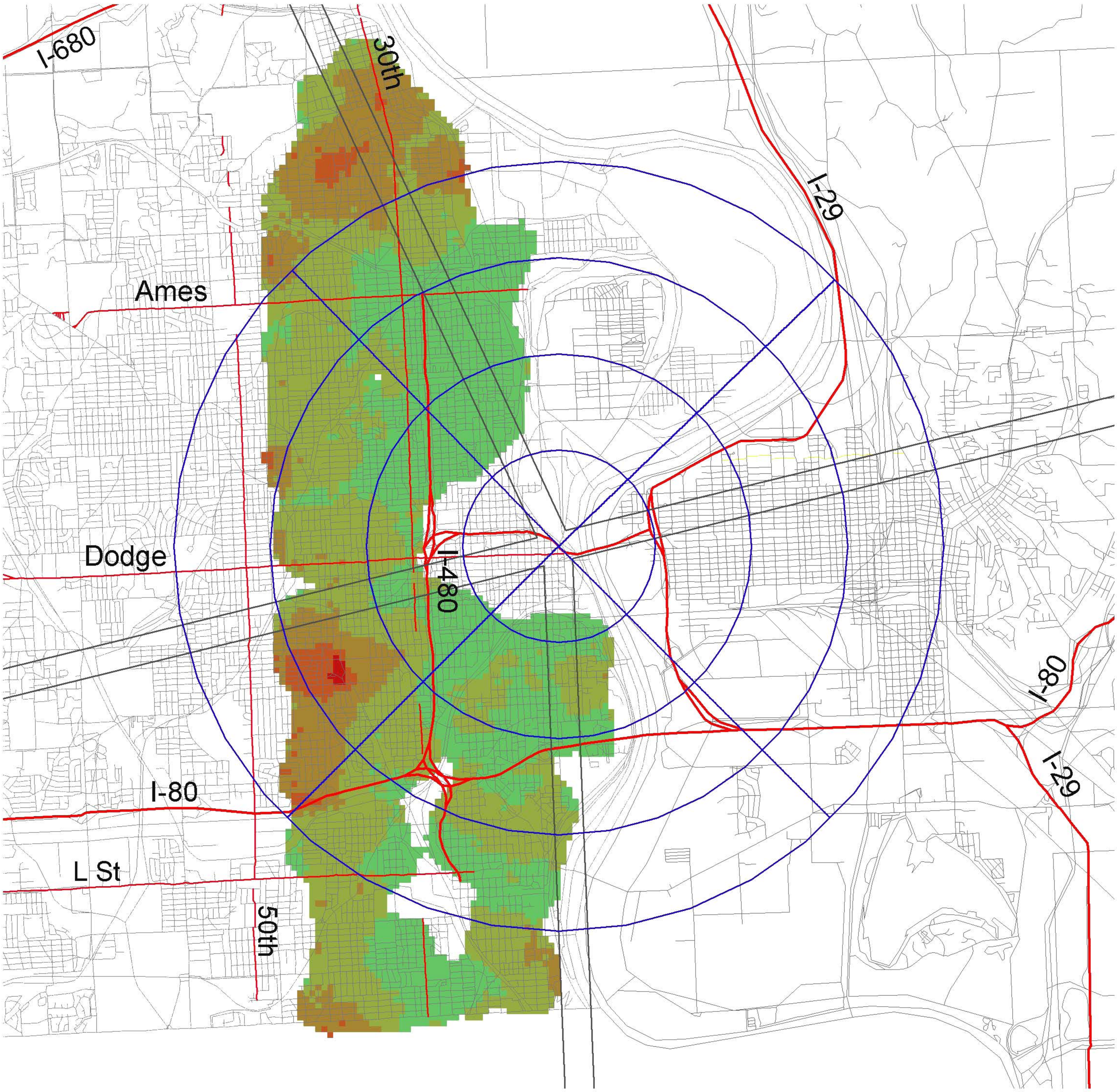
Unweighted Moving Average of Log Values for Arsenic YA Quadrant by XRF

2.0 - 2.2
2.2 - 2.4
2.4 - 2.6
2.6 - 2.8
2.8 - 3.1

6,258 distinct 100-sq-m cell locations used in analysis;
Data file: ejefigure3g; Maximum value represented = 3.06

1 0 1 Miles

N W E S



Omaha Lead Site

Unweighted Moving Average of Log Values for Arsenic by Laboratory

1.9 - 2.2
2.2 - 2.5
2.5 - 2.8
2.8 - 3.1
3.1 - 3.4

4,401 distinct 100-sq-m cell locations used in analysis;
Data file: ejefigure4g; Maximum value represented = 3.40

1 0 1 Miles

N W E S

Anomalous Arsenic Concentrations at Omaha Nebraska Superfund Site

For

USEPA Region 7

May 24, 2004

By

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Introduction

A small population (approximately 116 out of 1263 samples --9%) of residential soil samples collected as part of the Omaha lead site remedial action having anomalously high arsenic concentrations (> 40 mg/kg). I have been asked by EPA to determine if these elevated arsenic values could be attributed to the ASARCO facility, which has been determined to be the primary source of elevated lead values in the community. This report will be based on both limited data and time using a statistical review and speciation analyses.

Arsenic Geochemistry

Arsenic is found in many minerals and is typically enriched in soils originating from shales/schists and argillaceous sediments. Uncontaminated soils have mean concentrations of 1-6 mg/kg for arsenic (Fergusson, 1990), worldwide. The lowest levels are typically found in soils derived from volcanic or carbonate terrain, (andesites and limestones), and average 1-7 mg/kg As. The near neutral (6-8.5 pH) acidity of the local soils stimulate very low metal mobility, generally concentrating metals in the surface horizons by preventing there downward distribution over time. Mobility may be enhanced by irrigation, aeration, or by utilization of soil amendments (Logan and Chaney, 1983).

Numerous sources arsenic have historically led to elevated concentrations in surface soils. Table 1 is a compilation of the most common arsenic sources, speciation, and associated soil concentrations (data from Barzi et al., 1996, Kabata and Pendias, 1993; Fergusson, 1990; and Drexler, per. communication, 1998).

Table 1. Compilation of common arsenic sources and associated soil-metal concentrations.

Source	Arsenic Speciation	Associated Soils As mg/kg
Mining	Sulfosalts, As_2S_3, FeAsS	23-1023
Chemical Works	PbAsO, As_2O_3 ,R**AsO	10-2000
Metal Processing	As_2O_3, AsM*O, PbAsO	33-2500
Application of Pesticides	As_2O_3, PbAsO, R**AsO, Na-Ca arsenates	38-625
Gardens and orchards	PbAsO	38-892
Fly Ash	Unknown	1-9
Municipal Sludge	Unknown	1-6
Sheep/Cattle Dip/Tannery	As_2O_3	300-1000
Wood Preservatives	Cr-Cu arsenates	10-2000

**R = Organic compounds, *M = typically Pb, Ca, Cd, Zn, or Sb.

Speciation

Three samples were collected for metal spectiation using EMPA techniques. Two of the samples (13348 and 42638) contained high arsenic and low lead, while the third sample (47055) contained both elevated arsenic and lead. These two sample sets showed a

distinct difference in lead and arsenic speciation. The first set of samples indicated the relative arsenic mass was dominantly (90-95%) found as liberated arsenic trioxide particles and lead was found in MnOOH and phosphate (Figure 1a-b).

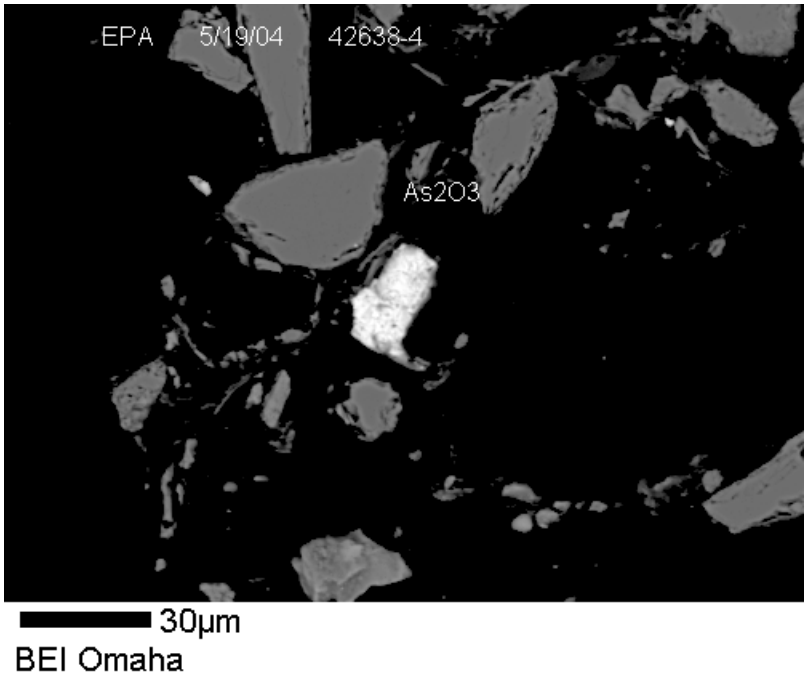
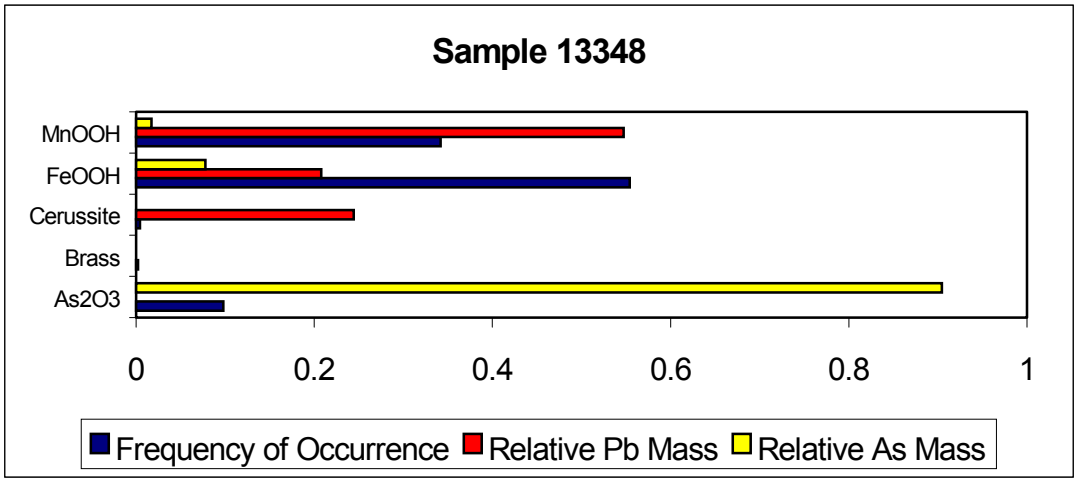
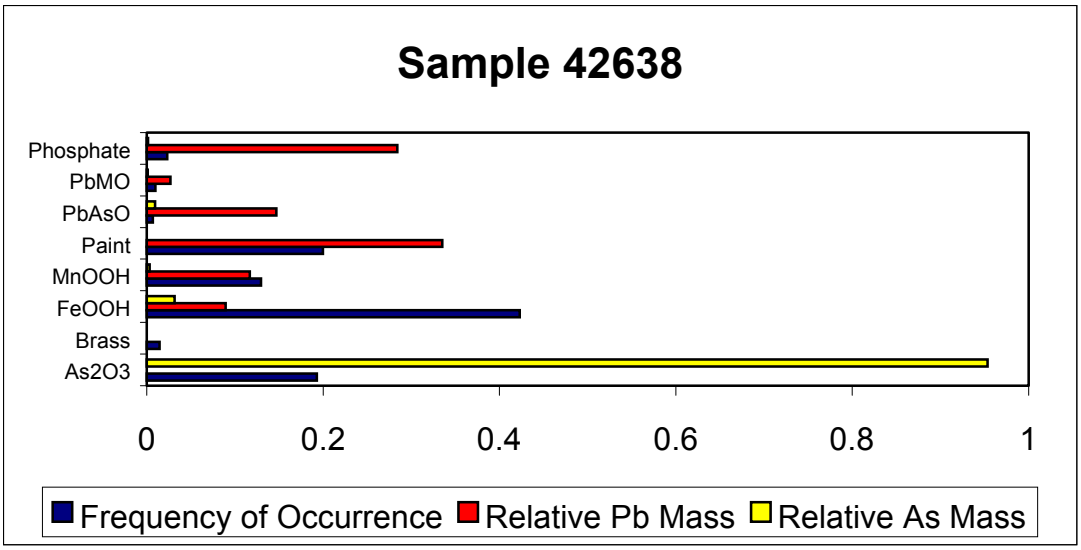


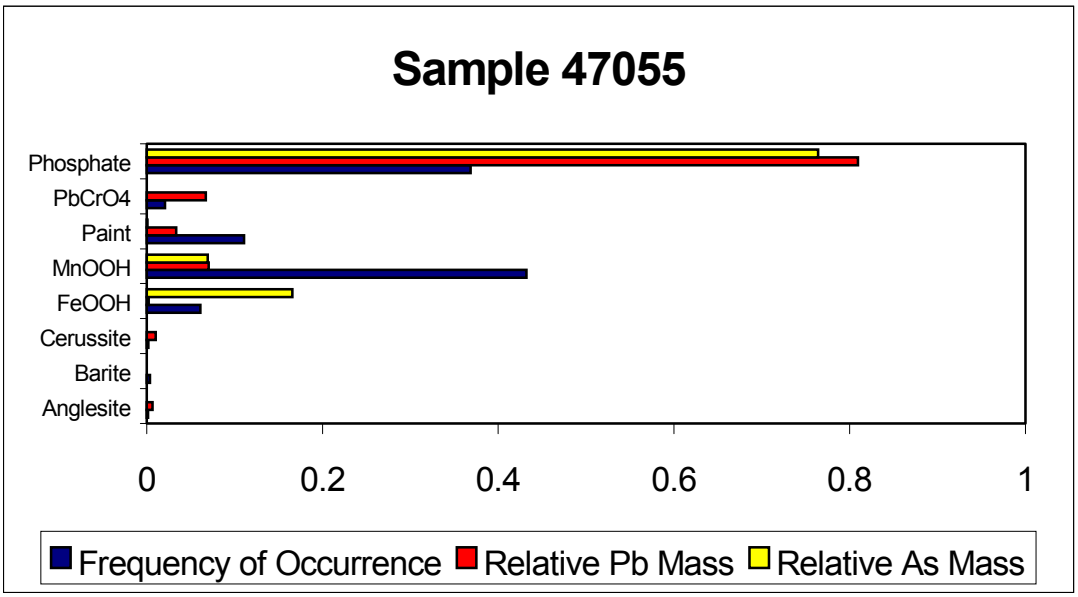
Figure 1.


Sample 13348
MnOOH
FeOOH
Cerussite
Brass
As2O3
0
0.2
0.4
0.6
0.8
1
Frequency of Occurrence
Relative Pb Mass
Relative As Mass


Sample 42638
Phosphate
PbMO
PbAsO
Paint
MnOOH
FeOOH
Brass
As2O3
0
0.2
0.4
0.6
0.8
1
Frequency of Occurrence
Relative Pb Mass
Relative As Mass

The second sample set has arsenic and lead relative mass dominated (75-80%, respectively) by phosphate particles Figure 2. No clear source to the metals was found, but it is likely the both originate from the same, soluble As-Pb compound(s).

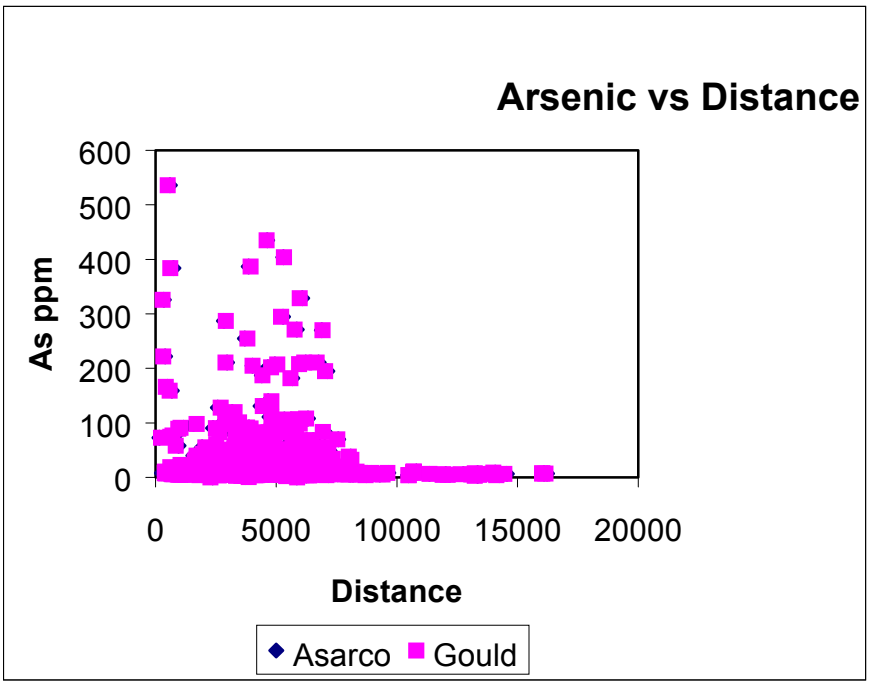
Figure 2.



Metal Concentration vs Distance

A comparison of arsenic and lead concentration with distance from the Asarco plant was made. The data, Figures 3a-b, show two populations, one indicates a series of samples with elevated arsenic and lead concentrations very near the plant, and both metal show a statistically significant increase in elevated metals concentration at between 4000-5000 meters from the plant center. This may suggest a "fugitive" and/or "stack" related portion to the overall metal concentration. Spatially, there is no clear distribution in elevated arsenic concentrations. Values are generally found randomly in all directions from the Asarco facility, Figure 4.

Figure 3.



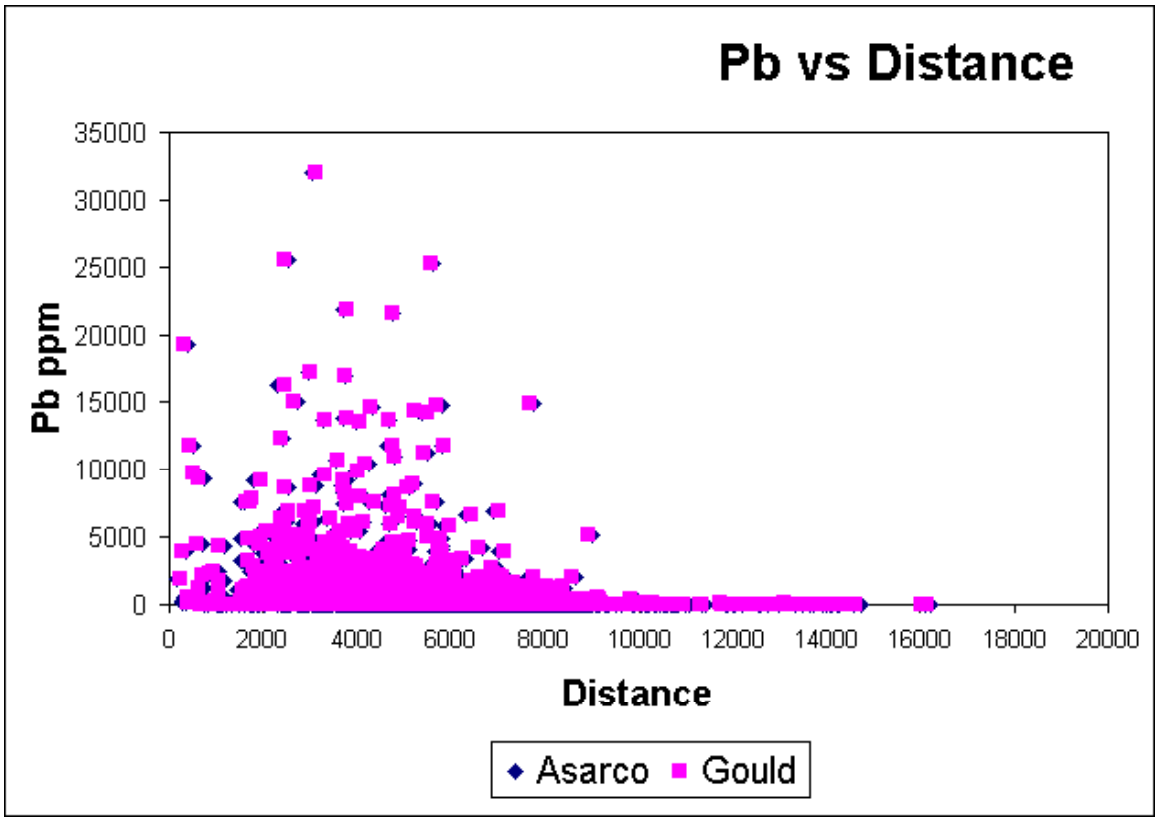
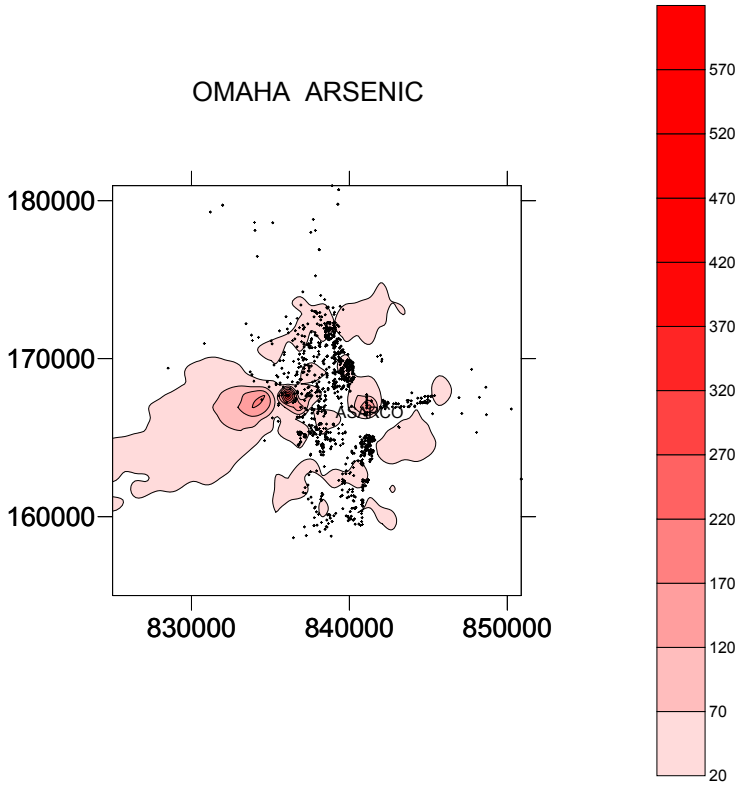

Pb vs Distance
Pb ppm
35000
30000
25000
20000
15000
10000
5000
0
0
2000
4000
6000
8000
10000
12000
14000
16000
18000
20000
Distance
Asarco
Gould

Figure 4


OMAHA ARSENIC
180000
170000
160000
830000
840000
850000
ASARCO
570
520
470
420
370
320
270
220
170
120
70
20

Metal Correlations

A correlation analysis using all of the available metals analyses (22 elements) was run on the data set. No significant correlation between arsenic and any of the tested metals can be found Table 2. This would suggest that not only is the arsenic not correlated (ie associated) with lead, but that no other metals are found to co-locate with arsenic. Thus, arsenic is of a rather "pure" form and may represent a commercial product instead of a industrial emission.

Table 2. Correlation coefficients for arsenic vs other metals.

Al	Sb	Ba	Be	Bi	Cd	Ca	Cr	Co	Cu	Fe	Pb	Mg	Mn	Ni	Se	K	Na	Tl	V	Zn
.1	.3	0	0	.4	0	.3	.4	0	.4	.1	.2	.2	.4	.2	0	0	.3	.1	.3	.1

Conclusions

Based on the following points:

1. There is No correlation with lead------ Not from Asarco facility nor a herbicide
2. There is No correlation with Cr and Cu----- not from CCA treated wood
3. There is No correlation with Ba or Zn----- not associated with paint
4. There is no clear spatial nor distance relation to Asarco facility

5. The singularly, predominant species of arsenic is a pure arsenic trioxide. A form of arsenic, which was never identified at the Asarco facility. At the Asarco facility arsenic was primarily associated with; PbAsO and PbMO, two forms that were virtually not found the three samples.

Therefore, I believe that the predominant source of the arsenic found in these yards is most likely from the use of an arsenic rodenticide.