STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

Use of XRF to Characterize Pre-Hanford Orchards in the 100-OL-1 Operable Unit

DOE-FIU SCIENCE & TECHNOLOGY WORKFORCE DEVELOPMENT PROGRAM

Date submitted:

October 17, 2014

Principal Investigators:

Christian Pino (DOE Fellow Student)
Florida International University

Amoret Bunn, Mentor
Pacific Northwest National Laboratory

Florida International University Program Director:

Leonel Lagos Ph.D., PMP®

Submitted to:

U.S. Department of Energy
Office of Environmental Management
Under Cooperative Agreement # DE-EM0000598

Applied Research Center
Florida International University

ABSTRACT

Prior to 1943, the Hanford Site as it is known today included several small towns with approximately 8,000 acres of agricultural development. About 5,000 of those acres were used for orchards, with lead arsenate (PbHAsO4) being the common pesticide for controlling coddling moths in fruit trees. To this day, trees and stumps are still visible in the old fields. Remediation actions and special studies on the Hanford Site have recorded high concentrations of lead and arsenic in the vicinity of the old orchards. U.S. Department of Energy's Richland Operating Office, Environmental Protection Agency, and Washington Department of Ecology agreed to investigate the lead arsenate residues under the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) and designated the pre-Hanford orchards as 100-OL-1 Operable Unit. Initial characterization activities included a pilot study to evaluate the use of a field portable x-ray fluorescence (XRF) analyzer and determine if the performance of the instrument provides results that meet quality assurance criteria for cleanup decisions. XRF has only previously been used for screening purposes at the Hanford Site. An optimization study was performed to evaluate the counting times and position of the XRF using soil collected from the orchards on the Hanford Site. Three soils with a range of lead and arsenic concentrations from low (~20 mg/kg lead and ~6 mg/kg arsenic), medium (~250 mg/kg lead and ~20 mg/kg arsenic) and high (~1000 mg/kg lead and ~100 mg/kg arsenic) were analyzed; the results indicated that 60 seconds was a sufficient count time for a sample with 3 repetitions being completed at each location. Transects were set up on the Hanford Site to evaluate field variability. The results demonstrated that the concentration of lead and arsenic changed considerably with even a 6-inch separation between two measurements. The optimization study confirmed that the variability in the field was more significant than operator or instrument variability. Upon completion of the optimization study, the surface soil at four Decision Units (DU) (OL-14, OL-32, OL-IU6-4 and OL-FR2-1) was evaluated with the XRF. The DUs vary in size from 28 to 250 acres. The past activities in each site are also distinct, as orchard activity may or may not have been present in every DU. Activities in the DUs after 1943 vary as well. OL-14 had a military camp in the 1950s; OL-FR2-1 is near the 100 F reactor area, and had more disturbances from remediation activities than the other DUs. The DUs together provide an adequate representation of the entire 100-OL-1 Operable Unit. Results indicated that there were areas in each DU with concentrations above the screening criteria for both lead (250 mg/kg) and arsenic (20 mg/kg).

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

The Hanford Site was created in 1943 under the *Second War Power Act* in order to create nuclear weapons for World War II. Much of the land before acquisition was used for agricultural development, especially orchard farming with over thousands of farmers covering thousands of acres of orchards. Various types of orchard farming was done on the land including apples, cherries, apricots, peaches, pears, plums and prunes; though the common denominator among these is with the use of lead arsenate ($PbHAsO_4$) pesticide beginning in 1890 (Figure 1). Lead arsenate had a number of applications per season; usually schedule I which included two applications and schedule II which included three applications of the pesticide. The form of application varied though predominantly included either 2.7 kg of paste or 1.4 kg of powder to 787 L of water.

Figure 1. Orchardist spraying lead arsenate.

With the coming of the 1920s and the great depression, many orchardists had to abandon their plots due to economic reasons as well as environmental factors such as drought. Orchardists would sometimes even cut down trees in order to sell for the production of paper, leading to stumps still being present today with the unique semi-arid environment present in eastern Washington. During the 1940s, a “Declaration of Taking” was issued, forcing the orchardists to abandon their land as it was being acquisitioned by the government, known now to be for the Manhattan Project. Though the use of lead arsenate would continue throughout the country until 1948 when it was largely replaced by DDT, it could have been used for even longer in some locations, depending on state law.

Lead arsenate contains both lead and arsenic which are heavy metals; these elements are very harmful to humans and animals and can lead to nerve damage, reproductive issues and hearing/vision impairment. The contamination will predominately remain within the topsoil up to a 6-inch depth as both these metals have little movement within soil and little solubility, thus remaining at high concentrations near the area where human/animal activity would occur. The screening criterion for humans is 250 mg/kg lead and 20 mg/kg arsenic with levels on the site exceeding the criteria. The Hanford Site is not and will not be open to the general public in the foreseeable future though the contamination can still affect those working in the site. This study could also be a basis for other areas with similar contamination.

This study will look at 5,000 total acres in the 100-OL-1 Operable Unit (OU) and include the optimization and pilot study which occurred in the summer of 2014, looking at 4 Decision Units (DU) covering over 350 acres. Each DU has been selected to give an accurate portrayal of the entire OU with different factors in each such as the presence of trees, the presence of past orchards and any disturbance in the area (Table 1).

Table 1. Decision Units

Decision Unit ID	***Acreage for Evaluation***	***Presence of Trees in 1943 Aerial Imagery?***	***WIDS Site within Decision Unit Boundaries?***	***Previously Sampled?***
OL-14	46.4	Yes	Yes	Yes
OL-32	28.7	Yes	No	Yes
OL-FR2-1	48.0	No	Yes	Yes
OL-IU6-4	250.6	Yes	Yes	Yes
WIDS is Waste Information Data System.				

A conceptual site model was created to demonstrate how the distribution of lead and arsenic was expected to occur throughout the site (Figure 2).

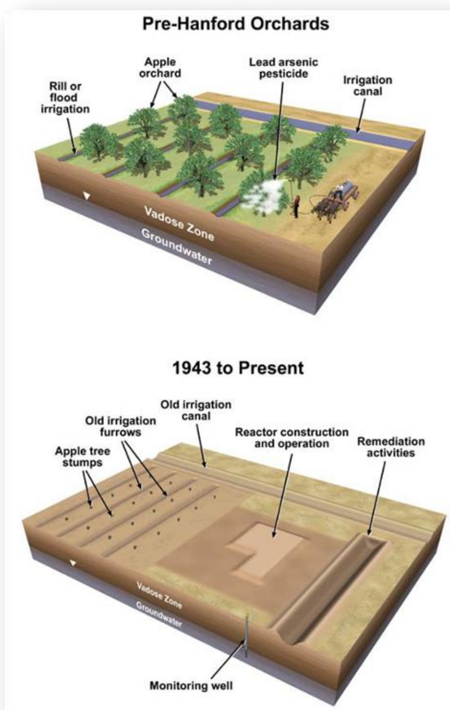

Figure 2. Conceptual site model.

The conceptual site model included the distribution of lead and arsenic occurring from the tree trunk and expanding outwards to the distance of the leaves to align with the prediction that the lead arsenate would fall from the leaves, producing a circular contamination area around the trunk.

X-Ray fluorescence (XRF) has previously only been used as a screening method at the Hanford Site. The XRF analyzer is a tool used to determine concentrations of elements in soil (or other surfaces) through either in situ or ex situ analysis (Figures 3 and 4).

In-Situ

Ex-Situ

Front View

Top View

Side View

Figure 3. XRF

X-rays are able to excite atoms in the sample and characteristic fluorescent x-rays are detected by the analyzer to determine the concentration.

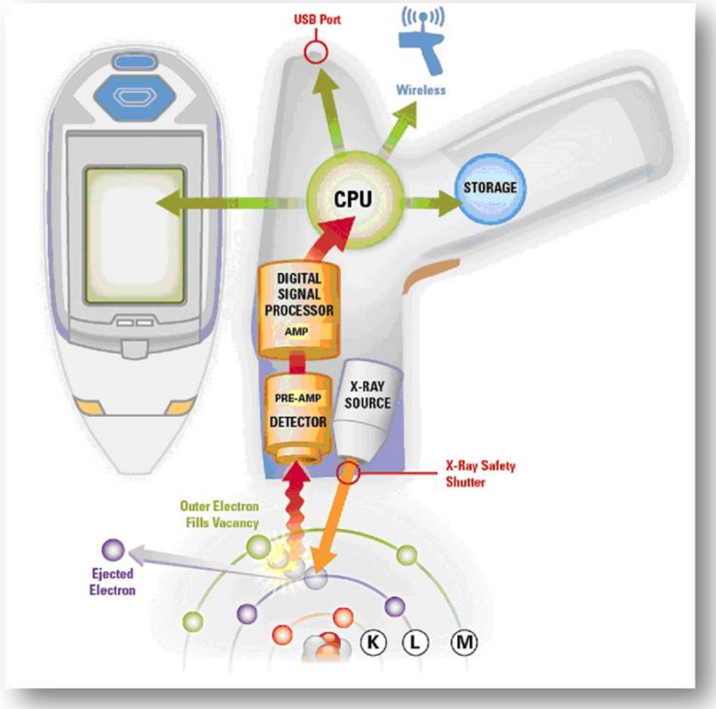

Figure 4. XRF analyzer.

A goal of the study is to prove that XRF can provide decision making capabilities. At the current time, the soil must also be collected after XRF screening to be sent for confirmatory analysis with ICP. By establishing the use of XRF as a decision making tool, decisions can be made much quicker more cost effectively without the need for ICP confirmation.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2014, a DOE Fellow intern Christian Pino spent 10 weeks doing a summer internship at Pacific Northwest National Laboratory under the supervision and guidance of Amoret Bunn, Ph.D and Field Team Lead Brad Fritz, Ph.D. The intern's project was initiated on June 2, 2014, and continued through August 14, 2014 with the objective of characterizing pre-Hanford orchards in the 100-OL-1 Operable Unit.

3. RESEARCH DESCRIPTION

Optimization Study

An optimization study was completed before field analysis could begin in order to determine the method to be used with the XRF such as count time, number of counts and any variability that may come under consideration.

XRF was used to screen locations where soil could be collected for analysis; the screening criteria as previously mentioned is 250 mg/kg for lead and 20 mg/kg for arsenic. Three samples were collected at each of two sites, OL-14 and OL-IU6-4, with each sample representing a low (below criteria), medium (at criteria) and high (above criteria) range (Figure 5). The samples were subdivided further into sample cups with three cups per concentration level (Figure 6). The samples were tested in a random order to determine if the instrument's precision improved or diminished.

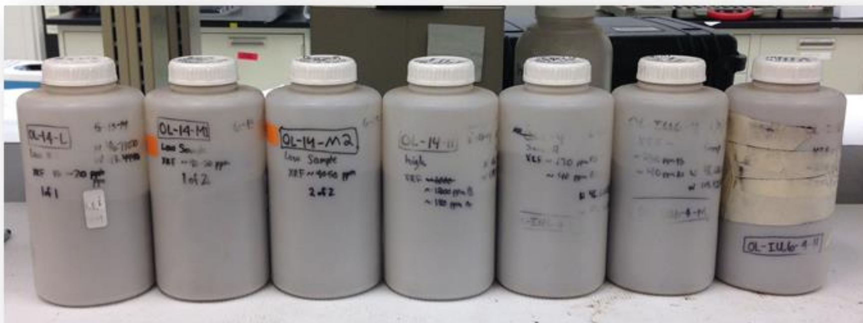

Figure 5. Soil samples.

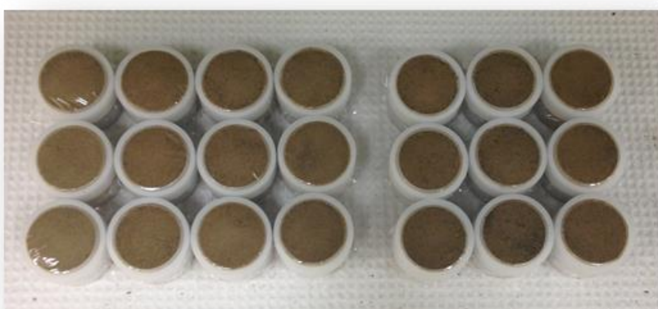

Figure 6. Cups for ex-situ analysis

After viewing the data, a selection was made for one low, one medium and one high sample to be representative of those values. The samples chosen were OL-14-L, OL-IU6-4-M, and OL-IU6-4-H as they clearly represented values below, at and above the screening criteria and show a clear linear relationship with ICP confirmatory data. A coefficient of variability analysis was done in order to further determine the duration of sampling to be done. In order to attain this data, OL-14-L and OL-IU6-4-H was analyzed in both a fixed and variable position for 15, 30, 45, 60, 90, 120, 150 and 180 seconds in triplicate measurements (Table 2).

Table 2. Analysis Time for Optimization Study

Count Time (seconds)	Number of Analyses in fixed position	Number of Analyses in varied positions	Minutes of count time
OL-IU6-4-H (high concentration sample)			
15	20	10	7.5
30	20	10	15
45	20	10	22.5
60	20	10	30
90	20	10	45
120	20	10	60
150	20	10	75
180	10	10	60
OL-14-L (low concentration sample)			
15	20	10	7.5
30	20	10	15
45	20	10	22.5
60	20	10	30
90	20	10	45
120	20	10	60
150	20	10	75
180	10	10	60
Minutes of instrument count time			630

Field variability was analyzed through the use of transects. A location was chosen as ground zero and points were analyzed in increasing distances radially of 0.5, 1, 2, 4, 8, 12, and 16 feet in triplicate. Ground zero would have 4 legs with the varying distances associated with them in order to create a circular transect. The transect study was done a total of three times with two completed at OL-14 and one completed at OL-IU6-4.

Finally, the method detection limit for the XRF was determined; the MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The XRF will give a <LOD (Less than Level of Detection) reading if a concentration value is too low. The MDL would replace this value as the lowest value the XRF can accurately detect. OL-14-M was analyzed for 60 seconds in a fixed position to determine the MDL.

Pilot Study

Once the Optimization Study was completed, and all variables that may occur had been accounted for, the field study (Pilot Study) began. This study included the four DUs with each DU having 40 locations selected within its area using Visual Sample Plan (VSP) with a random start and systematic grid pattern. Each location was analyzed with 3 replicates each with a 60 second count time. The blank and standard reference material (SRM) would be analyzed after every 20^{th} analysis to ensure accuracy. To further determine field variability, OL-14 was analyzed twice with an additional 40 locations equidistant from the initial 40.

4. RESULTS AND ANALYSIS

Optimization Study

The results of ICP analysis compared to XRF analysis yield a linear relationship (Figures 7 and 8).

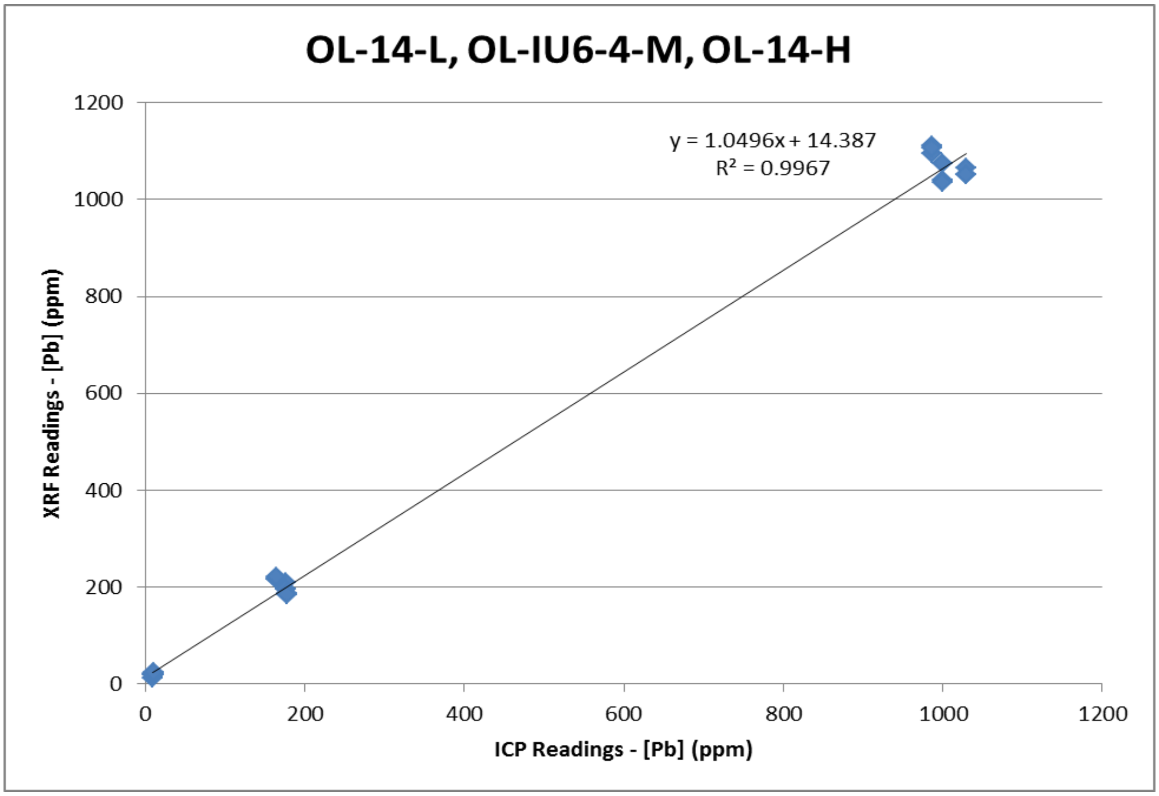

Figure 7. XRF vs ICP for Pb.

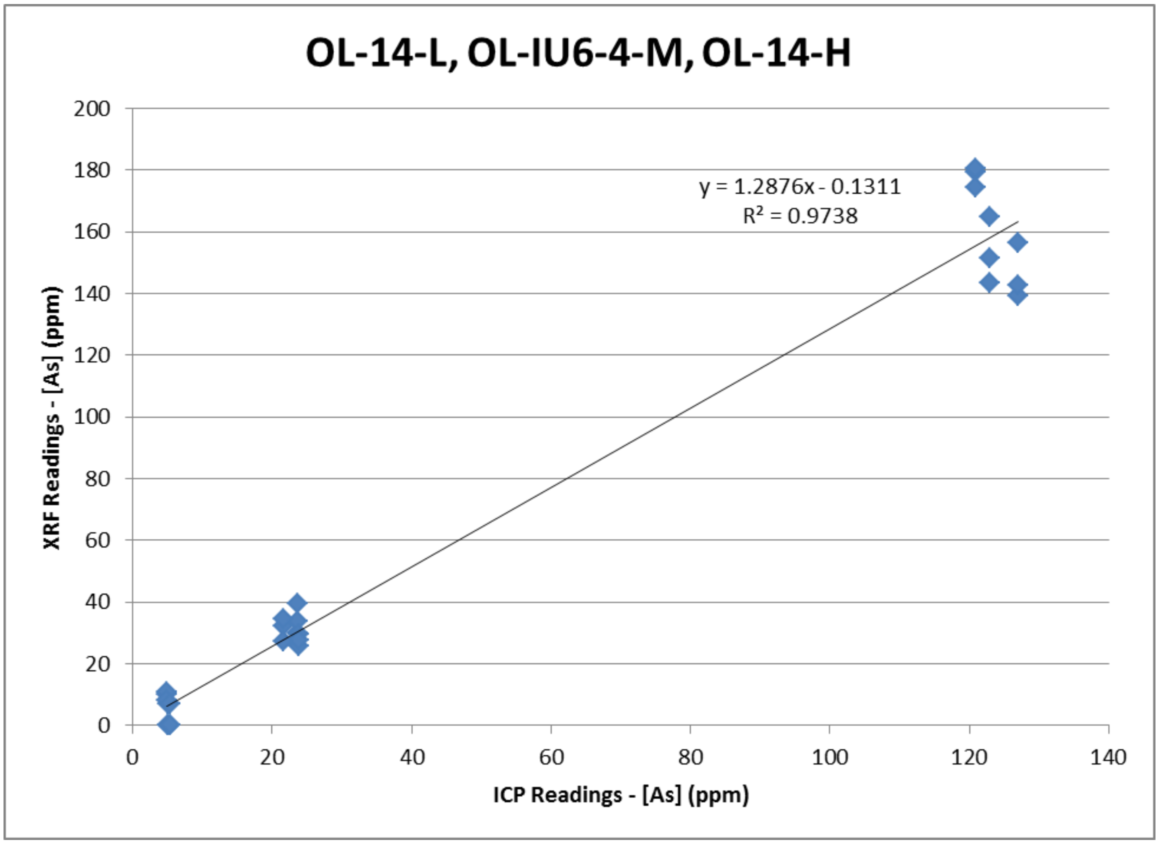

Figure 8. XRF vs ICP for As.

To further see this relationship, OL-14-M1 and Ol-IU6-4-L were selected to show that the XRF readings fall between a positive and negative 20% range when compared to ICP analysis (Figures 9 through 12).

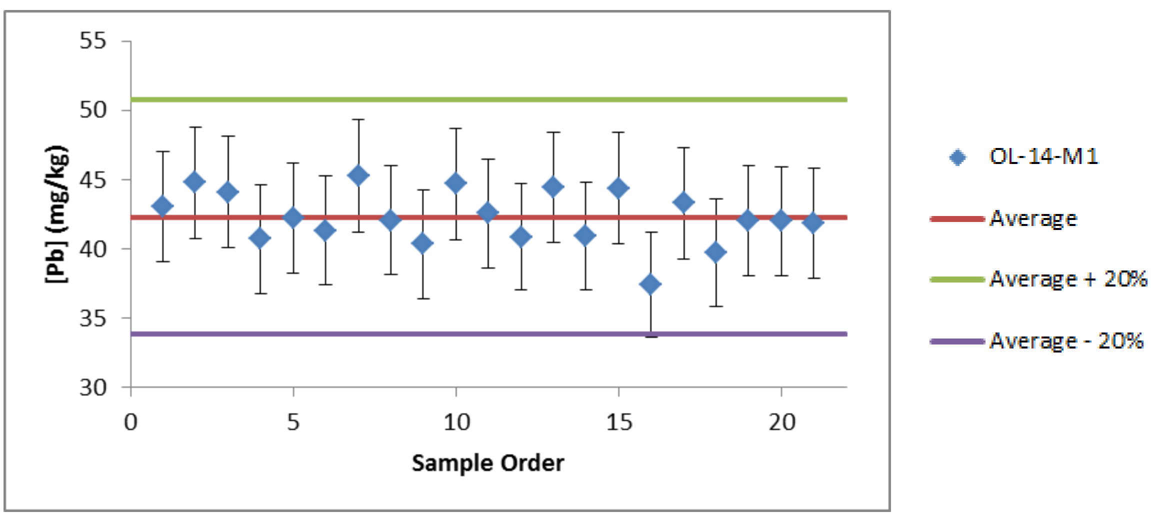

Figure 9. OL-14-M1 ±20% of ICP readings for Pb

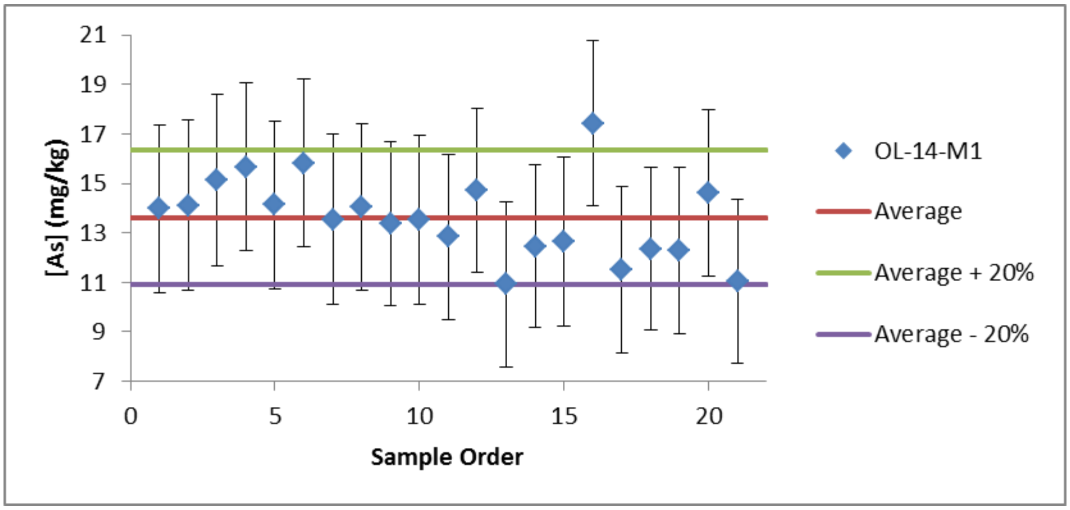

Figure 10. OL-14-M1 ±20% of ICP readings for As

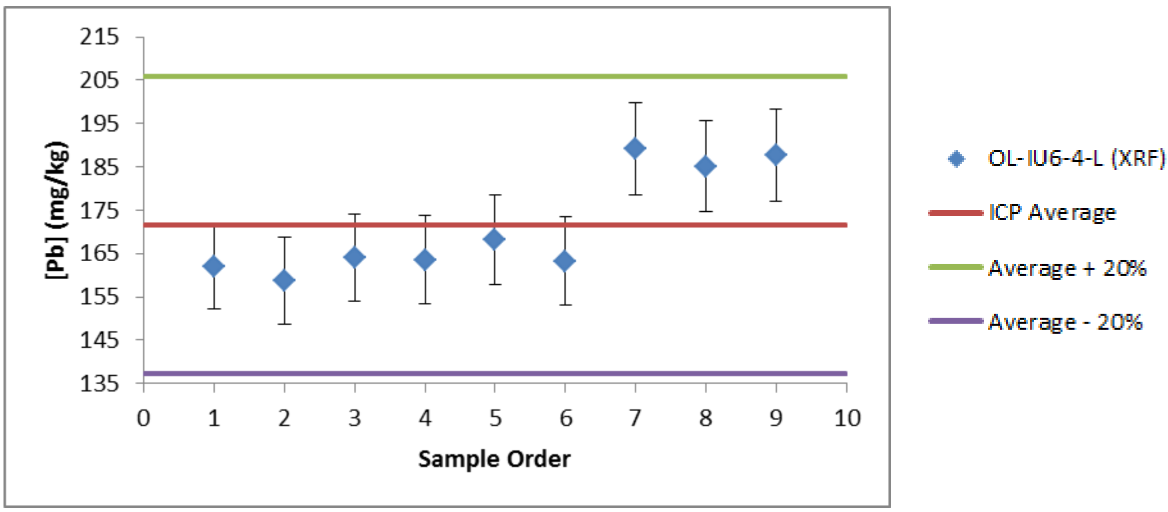

Figure 11. OL-IU6-4-L ±20% of ICP readings for Pb.

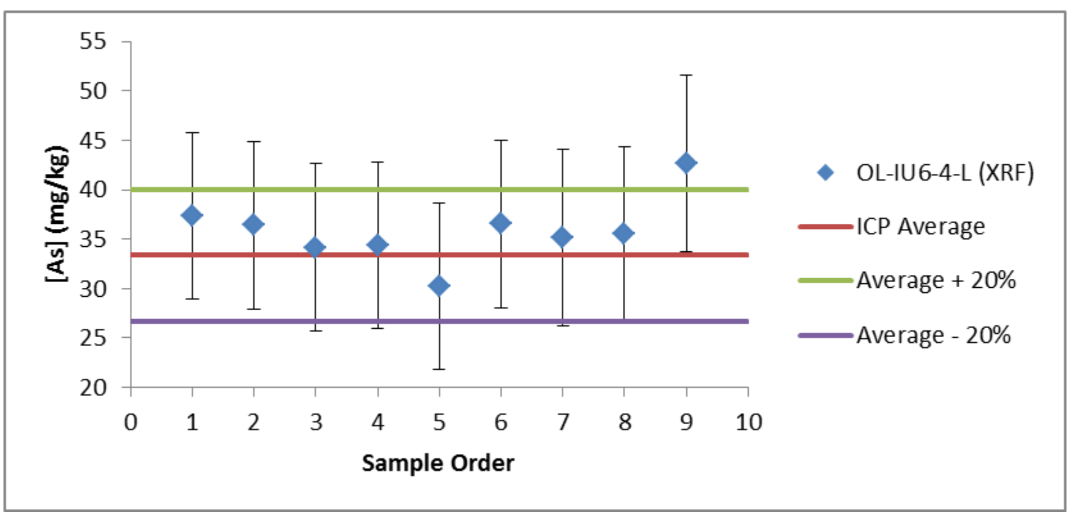

Figure 12. OL-IU6-4-L ±20% of ICP readings for As

The coefficient of variability analysis was done in order to determine the most efficient and accurate count time to be done in the field for analysis. Once count time analysis was done from 15 to 180 seconds in a fixed and variable position the results were plotted (Figure 13).

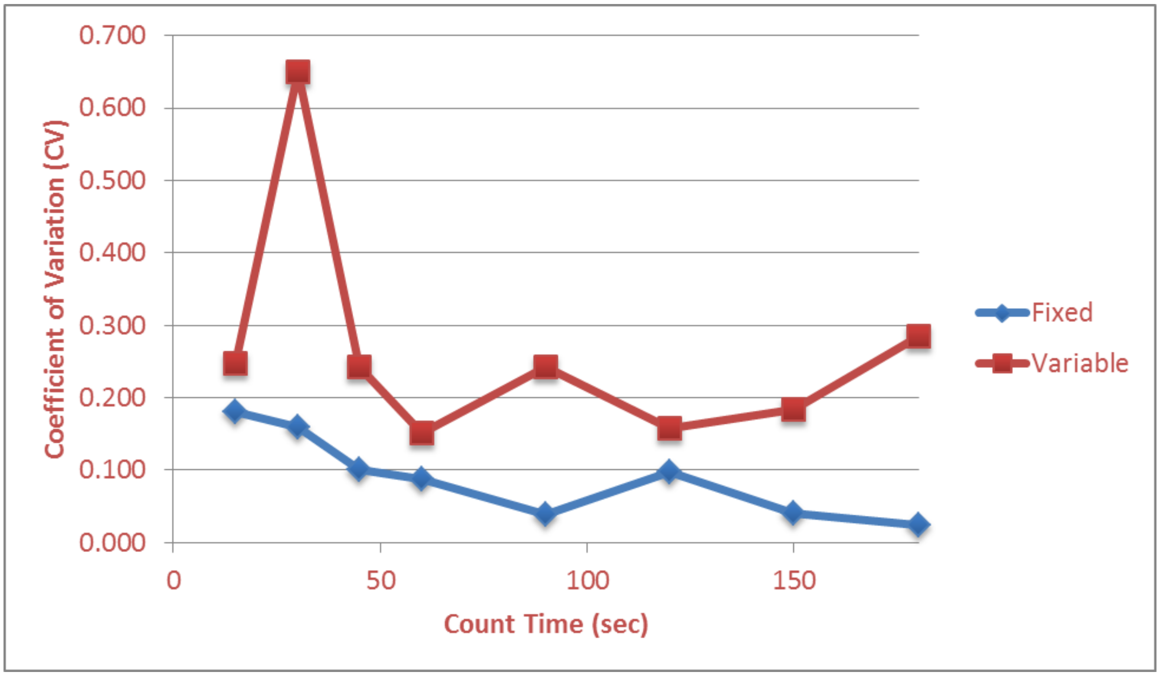

Figure 13. Coefficient of variability.

Three field transect studies were done to determine the variability present in the field. A visual plot was created to demonstrate the concentrations in the radial distance around ground zero for both lead and arsenic in OL-IU6-4 (Figures 14 and 15).

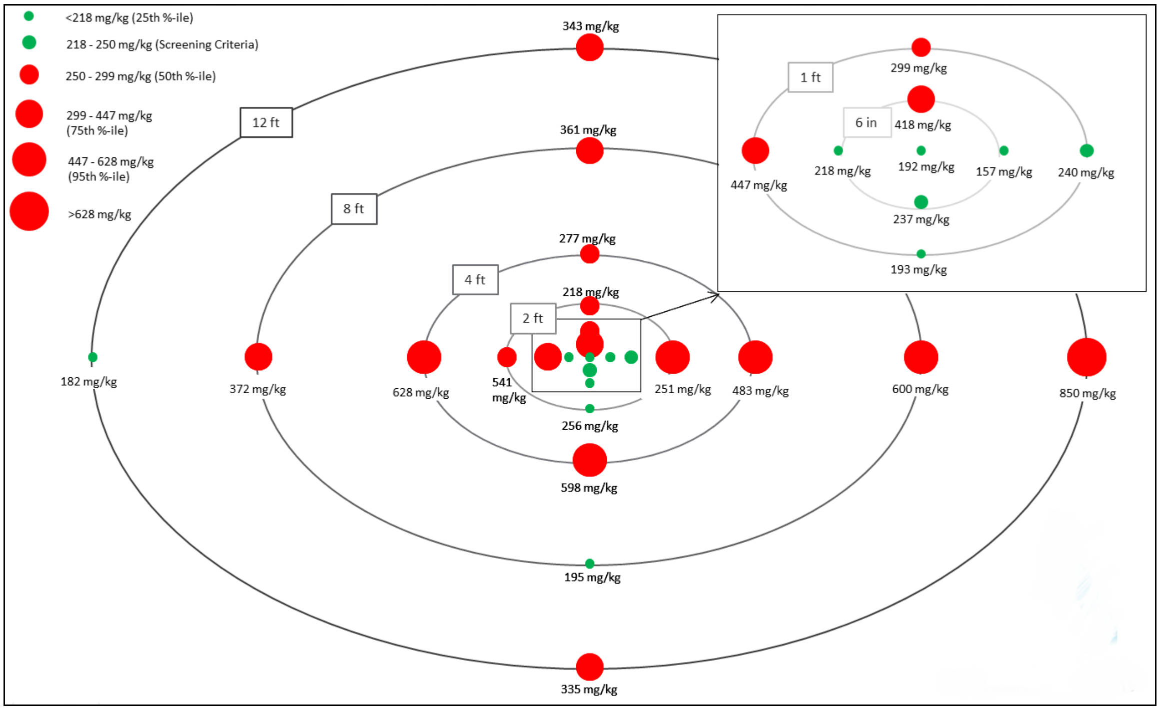

Figure 14. Transect for Pb.

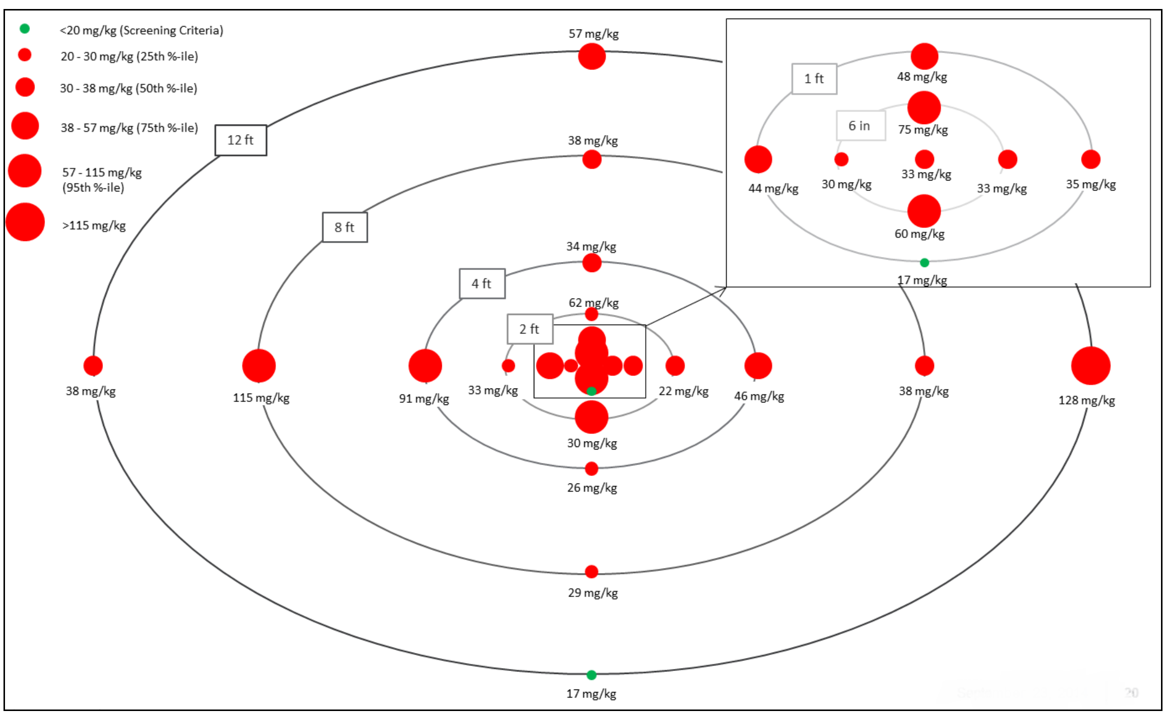

Figure 15. Transect for As.

MDL for lead and arsenic in the two soil samples was calculated using two methods. Both methods calculate the MDL by multiplying the standard deviation by the representative Student's T Value being that of samples-1 (n-1). The first method calculated the MDL based on the average in which the seven XRF readings for each distinct sample cup was averaged thus giving a total of seven new values for each sample cup. The results of the MDL using this method were as shown in Tables 3 and 4.

Table 3. Average Pb and As

Sample	Avg Pb	Avg As
OL-14-M1-A	41.46714	14.01857143
OL-14-M1-B	41.42714	15.23142857
OL-14-M1-C	44.47714	13.34571429
OL-14-M1-1	43.06429	14.62571429
OL-14-M1-2	42.25857	13.12714286
OL-14-M1-3	41.53571	13.12285714
OL-14-M1-4	42.21571	13.77285714
OL-14-L-A	17.93	6.52
OL-14-L-B	18.72143	6.485
OL-14-L-C	19.24857	6.725
OL-14-L-1	19.33857	6.24
OL-14-L-2	18.76143	6.394285714
OL-14-L-3	19.95714	6.1
OL-14-L-4	19.76714	5.5025

Table 4. MDL using 1st Method

Sample	MDL Pb from Averages	MDL As from Averages	Students T Value
OL-14-M	3.479963251	2.513625967	3.143
OL-14-L	2.179622326	1.250115423	

The second method calculated the MDL on the basis of the first measurement for each set of seven replicates. Thus, the first XRF reading from OL-14-M1-A, OL-14-M1-B, OL-14-M1-C, etc. would be used to calculate the standard deviation and the first MDL value. The 2nd measurement would then be used to calculate the 2nd MDL and the same process was repeated until all seven were completed. The results of the MDL using this method for OL-14-M are shown in Table 5.

Table 5. MDL using 2nd Method for OL-14-M

Sample	MDL Pb from 1st value of each set	MDL As from 1st value of each set	Students T Value
1	6.421338406	3.073060879	3.143
2	8.455465588	4.787152147	
3	7.004583243	6.111968143	
4	6.709021144	4.30616672	
5	7.626324589	5.386965954	
6	3.855051351	4.830403964	
7	5.464749961	4.169914514	

The results of the MDL using this method for OL-14-L are shown in Table 6.

Table 6. MDL using 2nd Method for OL-14-L

Sample	MDL Pb from 1st value of each set	MDL As from 1st value of each set	Students T Value
1	3.300883998	10.94309416	3.143
2	2.638230673	3.870395626	
3	4.201432579	11.23486379	
4	3.447544296	5.336739783	
5	6.364526035	9.491594858	
6	6.573716267	9.269805176	
7	4.95970313	8.783246449	

The MDL for the 30 and 45 second count times were also calculated, though only using the second method and only being completed for one set. These results are shown in Table 7.

Table 7. MDL for 30 and 45 Seconds using 2nd Method

Sample	MDL Pb for 30s	MDL As for 30s	Students T Value
OL-14-M	11.82405106	6.540151786	3.143
	MDL Pb for 30s	**MDL As for 30s**	
OL-14-L	6.197249747	2.390065	
	MDL Pb for 45s	**MDL As for 45s**	
OL-14-M	12.73699861	7.38264828	
	MDL Pb for 45s	**MDL As for 45s**	
OL-14-L	2.177523474	3.998033427	

Pilot Study

The 1943 aerial imagery for OL-14 shows black dots present in the northwest area; this has been determined to represent the orchards present at that time. Dots further to the east are still visible, though not as dark, and are also associated with orchards, though possibly not being cultivated this season. The results reveal a high concentration of both Pb and As in the northeast area which shows some past presence of orchards. The west area was expected to reveal a high concentration of Pb and As where the orchards are very clearly visible in the aerial imagery but it did not. The results still seem to show for this DU that orchard areas correspond significantly with increased Pb and As levels (Figures 16 and 17).

Figure 16. OL-14 2013 aerial imagery results.

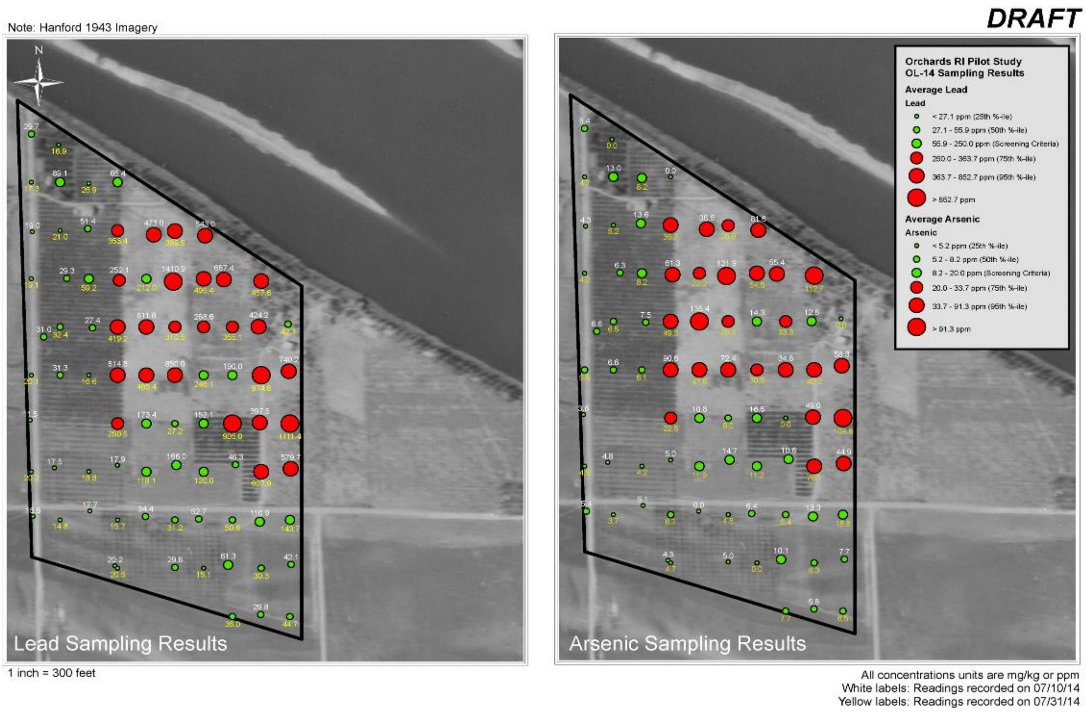

Figure 17. OL-14 1943 aerial imagery results.

OL-32 shows presence of past orchards in the southeast area although the highest Pb and As concentrations appear in the north and southwest areas which show little indication of past orchards. The site today actually reveals that the southern area still has stumps present while the northern area does not; we would assume the opposite when looking at the results (Figures 18 and 19).

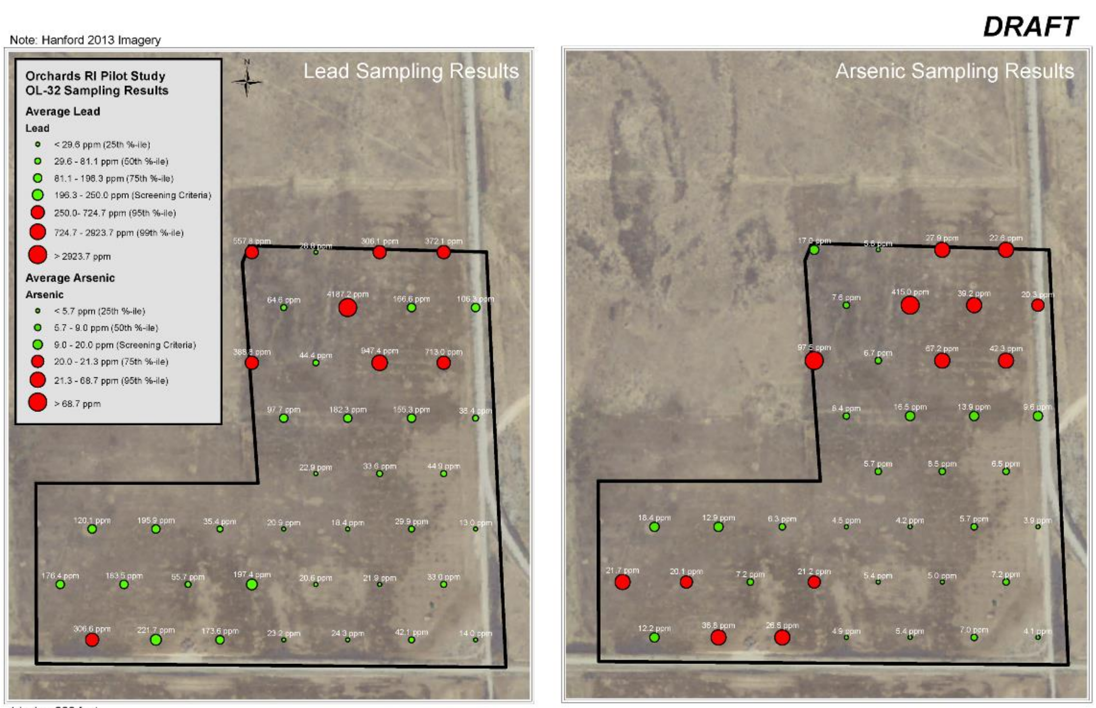

Figure 18. OL-32 2013 aerial imagery results.

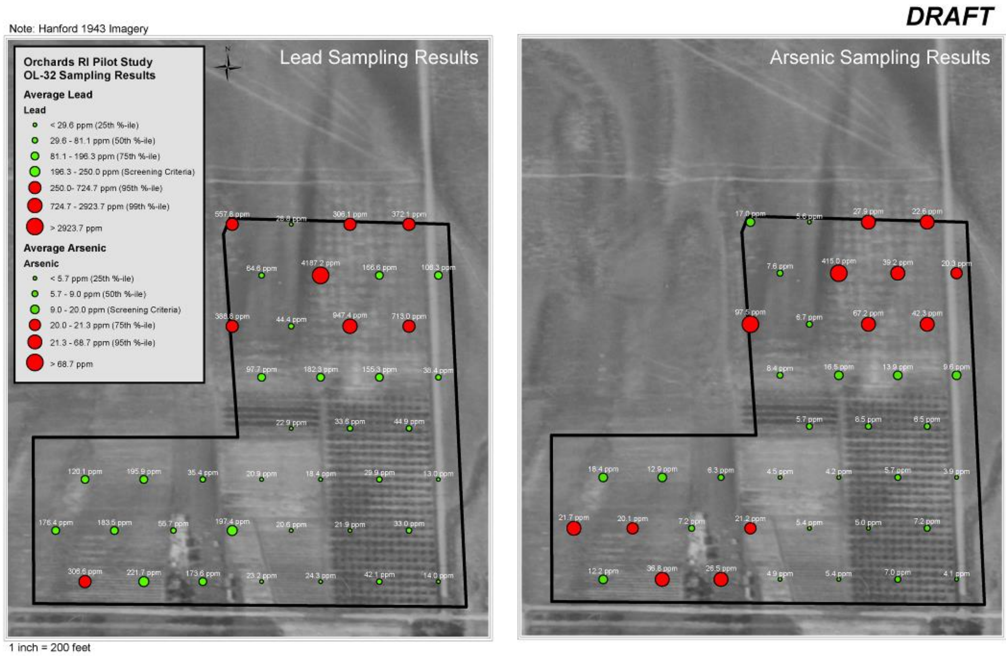

Figure 19. OL-32 1943 aerial imagery results.

OL-FR2-1 showed no indication of orchards being present in 1943 and almost all concentration values were below detection limit. Some outliers are present in the southern area (Figures 20 and 21).

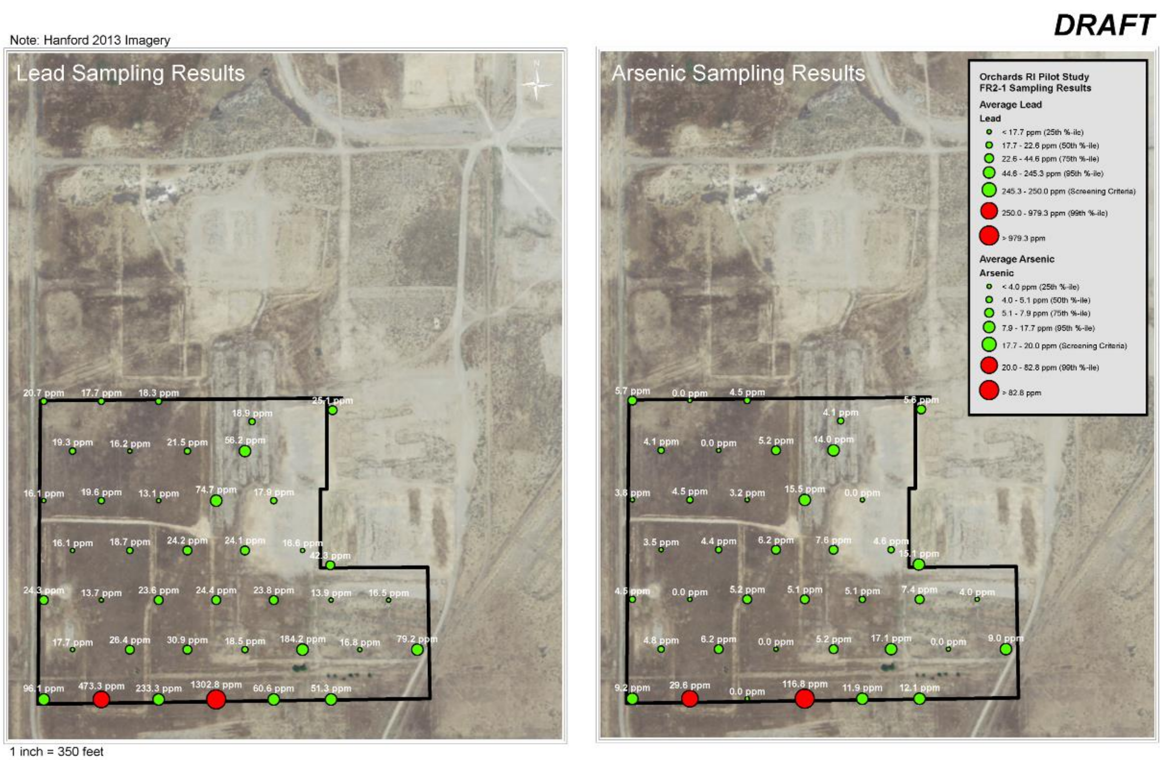

Figure 20. OL-FR2-1 2013 aerial imagery results.

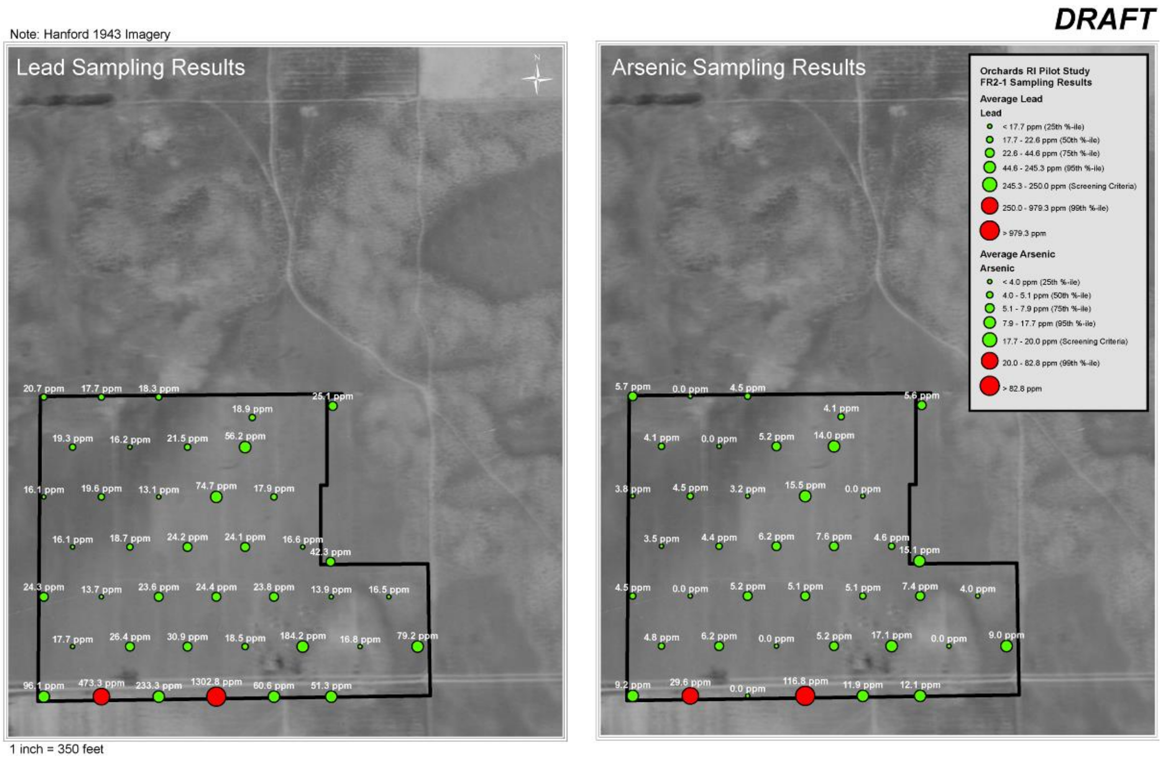

Figure 21. OL-FR2-1 1943 aerial imagery results.

OL-IU6-4 demonstrated high concentrations in the area where orchard stumps are still present today. The 1943 imagery unfortunately does not show any easily visible orchards present. Some high concentrations appear in the eastern area with this area having agricultural structures in 1943 (Figures 22 and 23).

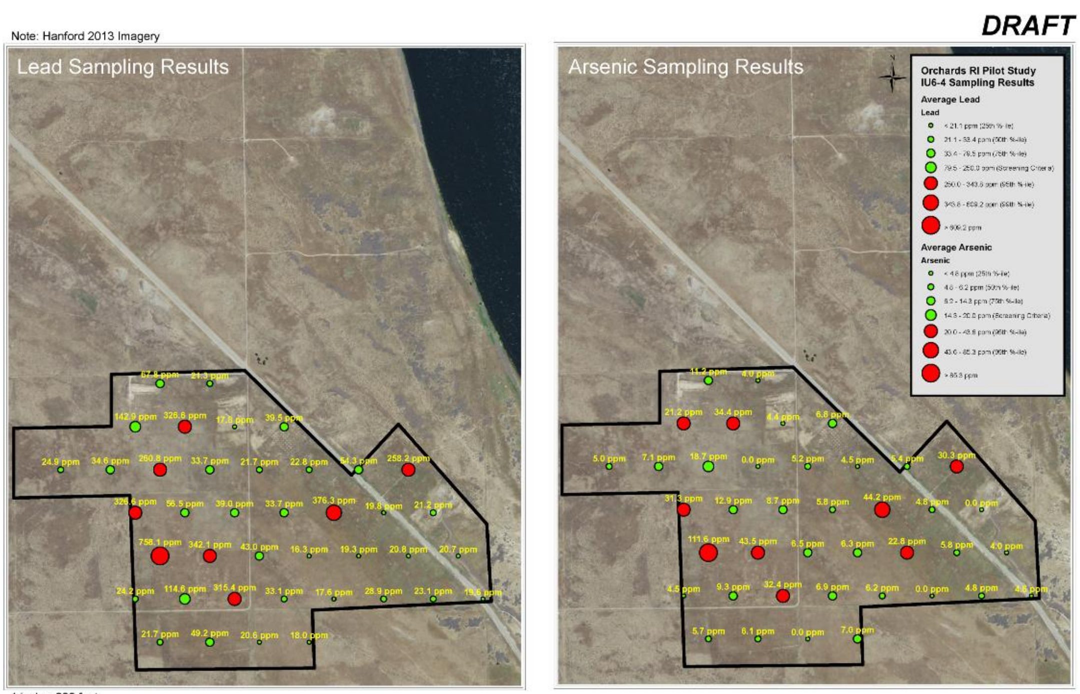

Figure 22. OL-IU6-3 2013 aerial imagery results.

Figure 23. OL-IU6-4 1943 aerial imagery results.

5. CONCLUSION

With the completion of the optimization study, various conclusions can be made. The linear relationship corresponding to the XRF vs ICP readings yielded an R^2 value of about .9735 which is much higher than expected and a good indication of precision and accuracy of the XRF relative to ICP. The MDL proved that the detection limits were much lower than the screening criteria; thus, no problem will arise with being unable to detect (reading <LOD) arsenic since it is well below the threshold. Further, with the XRF data falling ±20% within ICP values, it is a good indication that the XRF analyzer may be used for decision making.

When comparing results from OL-14 with the first 40 locations to OL-14 after 80 locations were analyzed, the same variability was seen; therefore, the size of the Decision Unit should not affect the number of samples measured.

According to the conceptual site model, we would expect the highest concentration of Pb and As to appear within the areas where past orchards were present; these results were seen in OL-14 although the other three DUs do not seem to accurately portray this model. The conceptual plan needs to be revised to explain this discrepancy.

6. REFERENCES

U.S. Code of Federal Regulations (CFR), "Protection of Environment," Part 136, Appendix B, Revision 1.11, "Definition and Procedure for the Determination of the Method Detection Limit."

Delistraty D and J Yokel. 2011. "Ecotoxicological Study of Arsenic and Lead Contaminated Soils in Former Orchards at the Hanford Site, USA." *Environmental Toxicology* DOI 10.1002/tox.20768.

EPA (U.S. Environmental Protection Agency). 2007a. *Method 6200: Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*. Office of Solid Waste and Emergency Response, Washington, D.C

Sharpe JJ. 1999. *Pre-Hanford Agricultural History: 1900-1943*. BHI-01326, Rev. 0, Bechtel Hanford, Inc., Richland, Washington.