EPA Triad Approach
Former Naval Petroleum Reserve No. 1
Arsenic in Soil Assessment

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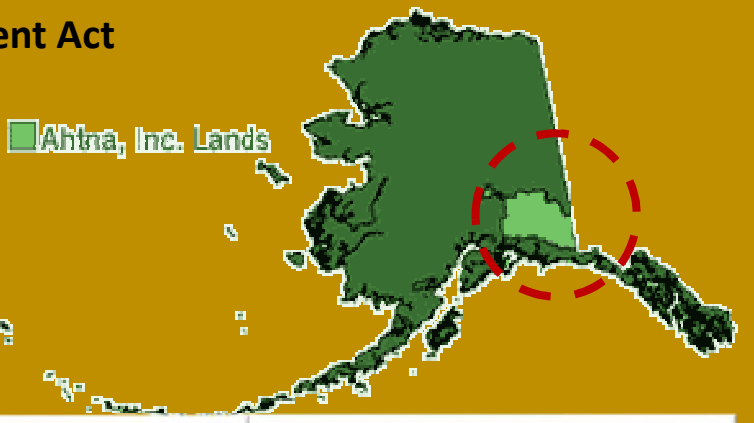
Presentation Overview

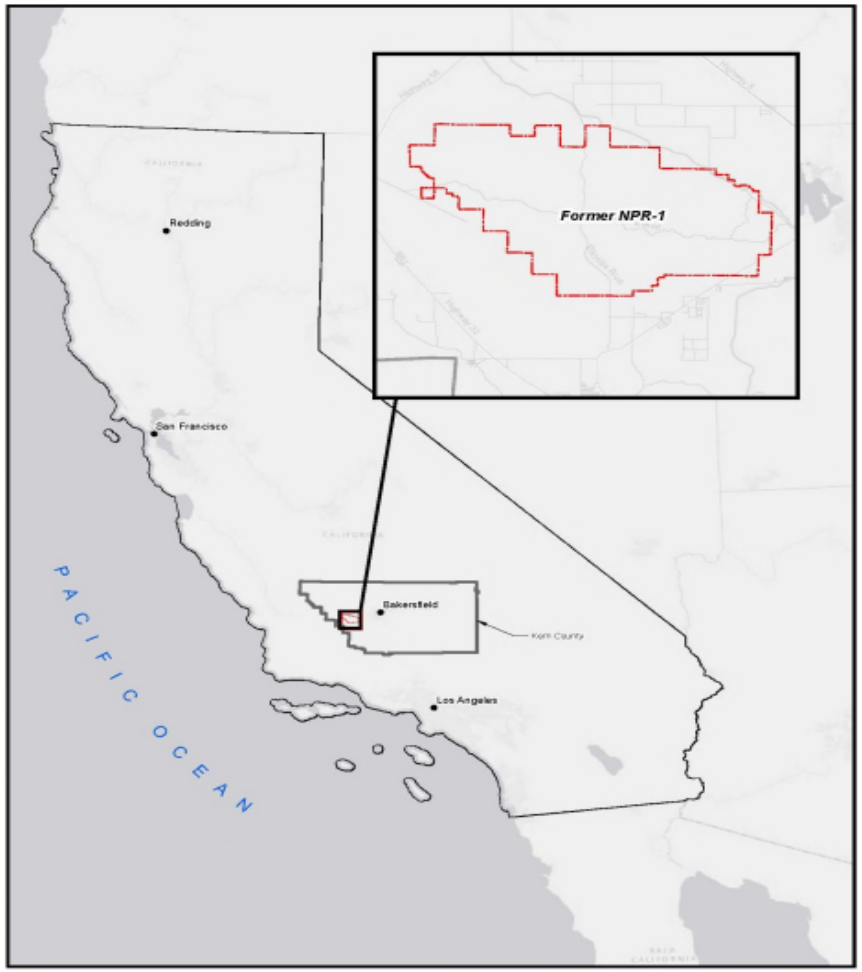
- Department of Energy (DOE) Former Naval Petroleum Reserve No. 1 (NPR-1)
- Area of Concern 130 – Arsenic at Well Pads
- Application of the EPA Triad Approach to characterize arsenic at over 700 separate sites
- XRF as a definitive site characterization tool
- Investigation Outcomes/Lessons learned

Ahtna Facility Services, Inc.

- **Ahtna Facility Services Inc. (Ahtna) is a wholly-owned subsidiary of Ahtna, Incorporated, an Alaska Native Corporation.**
- **Eight federally recognized tribes are members of the Ahtna Corporation**
- **Formed in 1971 under Alaska Native Claims Settlement Act**
- **14 Subsidiary Companies (AGSC, AES, AFSI etc.)**
- **Tribal Members are the Shareholders**



Former Naval Petroleum Reserve #1 - Elk Hills



Former NPR-1 Project

- AFSI, under contract to the DOE, is addressing environmental legacy issues under a Corrective Action Consent Agreement with California Department of Toxic Substances Control (DTSC)

- Elk Hills is one of the largest active oil fields in the lower 48 states and is the largest gas producing oil field in California

NPR-1/Elk Hills

NPR-1/Elk Hills

NPR-1/Elk Hills

Catch Basin

Catch Basin

Sump

Drainage Pathway

Oil Well Pads

Current Status

- Starting in 2013, AFSI conducted a soil boring and multi-incremental sampling (ISM) program
- Completed most of the initial characterizations at 131 Areas of Concern
- Obtained DTSC no further action status on 26 AOCs
- Metals (arsenic, lead, cadmium, chromium) PAHs, Dioxins, and VOCs comprise the most common COPC
- Moving into remediation phase for those AOCs with COC concentrations above risk-based screening levels
- Currently no groundwater impacts

Area of Concern (AOC) 130

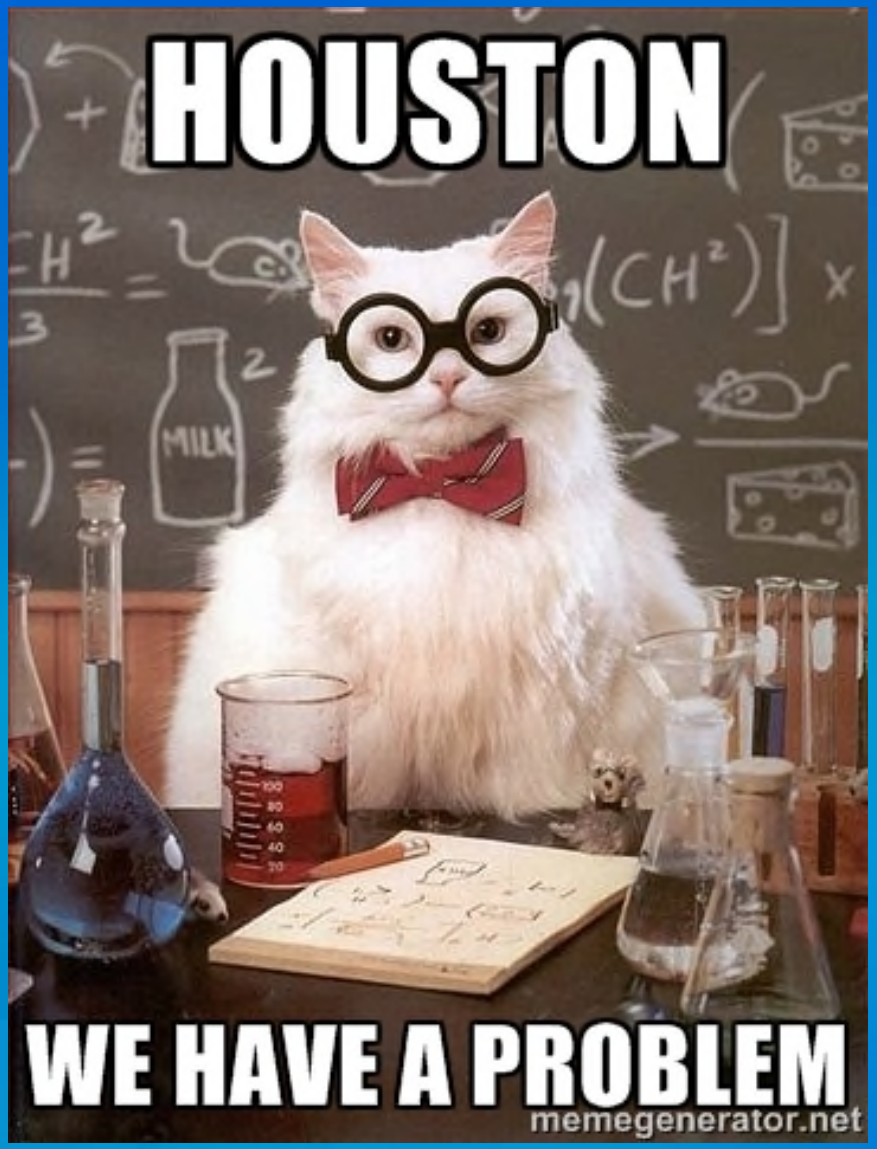
- AOC 130 is defined as “Arsenic at Well Pads”
- W-41 (Sodium Arsenite), was used during the 1950’s through early 1970’s as a corrosion inhibitor at some of the NPR-1 oil extraction wells.
- W-41 solution was introduced into the wells in what was *reported* to be a closed loop system
- 764 (out of several thousand) former or current well pads possibly impacted by the use of W-41

Initial Assessment (2013)

- Objective: Determine if arsenic concentrations in soil were above the site-specific action level
- Sampling Plan
  - 40 “locations” (well pads) were calculated to represent the total population of potentially impacted wells
  - Randomly selected 40 out of about 700 well pads for sampling
  - Collected 4-point composite samples around each well head location for arsenic analysis

Initial Assessment Outcome

- Arsenic in 18 of the 40 composite samples (45%) were above the site-specific background and action levels
  - Background level established at 16 mg/kg
  - Action level established at 26 mg/kg
  - Residential RBSL of 0.07 mg/kg
  - 0.24 mg/kg commercial/industrial RBSL


HOUSTON
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Supplemental Assessment

Conducted a pilot investigation study of 5 well pads to inform us on how to best proceed with tackling a large effort

- Multi-increment (ISM) sampling was not acceptable to the regulator due to lack of “hot spot” resolution
- Combination of discrete sample results and 95 UCL calculation of the aggregate well pad results would meet regulator requirements
- Developed and evaluated sample processing and XRF method protocol to produce data comparable to EPA Method 6020A
- Prepared a comprehensive Work Plan to characterize 764 well pad sites using an enhanced XRF method

EPA's Triad Approach

Ahtna Facility Services, Inc.

Systematic Planning

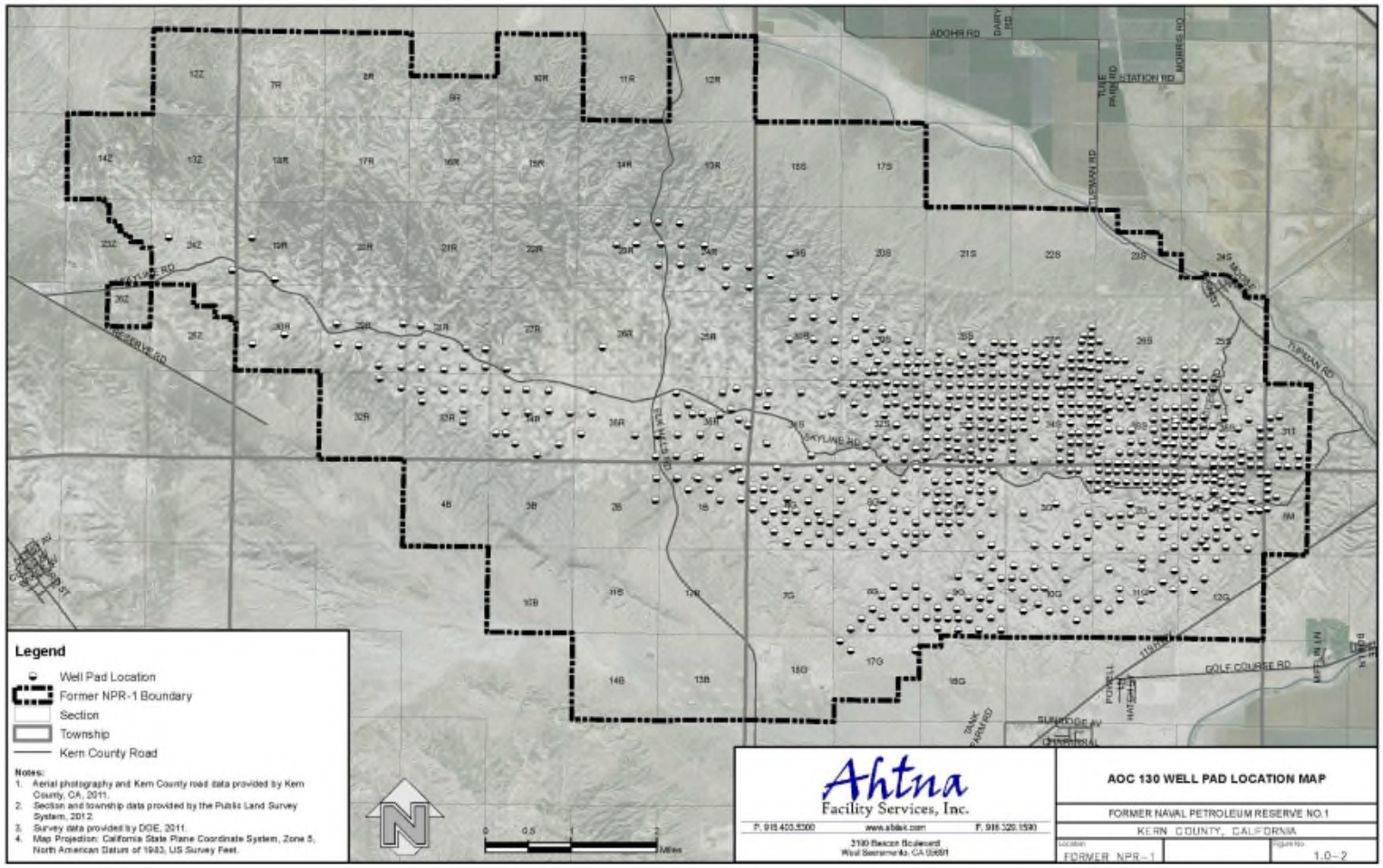
Dynamic Work Strategies

Real-Time Measurement Technologies

Systematic Work Plan

- Well head coordinates from California Division of Oil and Gas Resources (DOGGR) database loaded to the GIS
- Created a well pad sampling grid in the GIS and transferred coordinates to hand held GPS (Trimble) devices
- Deployed sampling analytical teams of 2-3 people and a mobile laboratory trailer to well pad areas
- Established the sampling grid and collected discrete samples at each grid node (~ 30 per ½ acre well pad)
- Used bar code sample labels and wireless bar-code devices to:
  - Link sample IDs to location coordinates
  - Prepare COC forms
  - Populate instrument files

Well Pad Identification



Aerial View of Well Pads

Well Pad Identification

Well Pad Identification

Establish Sampling Grid

Establish Sampling Grid

Establish Sampling Grid

Systematic Project Plan
Sample Heterogeneity

- Contaminants adsorbed to distinct particles form "nuggets" of high concentration
- Depending on where the XRF beam is directed, or the laboratory "scoop" is taken, the analysis may include more or less of the arsenic nuggets.

Arsenic (whitish color) sorbed to iron hydroxide particles

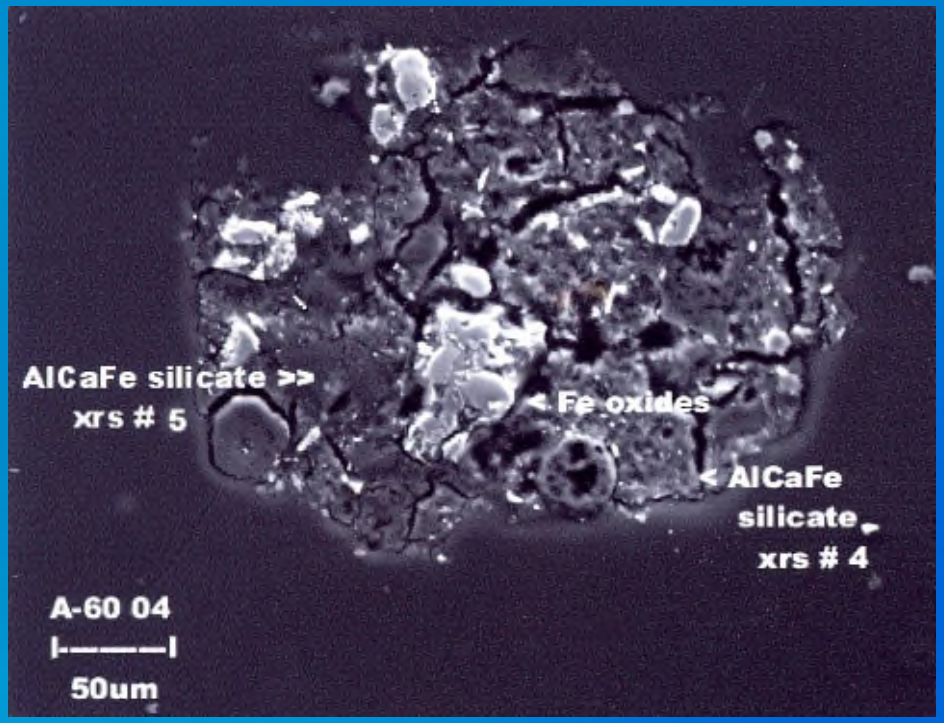
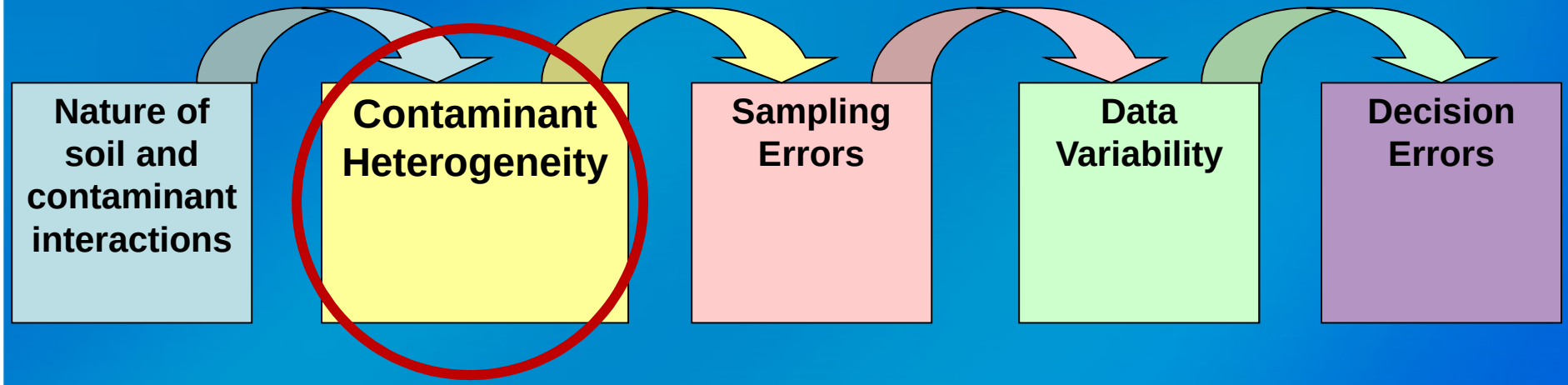


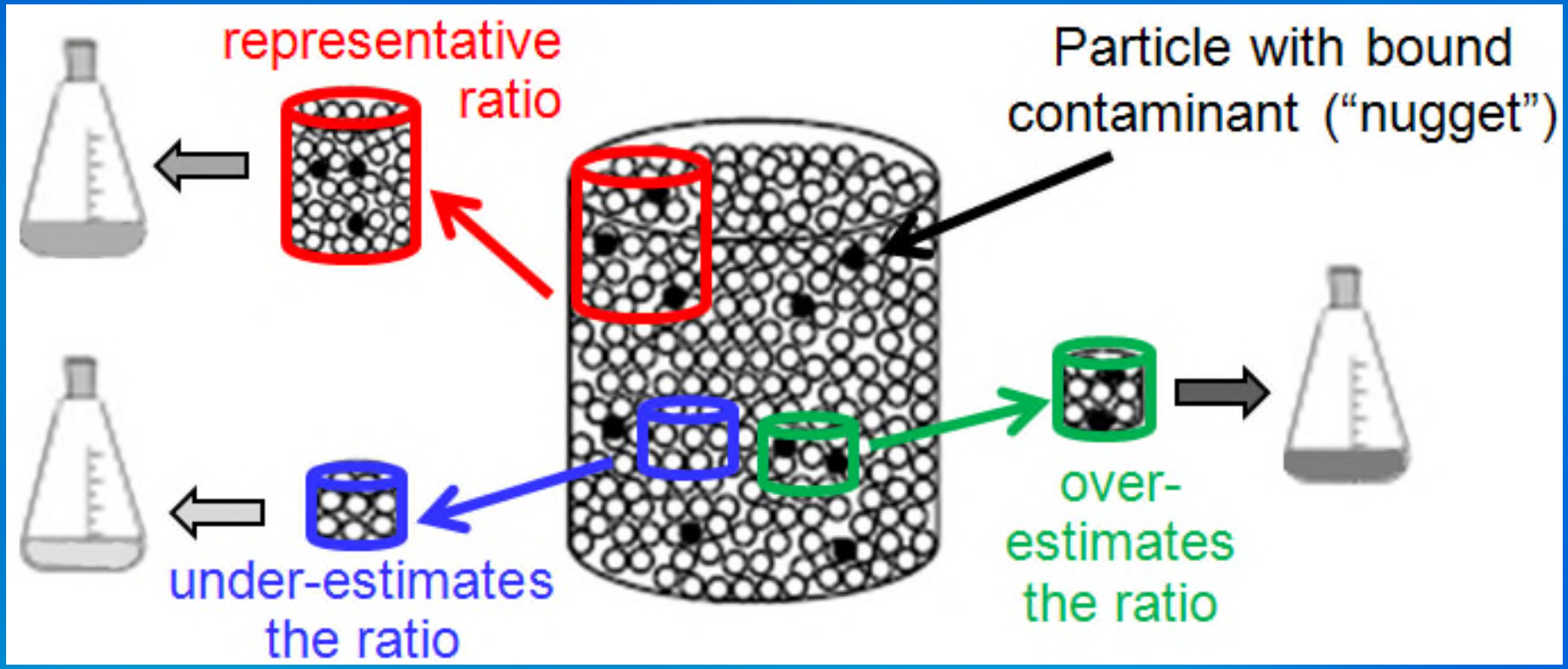
Photo courtesy of William Cutler, Integral Consulting

Particulates in Solid Matrices "Micro-Heterogeneity"



- "Micro-heterogeneity" is non-uniformity within the sample container
- Important because contamination is heterogeneous at the same spatial scale as sample analysis

Sampling Size Induced Error



- Illustration of sampling error: For the blue and green samples, the proportion of nuggets in the samples do not represent the nugget proportion of the population (the large container)

Planned for Real Time XRF Measurement

- 24,000 samples in 6.5 months (900 samples/week)
- Developed Field XRF SOP based on EPA Method 6200
  - Definitive, representative and fully defensible data for supporting risk assessment decisions
- Used wireless bar code devices to upload sample IDs into GPS and XRF instruments
- Analyzed each discrete sample in triplicate by the XRF (30 second acquisition time) with homogenization between each analysis

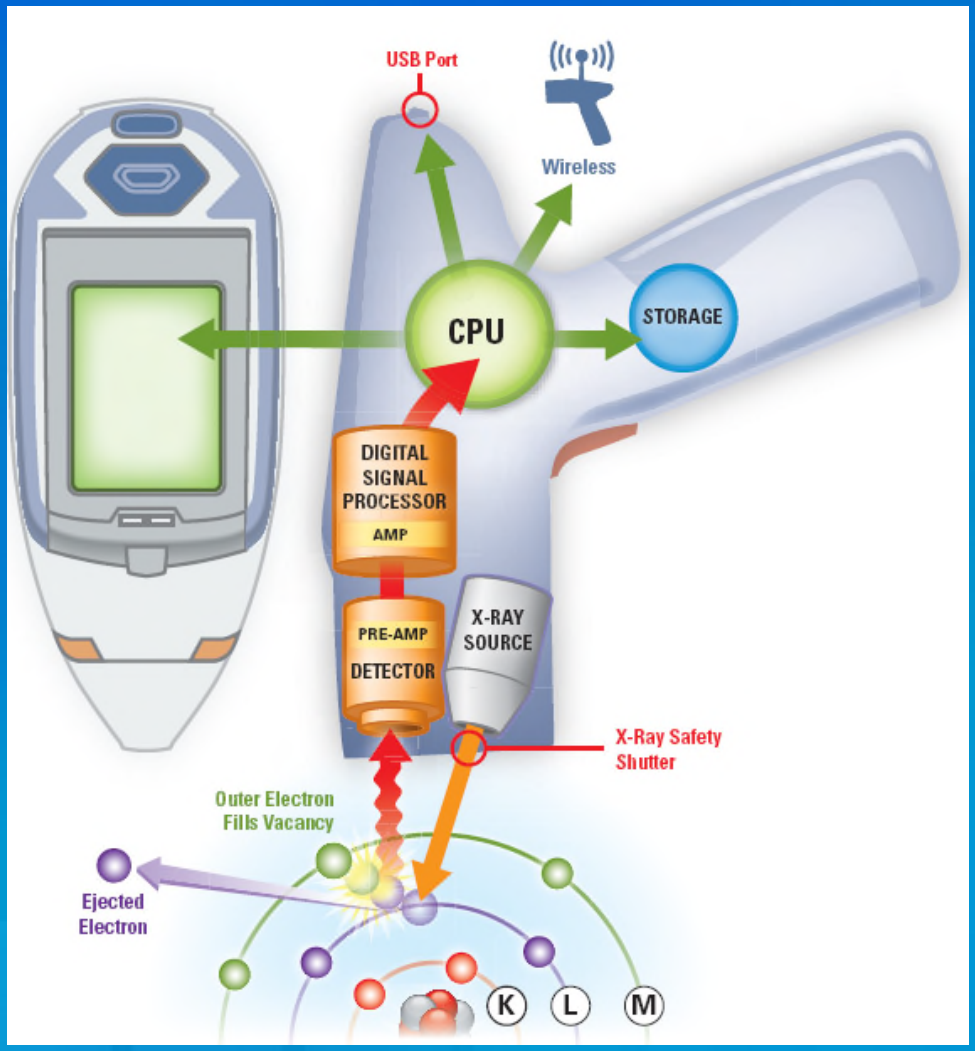
Sample Collection

- Surface samples (0-6 inches)
- Discarded top layer of vegetation and rocks
- Used stainless steel trowel to mix soil in place to a depth of 6 inches
- Pre-printed bar code sample labels affixed to zip seal plastic bags (e.g., Thin zip-seal “snack” bags)
- Automated bar-coded COC forms

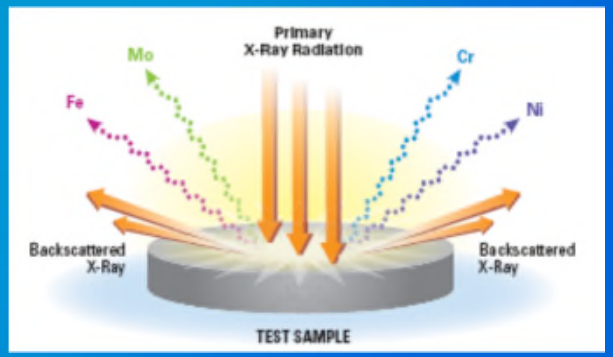
Dynamic Work Strategy

- Measured XRF concentration for each discrete grid sample and created preliminary site map
- Collected “step-out” samples at margin of well pads where arsenic concentrations were > 26 mg/kg
- Conducted a complete site characterization in a single mobilization in less than 1 day

XRF Theory/Operation



- Each individual element produces its own set of characteristic x-rays; the basis for qualitative analysis
- By counting the number of characteristic x-rays of a given element we can determine its concentration; the basis for quantitative analysis



Comparison of XRF/ICP-MS

XRF (EPA Method 6200/SOP)

- No sample digestion
- 30 second measurement
- 5 gram sample (approximately)
- Factory calibration
- Highly linear response – no dilutions required
- 4-12 mg/kg RL
- Non-destructive test
- Low cost/analysis
- Moderate instrument cost

ICP-MS (EPA Method 6020A)

- Sample digestion
- 24 hour (or longer) analysis turnaround
- 1-5 gram sample
- Lab calibration
- Dilutions required due to high salt or arsenic concentrations
- 1 mg/kg RL (0.26 MDL)
- Destructive
- $15-20/sample
- High instrument cost

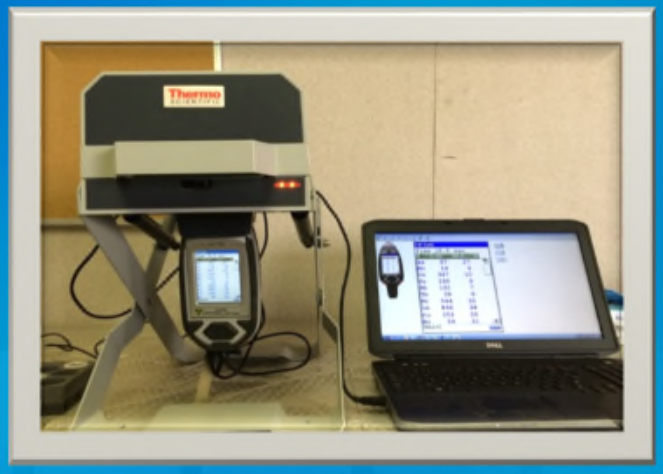
XRF Arsenic Method Components

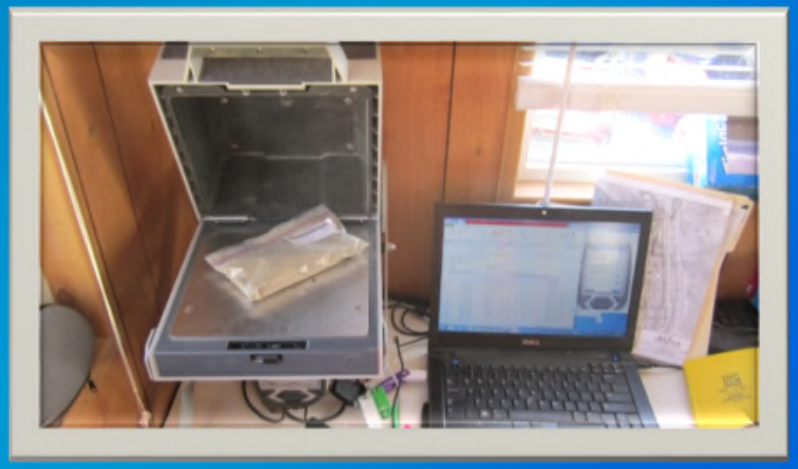
- XRF Instrument Factory Calibration (ICAL)
- Daily calibration verification: CRM (10, 111 and 500 mg/kg: 75-125% QC Limit) – mid point every 4 hours
- Certified blank: < LOD (< 4-6 mg/kg)
- Triplicate XRF analyses: 30 second sample scan
- Analyzed samples in the zip seal bag
- Mixed sample in bag between replicate analyses
- If RSD > 25%, take three additional measurements
- Converted XRF average value to a lab equivalent concentration using a XRF/6020A calibration curve

Data Processing

- Generated an electronic data deliverable (EDD) and laboratory report from GIS and XRF data files for database upload
- Evaluated discrete results and calculated 95 UCL concentration from 30 (or more) discrete grid sample results
- Prepared final well pad figure from GIS showing sampling grid, discrete sample results, and 95 UCL calculation
- < 5 day TAT from sample collection to final data package and map for decision making at each site
- 25-30 well pad sites (750-900 samples) characterized per week, for 26 weeks in a row

Sample Analysis
Thermo Scientific Niton XL3-950





Sample Collection

Sample Collection

Sample Collection

Sample Location Coordinates

Field Maps

Sample Processing

Sample Processing

Sample Processing

Sample Processing

Sample Processing

Sample Analysis

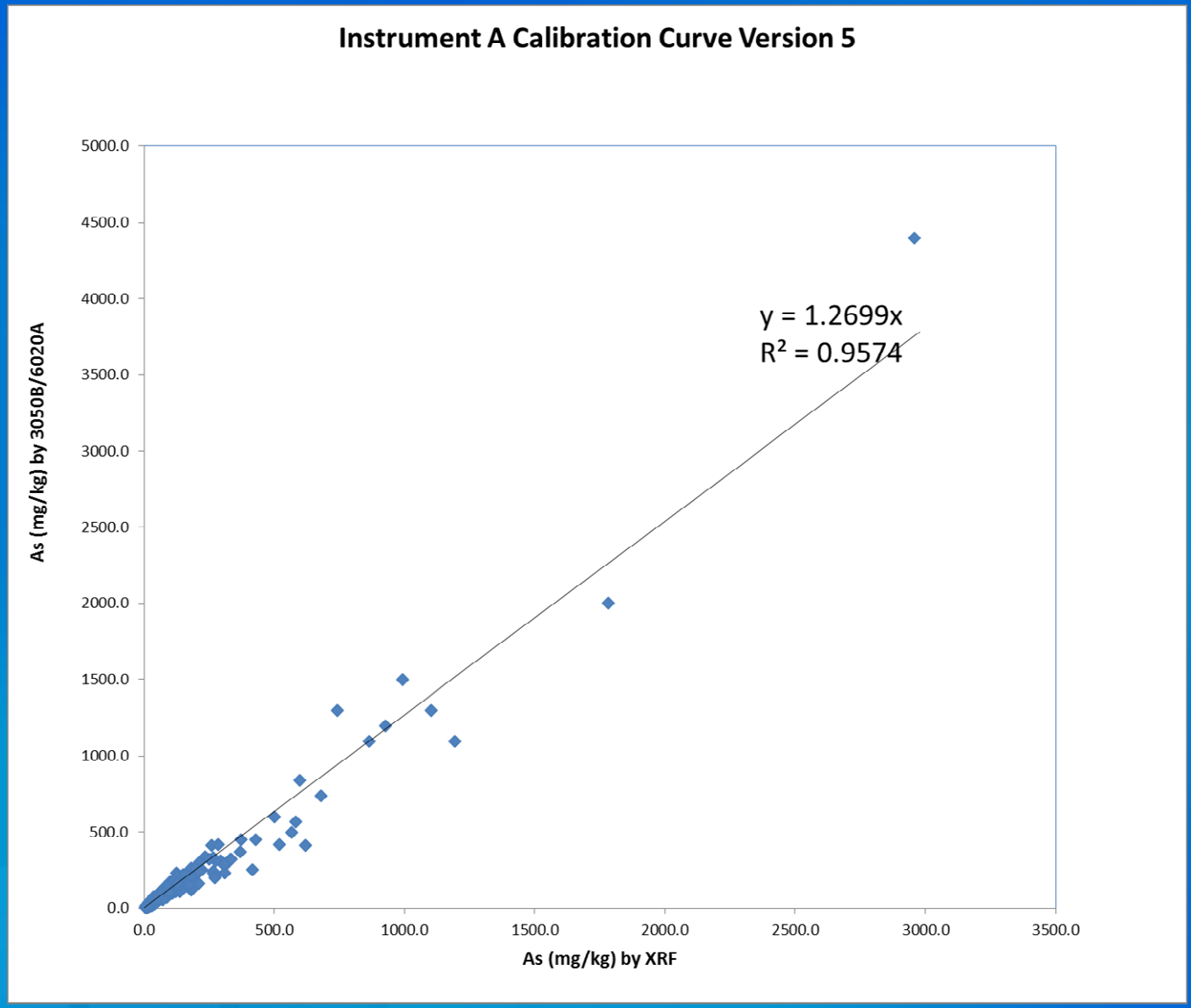
Sample Analysis

Field Data Processing

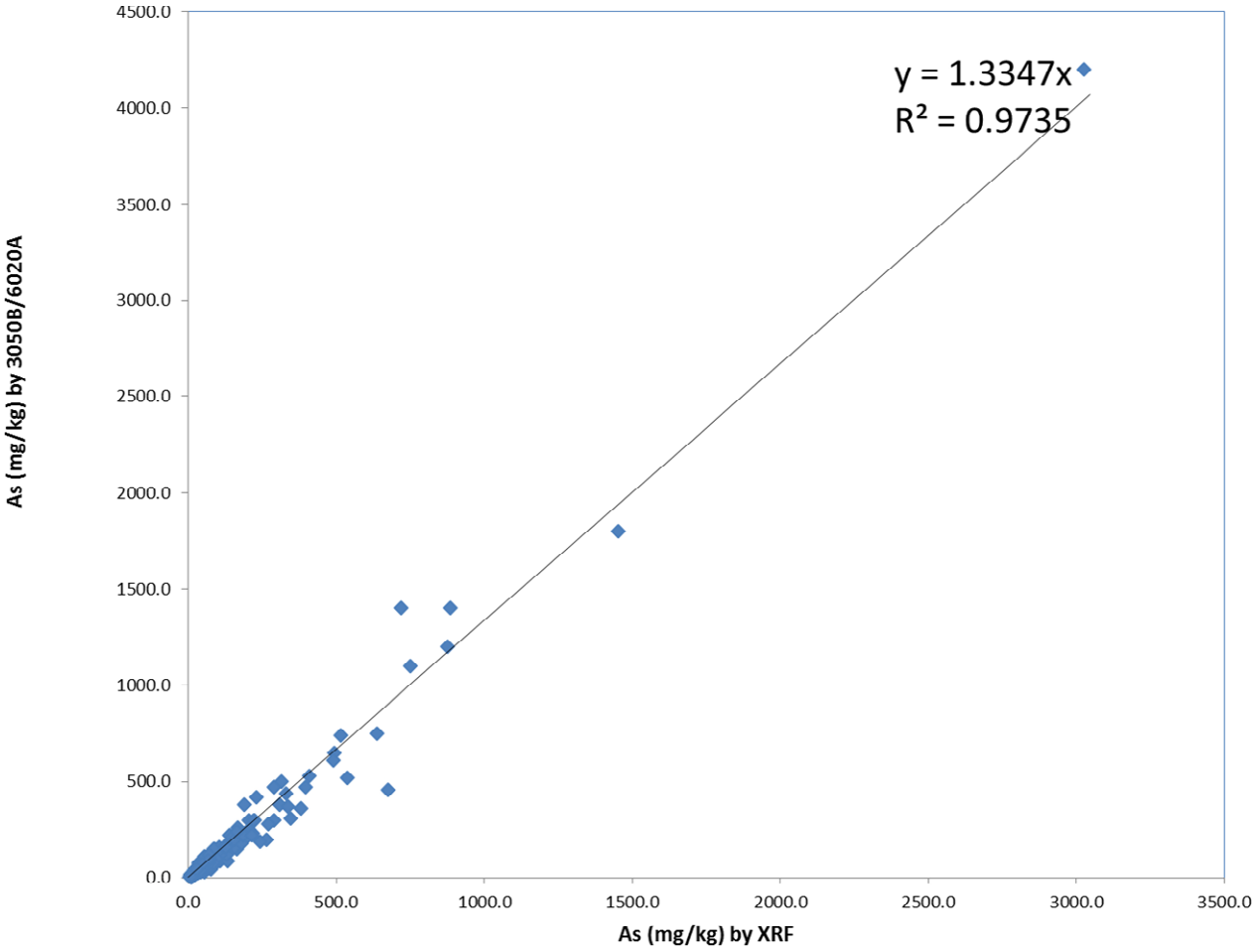
XRF Calibration Curves

- Calibration curves were prepared for each XRF instrument to convert XRF result into a “lab equivalent” concentration
- Linear regression from split sample XRF and 6020A results
- Linear correlation coefficients of 0.87 to 1.33 with an average of 1.05 (Y value; strength and direction of the linear relationship)
- Coefficient of determination (R^2) of 0.90 to 0.98 with an average value of 0.96 (R^2 of 1.00 = ideal fit)

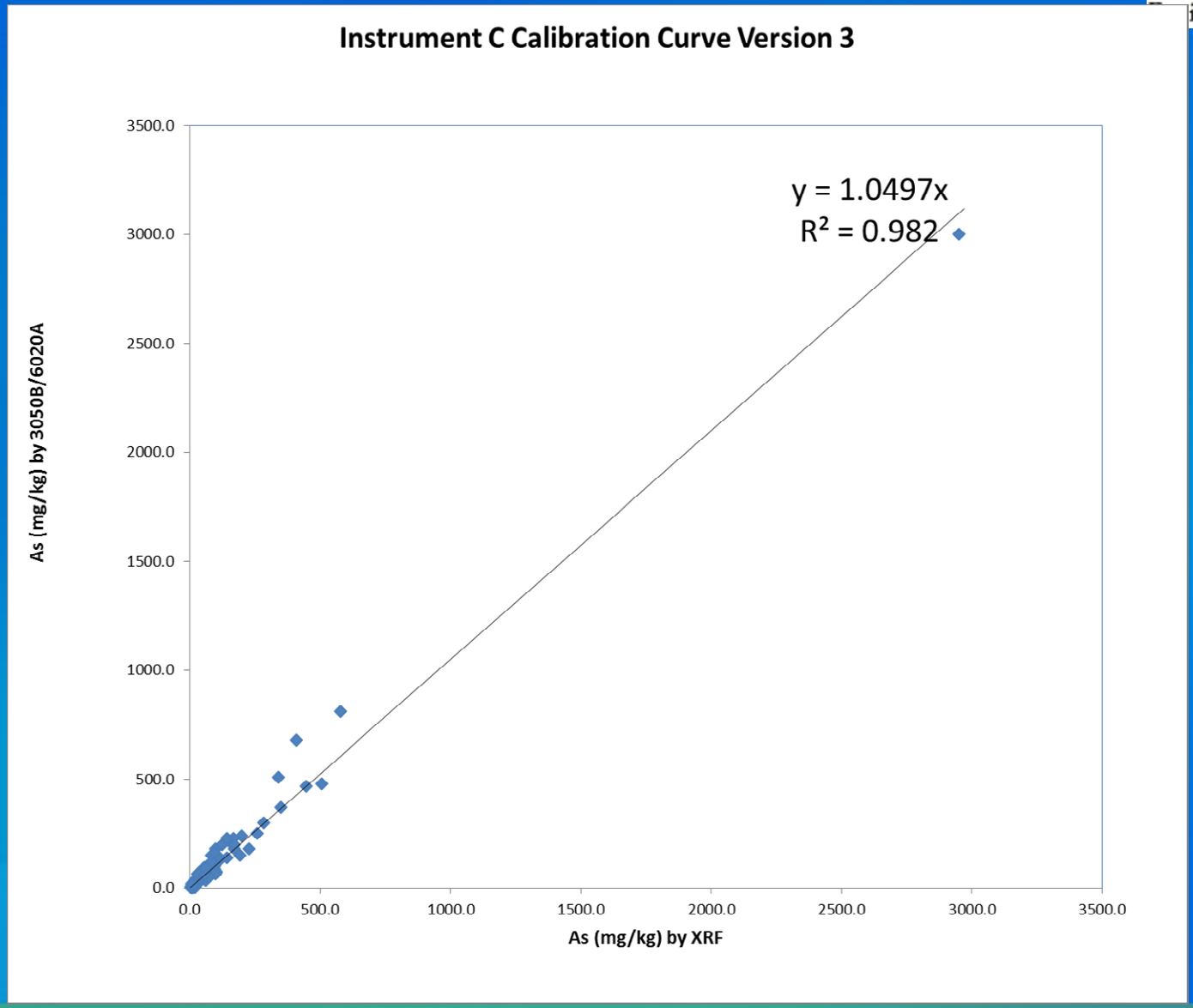
XRF Calibration Curve: 631 split samples



XRF Calibration Curve: 523 split samples



XRF Calibration Curve: 223 split samples



RSD of Replicate Analyses

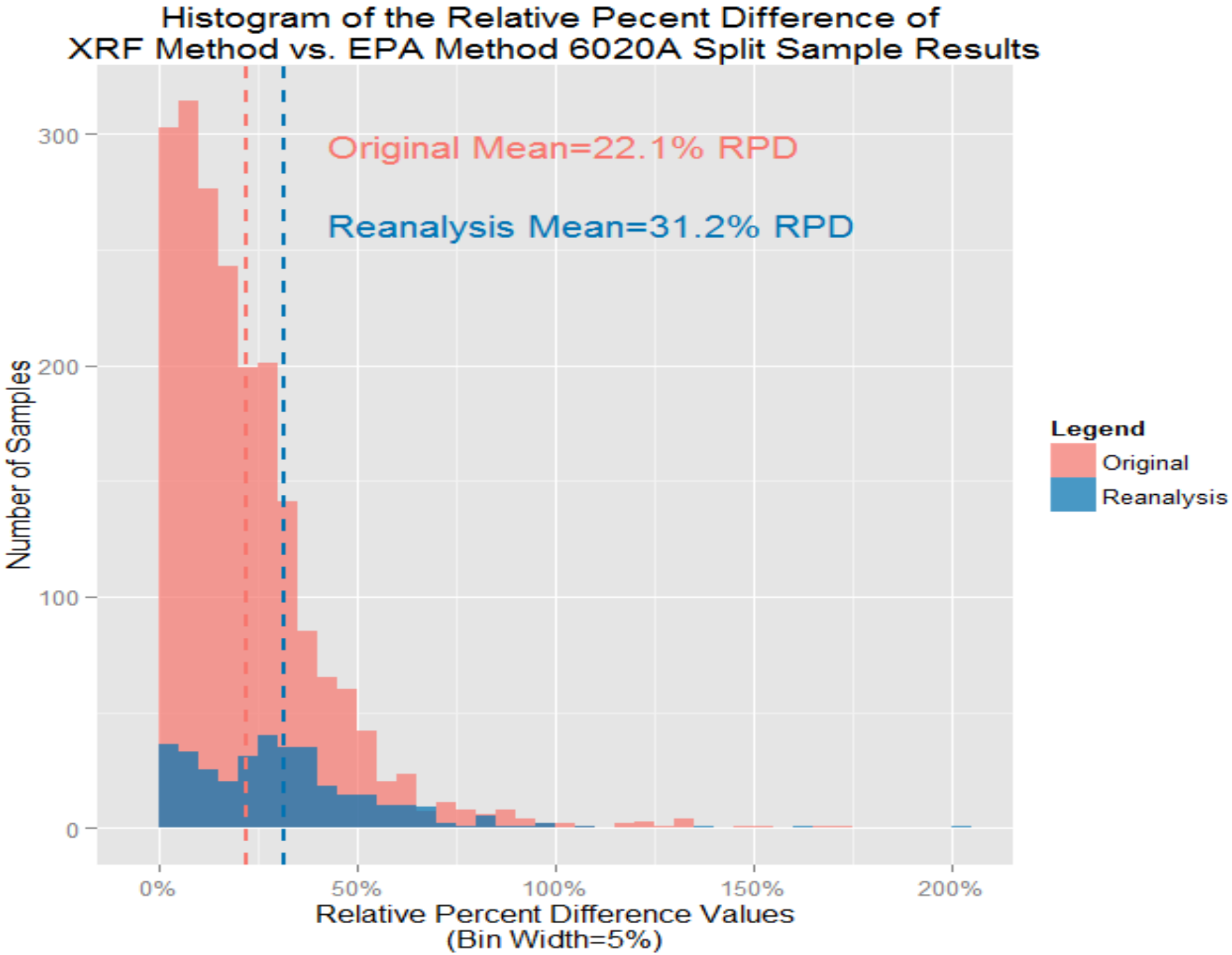
- Each sample was analyzed a minimum of 3 times, with homogenization in the sample bag between analyses
- RSD > 20%, conducted additional triplicate analyses
- 197 sample results out of 23,895 (0.82%) had RSDs greater than 20% (from six analyses)
- Sample homogenization and replicate XRF analytical processes adequately controlled inherent sample variance in the soil matrix

Split Sample Results

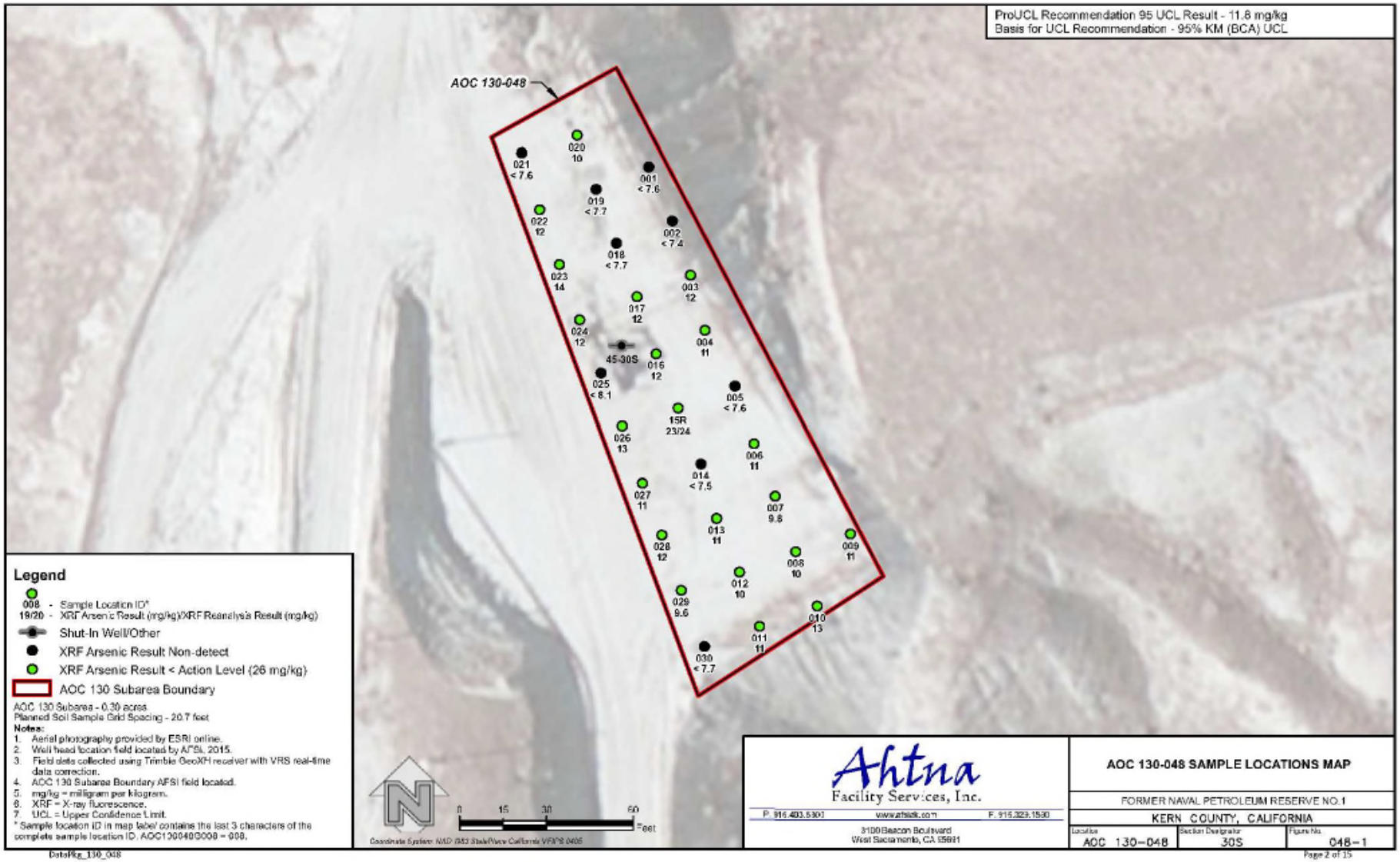
- ~ 10% split samples analyzed by EPA Method 3050B/6020A (ICP/MS)
- Low, medium, and high concentration samples from each well pad selected for split analysis
- Calculated the relative percent difference (RPD) between XRF and ICP/MS results
- Evaluated against 35% RPD criterion
- Reanalyzed samples by both methods if RPD > 35%

Split Sample Results

- 2492 split samples analyzed out of 23,895 total samples (10.4%)
- Average RPD was 22.1%
- 85.6% RPDs < 35%
- 14.4% of the RPDs > 35% - reanalyzed
- Average RPD of reanalyzed samples was 31.2%


Histogram of the Relative Pecent Difference of
XRF Method vs. EPA Method 6020A Split Sample Results
Original Mean=22.1% RPD
Reanalysis Mean=31.2% RPD
Number of Samples
300
200
100
0
0%
50%
100%
150%
200%
Relative Percent Difference Values
(Bin Width=5%)
Legend
Original
Reanalysis

ProUCL Recommendation 95 UCL Result - 11.6 mg/kg
Basis for UCL Recommendation - 95% KM (BCA) UCL



Legend

008 - Sample Location ID*
19/20 - XRF Arsenic Result (mg/kg)/XRF Reanalysis Result (mg/kg)
Shut-In Well/Other
XRF Arsenic Result Non-detect
XRF Arsenic Result < Action Level (26 mg/kg)
AOC 130 Subarea Boundary

AOC 130 Subarea - 0.30 acres
Planned Soil Sample Grid Spacing - 20.7 feet

Notes:
1. Aerial photography provided by ESRI online.
2. Well head location field located by AFSI, 2015.
3. Field data collected using Trimble GeoXH receiver with VRS real-time data correction.
4. AOC 130 Subarea Boundary AFSI field located.
5. mg/kg = milligram per kilogram.
6. XRF = X-ray fluorescence.
7. UCL = Upper Confidence Limit.

* Sample location ID in map label contains the last 3 characters of the complete sample location ID. AOC130048O008 = 008.

0 15 30 60 Feet

Coordinate System: NAD 1983 StatePlane California VI FIPS 0406

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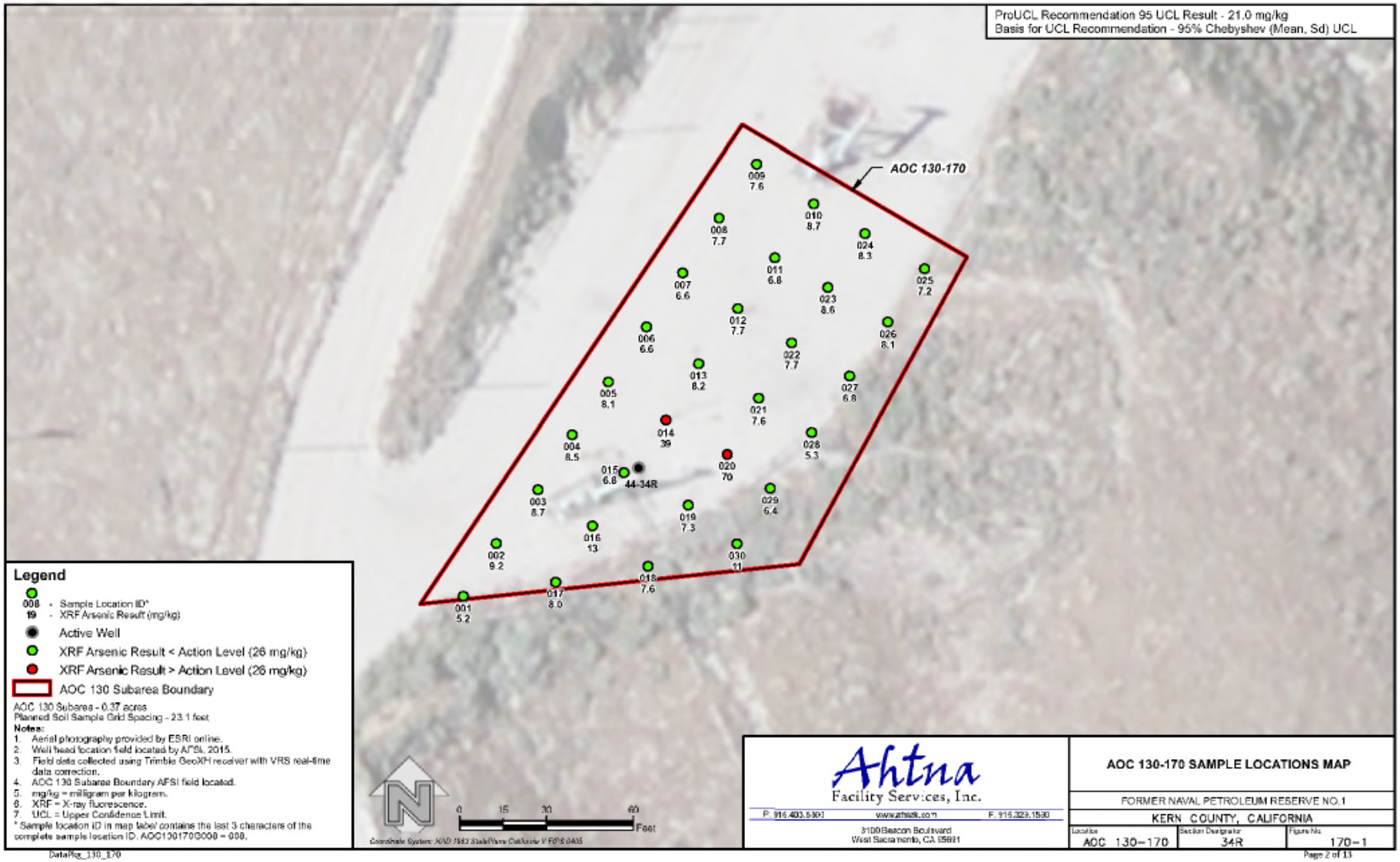
AOC 130-048 SAMPLE LOCATIONS MAP

FORMER NAVAL PETROLEUM RESERVE NO.1
KERN COUNTY, CALIFORNIA

Location	Section Designator	Figure No.
AOC 130-048	30S	048-1


ProUCL Recommendation 95 UCL Result - 21.0 mg/kg
Basis for UCL Recommendation - 95% Chebyshev (Mean, Sd) UCL
AOC 130-170
009 7.6
010 8.7
008 7.7
024 8.3
011 6.8
025 7.2
007 6.6
023 8.6
012 7.7
026 8.1
006 6.6
022 7.7
013 8.2
027 6.8
005 8.1
021 7.6
014 39
004 8.5
028 5.3
020 70
015 6.8
44-34R
003 8.7
029 6.4
019 7.3
016 13
002 9.2
030 11
018 7.6
017 8.0
001 5.2
Legend
008 - Sample Location ID*
19 - XRF Arsenic Result (mg/kg)
Active Well
XRF Arsenic Result < Action Level (26 mg/kg)
XRF Arsenic Result > Action Level (26 mg/kg)
AOC 130 Subarea Boundary
AOC 130 Subarea - 0.37 acres
Planned Soil Sample Grid Spacing - 23.1 feet
Notes:
1. Aerial photography provided by ESRI online.
2. Well head location field located by AFSI, 2015.
3. Field data collected using Trimble GeoXH receiver with VRS real-time data correction.
4. AOC 130 Subarea Boundary AFSI field located.
5. mg/kg = milligram per kilogram.
6. XRF = X-ray fluorescence.
7. UCL = Upper Confidence Limit.
* Sample location ID in map label contains the last 3 characters of the complete sample location ID. AOC130170008 = 008.
0 15 30 60
Feet
Coordinate System: NAD 1983 StatePlane California V FIPS 0405
Ahtna
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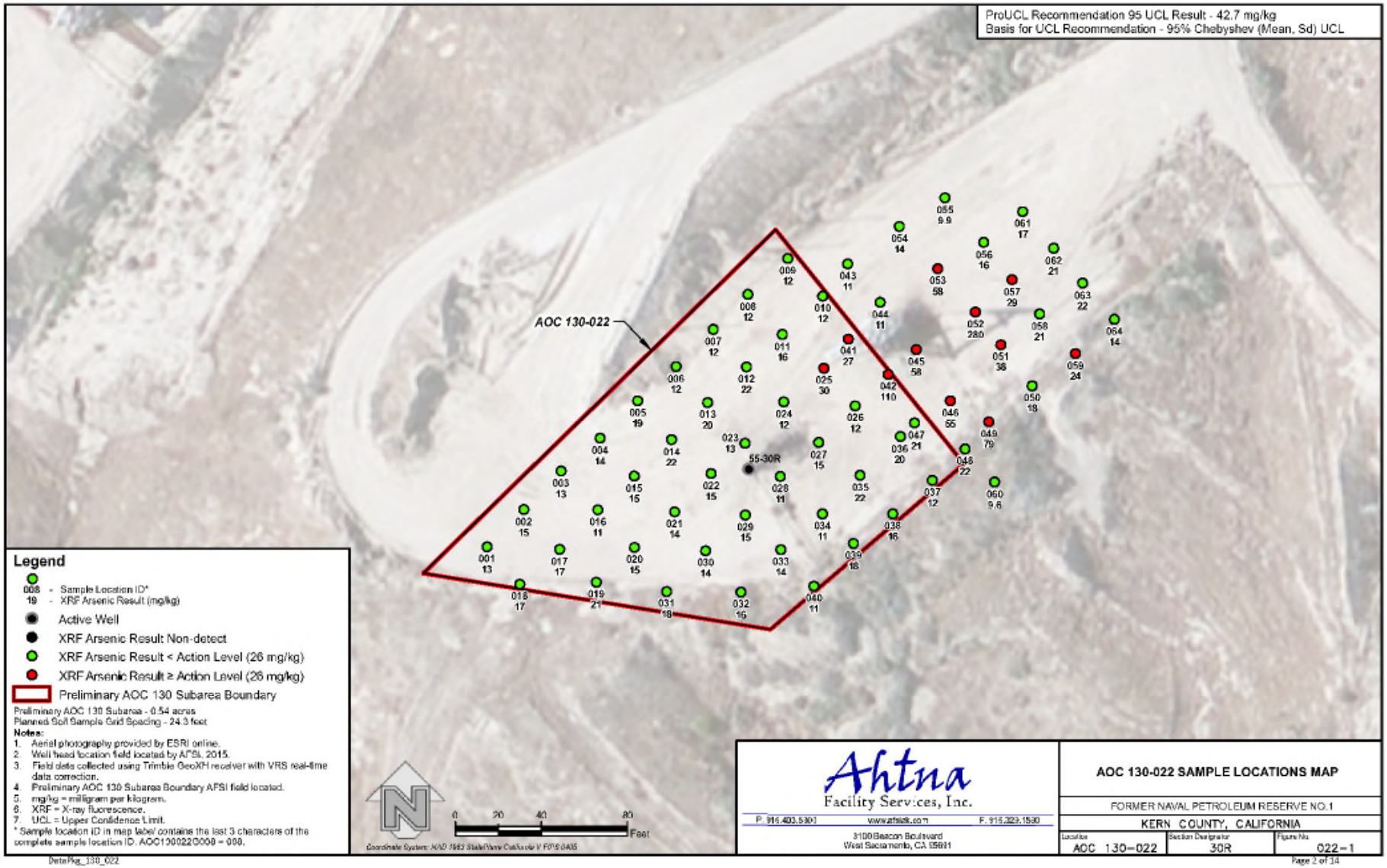
AOC 130-170 SAMPLE LOCATIONS MAP
FORMER NAVAL PETROLEUM RESERVE NO.1
KERN COUNTY, CALIFORNIA
Location AOC 130-170
Section Designator 34R
Figure No. 170-1


ProUCL Recommendation 95 UCL Result - 42.7 mg/kg
Basis for UCL Recommendation - 95% Chebyshev (Mean, Sd) UCL
AOC 130-022
55-30R
Legend
008 - Sample Location ID*
19 - XRF Arsenic Result (mg/kg)
Active Well
XRF Arsenic Result Non-detect
XRF Arsenic Result < Action Level (26 mg/kg)
XRF Arsenic Result ≥ Action Level (26 mg/kg)
Preliminary AOC 130 Subarea Boundary
Preliminary AOC 130 Subarea - 0.54 acres
Planned Soil Sample Grid Spacing - 24.3 feet
Notes:
1. Aerial photography provided by ESRI online.
2. Well head location field located by AFSI, 2015.
3. Field data collected using Trimble GeoXH receiver with VRS real-time data correction.
4. Preliminary AOC 130 Subarea Boundary AFSI field located.
5. mg/kg = milligram per kilogram.
6. XRF = X-ray fluorescence.
7. UCL = Upper Confidence Limit.
* Sample location ID in map label contains the last 3 characters of the complete sample location ID. AOC130022C008 = 008.
0 20 40 80 Feet
Coordinate System: NAD 1983 StatePlane California V FIPS 0405
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AOC 130-022 SAMPLE LOCATIONS MAP
FORMER NAVAL PETROLEUM RESERVE NO.1
KERN COUNTY, CALIFORNIA
Location AOC 130-022
Section Designator 30R
Figure No. 022-1
DataPkg_130_022
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Project Summary

Utilized EPA's Triad Approach to characterize 764 Arsenic Contaminated Sites

- Systematic investigation strategy
- Clearly defined decision criteria
- Integrated geospatial, analytical, and data management systems
- Sampling and analytical procedures designed to address soil heterogeneity issues
- Field XRF analytical protocol equivalent to "industry standards" for definitive site characterization data

Project Summary

- Successful application of real time analysis and dynamic field decision methodology for making accurate and reliable site characterization decisions
- Properly utilized, XRF is not just a screening tool, and can provide data for making better decisions than relying on “traditional” lab methods
- Moving into remedial evaluation phase – much more XRF work in our future
  - Risk management approaches
  - Remedial alternatives
  - Remediation

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David Jaske, Data Manager
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Questions?

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