The Unexpected Nature and Extent of Arsenic in Soil, Based on the RCRA Facility Investigation at the Elk Hills Oilfield, Former Naval Petroleum Reserve No. 1, Kern County, California*

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Abstract

A Resource Conservation and Recovery Act (RCRA) Facilities Assessment was prepared by California Department of Toxic Substances Control Board (DTSC) identifying 131 Areas of Concern (AOCs) at the Former Naval Petroleum Reserve-1, resulting in a consent agreement between DTSC and the US Department of Energy (DOE) to evaluate potential releases of hazardous constituents and implement corrective measures as appropriate.

Polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) were anticipated to be the chemicals of potential concern (COPCs) driving the need for corrective action. Metals were also anticipated COPCs; therefore, a study to determine the site-specific background concentrations of metals, including arsenic, was conducted. Historical information indicated that four AOCs would likely be impacted with arsenic due to historical use of an arsenic containing corrosion inhibitor, W-41.

During the RCRA Facilities Investigation, arsenic concentrations in soil were shown to require additional investigation at over 700 separate sites. Innovative sampling and analytical techniques using a field-based X-Ray Fluorescence analyzer (XRF) were utilized to analyze over 20,000 individual samples. EPA's Triad Approach, which consists of Systematic Project Planning, Real Time Data Acquisition, and Dynamic Work Strategies, was used to efficiently characterize each site in a single mobilization. Over 450 sites have arsenic in soil greater than background concentrations, resulting in a greater number of AOCs requiring corrective measures than initially anticipated.

Rapid site characterization for metals, risk evaluation strategies, and innovative data collection and data processing techniques will be presented, give attendees specific knowledge how to successfully use field-based XRF analyzers to generate data suitable for supporting human health risk evaluations.

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American Association of Petroleum Geologists
Annual Conference and Exhibition
May 23, 2018
Salt Lake City, Utah

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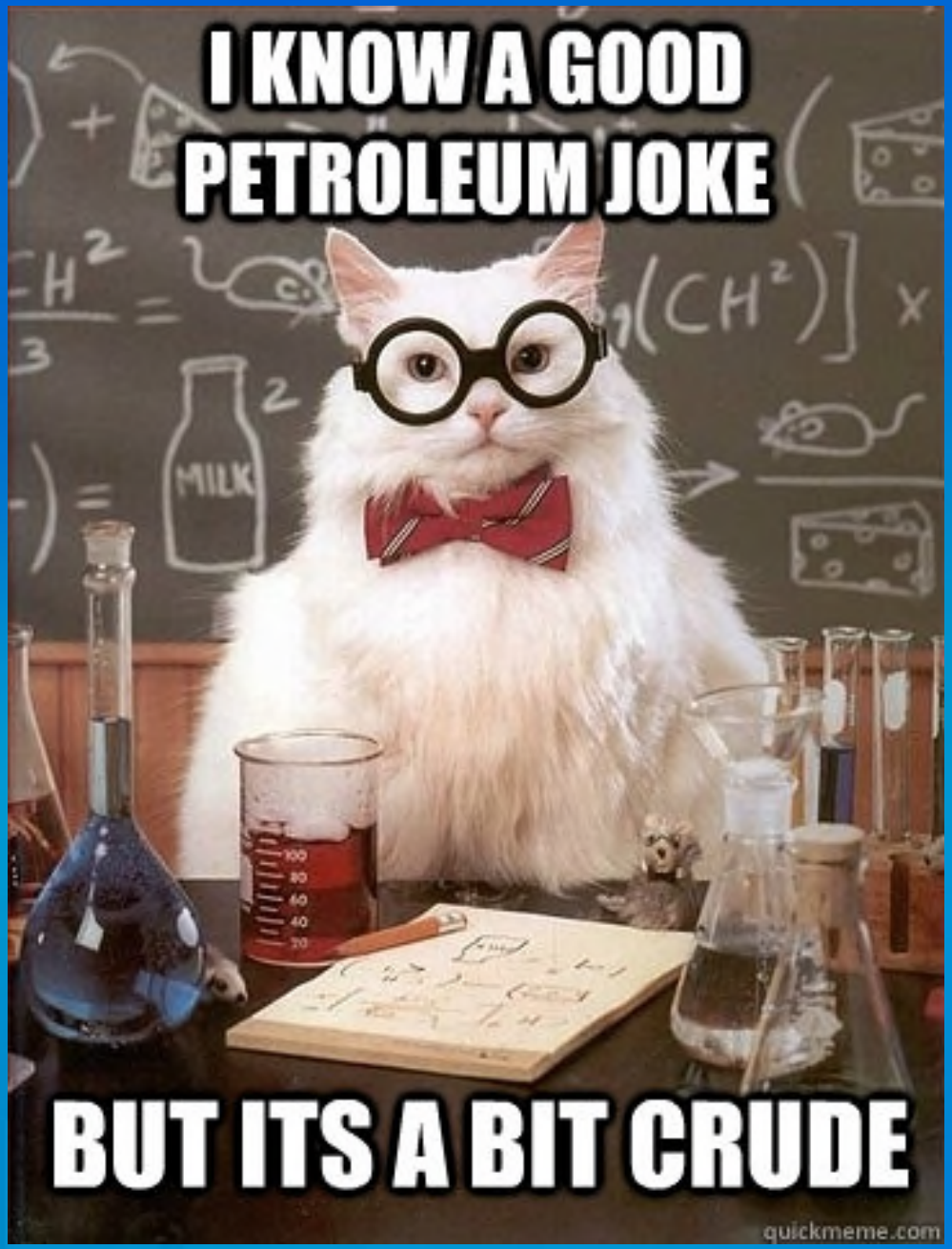
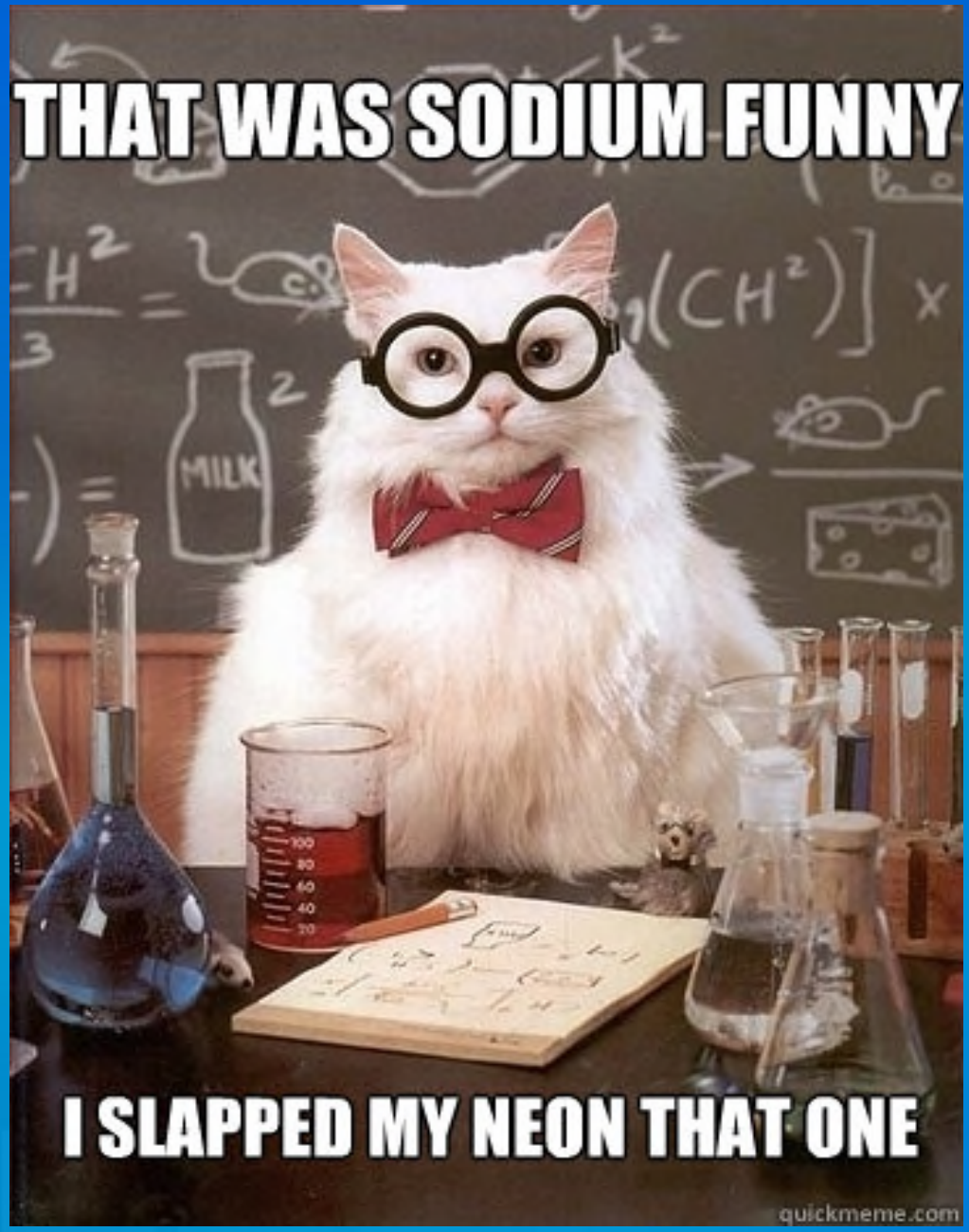
Presentation Objectives

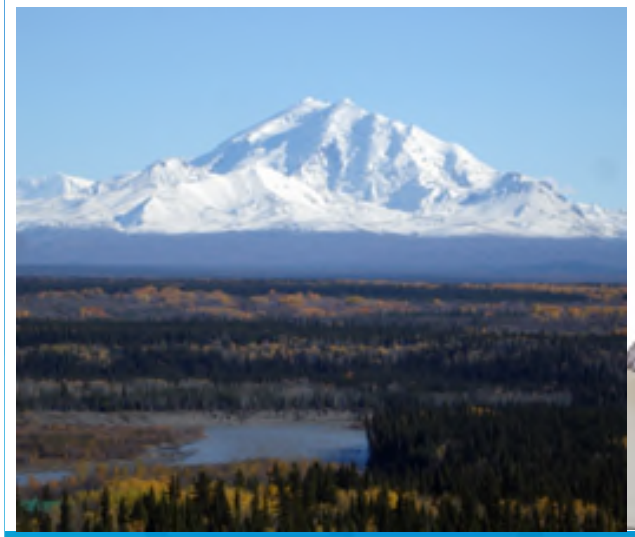
- Systematic oil field environmental assessment approach
- The unexpected nature and extent of arsenic contamination in soil from prior corrosion inhibitor usage
- Dynamic work strategies for rapid arsenic site characterization


I KNOW A GOOD PETROLEUM JOKE
MILK
BUT ITS A BIT CRUDE
quickmeme.com

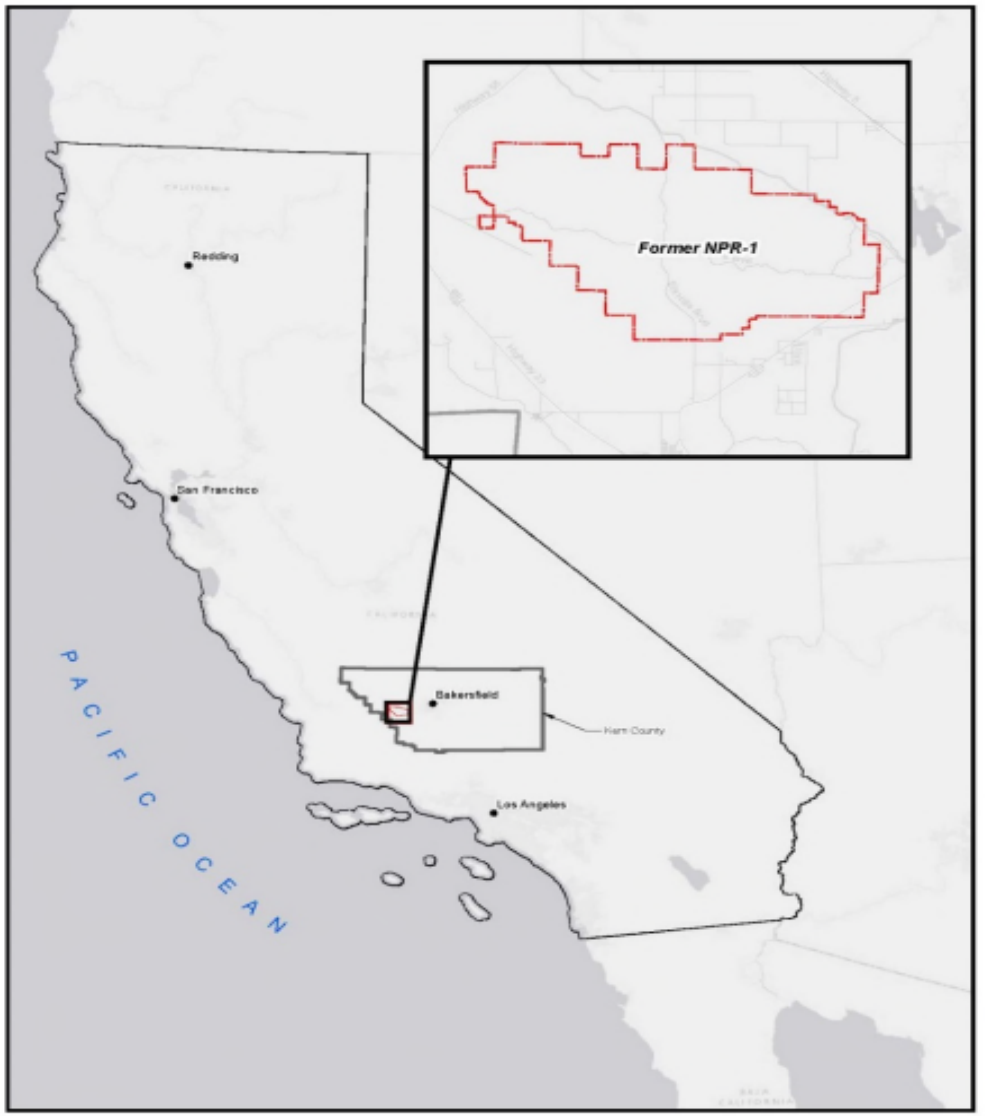

THAT WAS SODIUM FUNNY
MILK
I SLAPPED MY NEON THAT ONE
quickmeme.com

Ahtna Facility Services Inc.

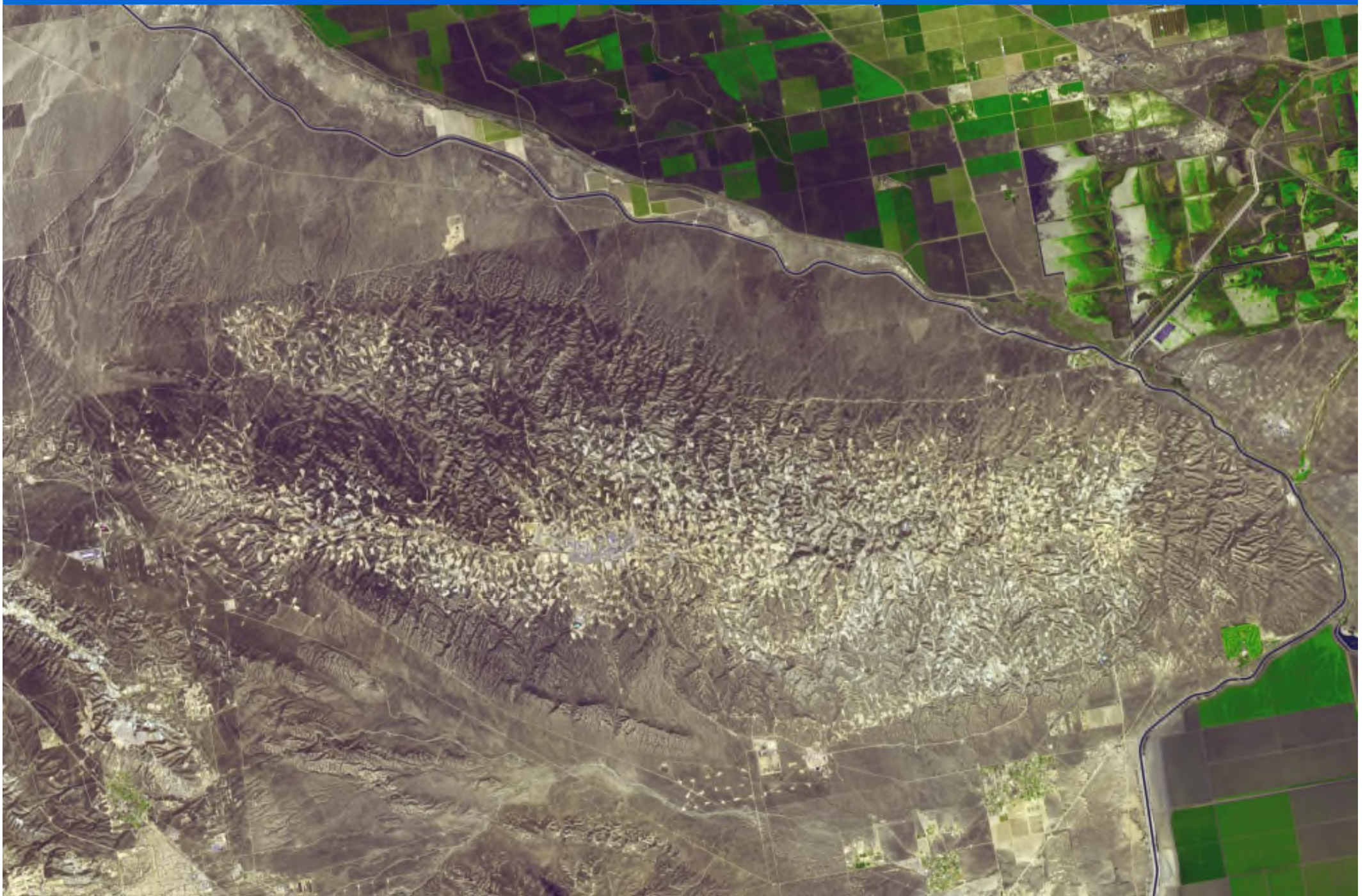
- **Ahtna Facility Services Inc. (AFSI) is a wholly-owned subsidiary of Ahtna, Incorporated, an Alaska Native Corporation (ANC).**
- **Ahtna is one of the original 13 regional ANCs**
- **100 % Native Shareholder-owned. Focus on land stewardship, and maintaining tribal heritage**
- **14 Subsidiaries offering a variety of services**
- **38 years on the Trans-Alaska pipeline System**
- **Diverse Federal Government and Commercial Client Base**



Former Naval Petroleum Reserve No. 1 (NPR-1)

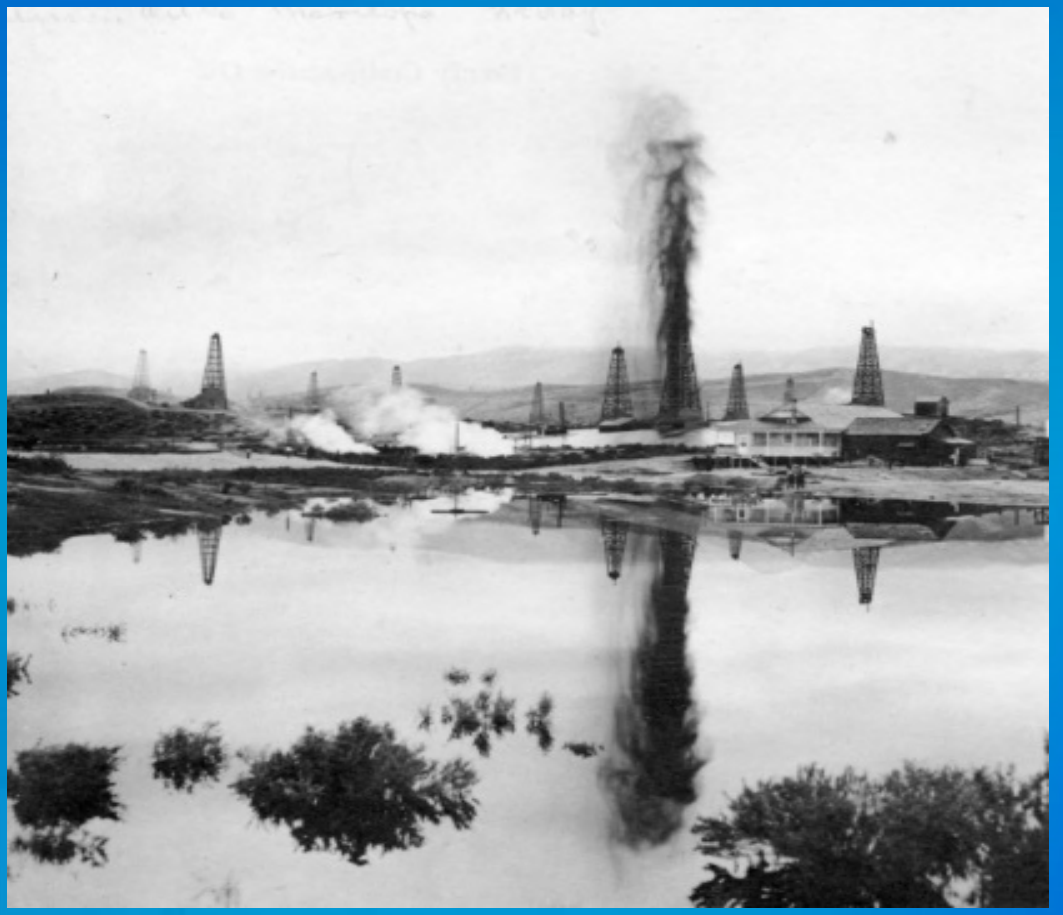


Former Naval Petroleum Reserve No. 1



NPR-1 (Elk Hills) History

- 1910 – Nearby Lakeview Gusher: 18 month eruption released 9 million barrels of crude oil



NPR-1 (Elk Hills) History

- 1911 – Discovered by Associated Oil Company
- 1912 - President Taft executive order set aside NPR
- Held as a reserve until the mid-1970's
- 1973-1974 Arab Oil Embargo: Navy opened up the oil field to development through private contractors
- 1975: Transferred from the Navy to Department of Energy (DOE)

Project History

- 1997: Sold by DOE to Occidental Petroleum Corporation
- 1997- 1998: California Department of Toxic Substances Control (DTSC) completed a Resource Conservation Recovery Act (RCRA) Facility Assessment
- 2008: DOE/DTSC Corrective Action Consent Agreement
  - Requires further investigations and corrective measures for protection of the environment and public health at 131 Areas of Concern (AOC)

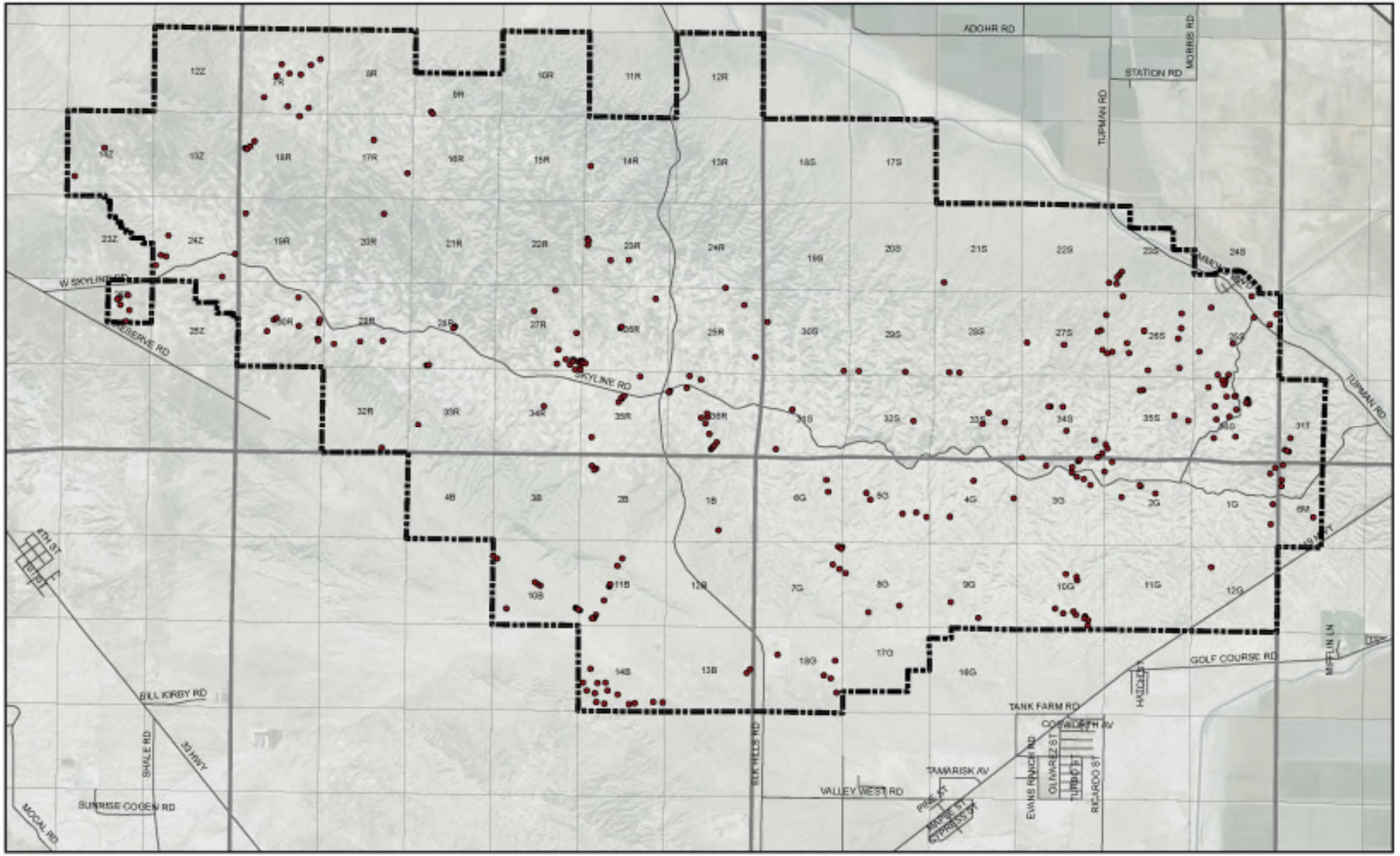
Current Status

- 2010: AFSI receive contract from DOE to address investigation and cleanup requirements required by the corrective action consent agreement
- Currently operated by California Resources Corporation – spinoff from Occidental Petroleum
- One of the largest active oil fields in the lower 48 states
- Largest natural gas producing oil field in California

Current Status

- Most initial characterization work completed at the 131 AOCs
  - Multi-increment surface soil sampling (ISM)
  - Discrete surface and soil boring sampling
- Exempt Aquifer: No water impacts or sampling required
- No further action status on 86 of the 131 AOCs
- Remediation phase based on identified risks to human health

131 Areas of Concern



Catch Basin

Catch Basin

Sump

Sump

Waste Management

Tanks/Facilities

Well Pad(s)

Chemicals of Potential Concern

- Polycyclic aromatic hydrocarbons (PAHs)
- Heavy metals (Arsenic, Cadmium, Chromium, Lead)
- Hexavalent Chromium
- No refined petroleum products except at a few dispensing locations
- Some VOCs/chlorinated hydrocarbons
- Dioxins (burn sites)

Chemicals of Potential Concern

- Polycyclic aromatic hydrocarbons (PAHs)
  - May be present in crude oil at concentrations above risk based screening levels (RBSLs)
  - Widespread presence of crude oil in surface soils and disposal areas – TPH clean up not required
  - Highly weathered in the natural environment
  - Primarily at concentrations below RBSLs
  - Some remediation required – mostly in sumps

Arsenic

- W-41: Sodium Arsenite – 41% arsenic
- Corrosion inhibitor used from the 1920s through the early 1970s
- Reportedly used in closed loop systems for rod pump extraction wells
- 764 former or current well pads identified as possibly impacted by the use of W-41
- Disposal areas (catch basins/sumps) also impacted
- Soil is transported throughout the environment through natural processes and oil field activities

Arsenic Decision Criteria

- Naturally occurring in native soil at concentrations greater than RBSLs
  - *0.11 mg/kg residential, 0.24 mg/kg commercial/industrial: 1.0E-06 risk factor*
- Site-specific background levels approved by DTSC using a two tiered approach
  - *Arsenic Action Level = 26 mg/kg: Upper prediction limit: 2.4E-04 Risk Factor*
  - *Arsenic Background = 16 mg/kg: Upper limit – clean up goal: 1.5E-04 Risk Factor*

Initial AOC 130 Assessment
Arsenic at well pads

- Conducted soil sampling at a random selection of 40 out of 764 well pads
- Arsenic concentrations in 18 out of 40 composite surface samples (45%) > 26 mg/kg
- Indicated that there could be close to 400 individual well pad sites (approximately ½ acre) with arsenic soil concentrations that require further sampling and eventual remediation

AOC 130 Conceptual Site Model

- Wells/Well Pads where W-41 was used
  - Spills/direct releases
  - Surface soil/exposed subsurface soil
  - Soil disturbance to outdoor air: inhalation risk to site workers
  - Re-deposition to soil: ingestion and dermal risk to site workers

AOC 130 Conceptual Site Model

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EPA's Triad Methodology Applied

Systematic Planning

Dynamic Work Strategies

Real-Time Measurement Technologies

Systematic Planning

- Developed XRF arsenic method for rapid characterization in lieu of offsite analysis using EPA Method 6020A
- Evaluated different sampling and sample processing strategies to enhance decision quality
- Used findings to prepare a Work Plan designed to:
  - Assess arsenic at 764 well pads with minimal mobilizations
  - Eliminate well pads from further action consideration
  - Inform future corrective measure approaches

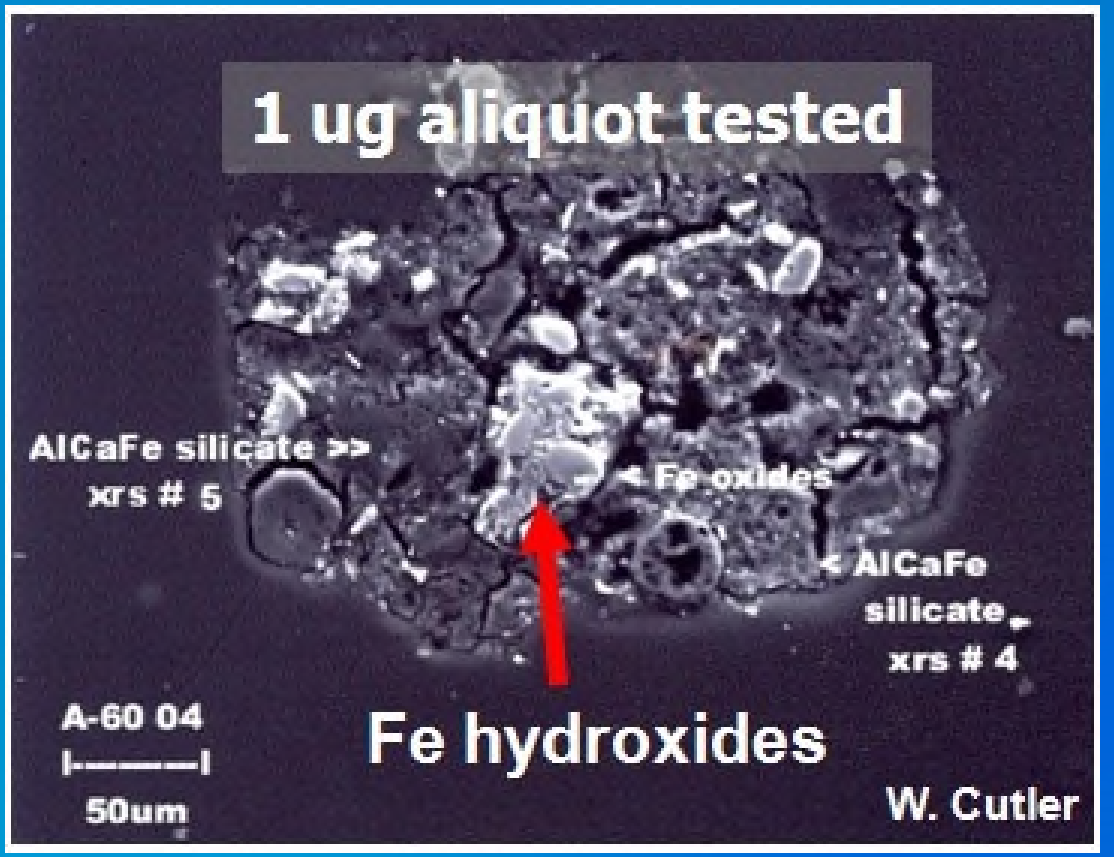
Systematic Planning

- California Division of Oil, Gas & Geothermal Resources (DOGGR) well coordinates uploaded to the GIS
- Grid sampling design
- Sample homogenization/processing
- Real-time mobile lab XRF method protocol
- Data management and reporting systems
- Dynamic field decision processes
- Regulator approval

Heterogeneity is the Norm
The Nugget Effect

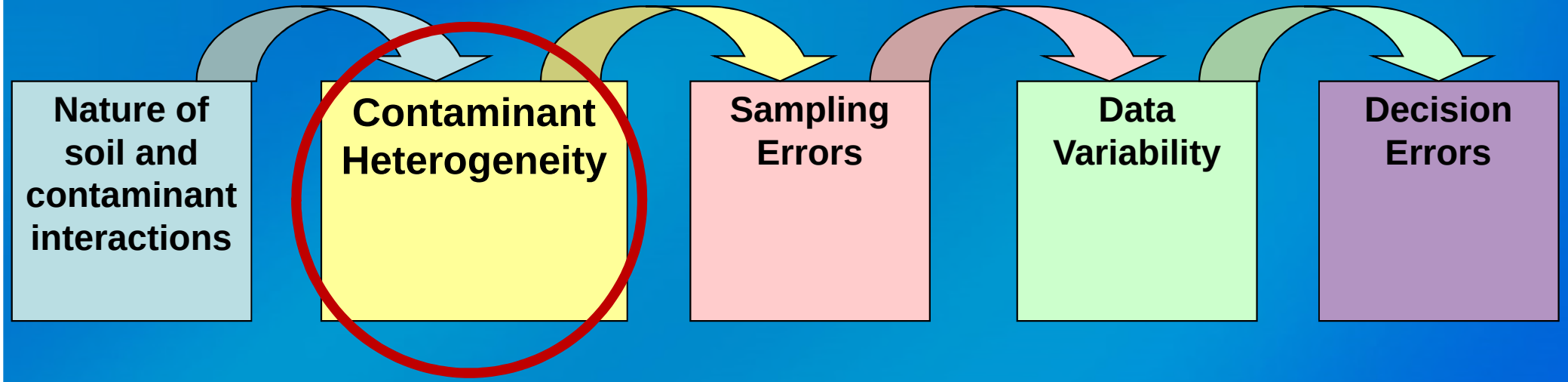
- Contaminants adsorbed to distinct particles form “nuggets” of high concentration
- Depending on where the XRF beam is directed, or the laboratory “scoop” is taken, the analysis may include more or less of the arsenic nuggets.

Arsenic (whitish color) sorbed to iron hydroxide particles



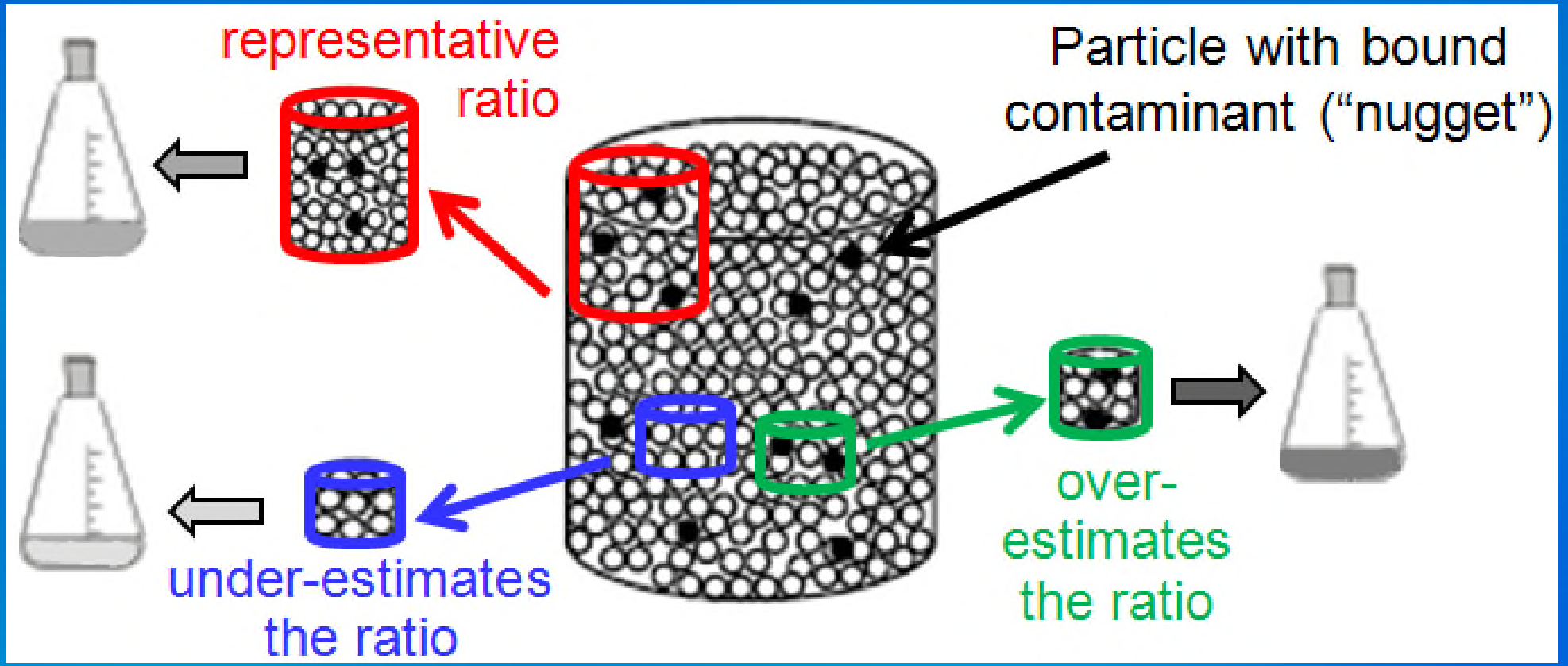
Particulates in Solid Matrices

"Micro-Heterogeneity"



- Non-uniformity within the sample container
- Contamination is heterogeneous at the same spatial scale as sample analysis

Sampling Size Induced Error



Real Time Measurement

- Scale-up considerations; 23,000 samples in 6.5 months!
- Hand-held GPS integrated with GIS
- Barcode sample and location identifications
- Field XRF protocol (SOP) based on EPA Method 6200
  - Definitive, representative, decision quality data
- Data processing and management systems
- Staffing: 8 full time staff plus office support

XRF Method Protocol

- Seived samples < 2 mm, thoroughly homogenized
- Create instrument-specific calibration curve
  - Regression analysis between EPA 6020A and XRF values
- Daily calibration verification using certified reference material (10, 111 and 500 mg/kg, blank)

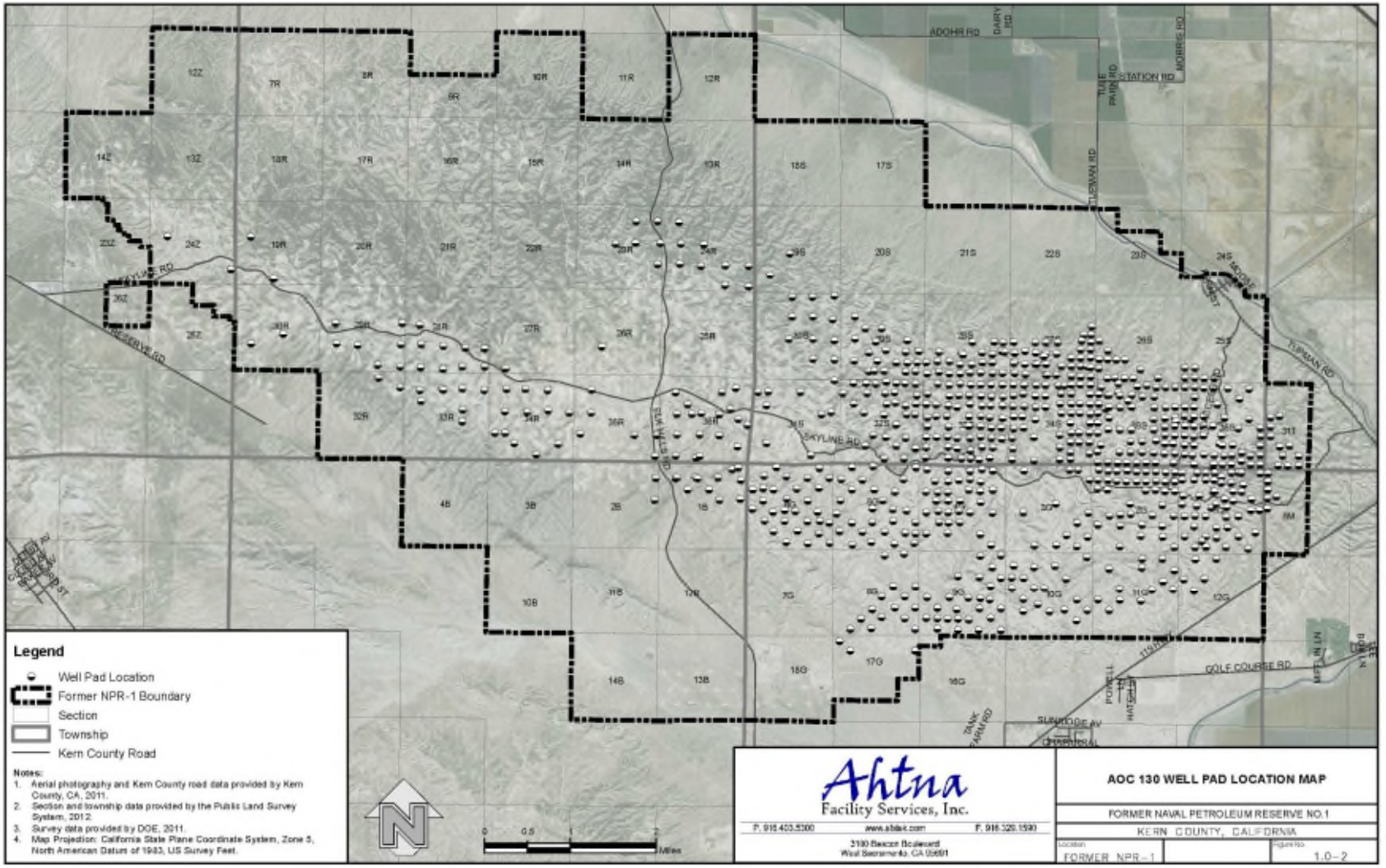
XRF Method Protocol

- Triplicate XRF analysis using 30 second sample scan
- Samples stayed in the zip seal bag
- Mixed sample between analyses
- RSD > 25%, additional triplicate analysis
- Convert XRF average value to a “lab equivalent” concentration using calibration curve

QA - Split Sample Results

- 2200 (10 %) split samples analyzed by XRF and EPA Method 6020A
- Average calculated RPD = 24%
- 20% of the RPDs were greater than 35% and were reanalyzed
- Most of the reanalyzed split samples were within 35% RPD
- Sample heterogeneity is the primary contributor to variance between split samples

Well Pad Identification



Aerial View of Well Pads

Well Pads

Determine Well Pad Boundary

Establish Sampling Grid

Establish Sampling Grid

Establish Sampling Grid

Sample Collection

Sample Collection

Sample Location Coordinates

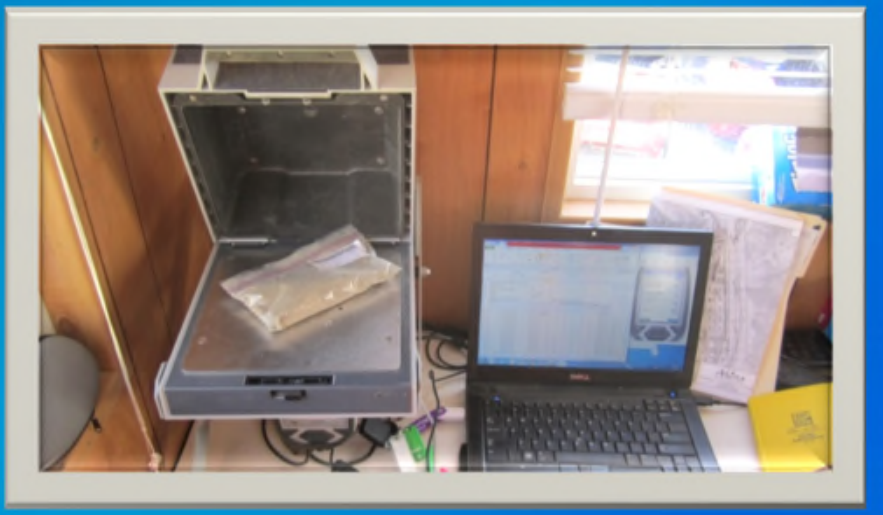
Field Mapping

Sample Processing

Sample Processing

Sample Processing

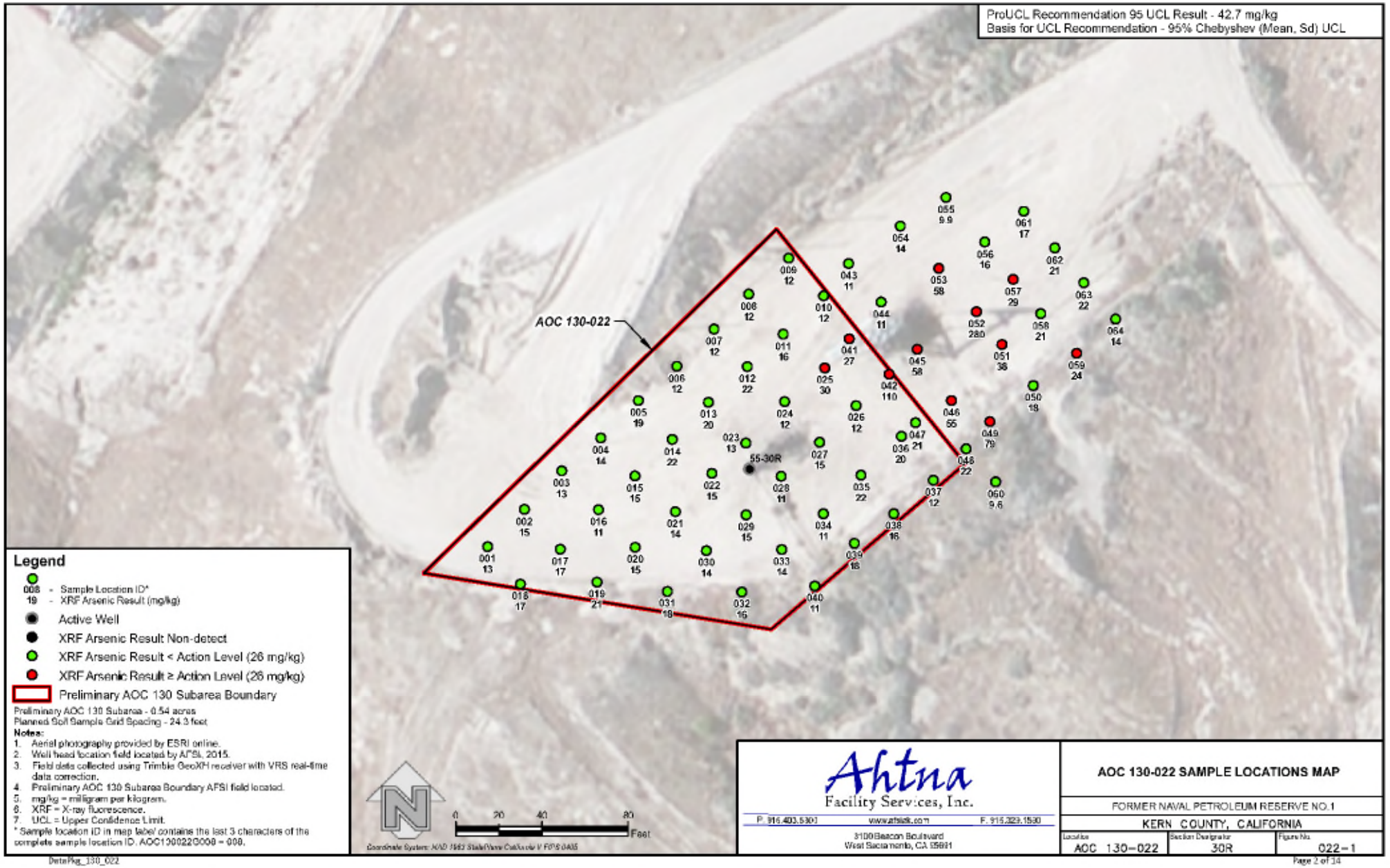
Sample Analysis
Thermo Scientific Niton XL3-950



Sample Analysis

Sample Analysis

Field Data Processing


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. AOC130022G008 = 008.
0 20 40 80
Feet
Coordinate System: NAD 1983 StatePlane California V FIPS 0405
Ahtna
Facility Services, Inc.
P. 916.403.5301 www.afsisk.com F. 916.323.1530
3100 Beacon Boulevard
West Sacramento, CA 95691
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

Arsenic Investigation Summary

- Arsenic concentrations ranged from 4.3 to 3500 mg/kg
- 77/764 well pads proposed for NFA due modified land surface
- 190 well pads proposed for NFA due to sample results less than 26 mg/kg arsenic
- 497 well pads proposed for further action due to sample results greater than or equal to 26 mg/kg

Other Arsenic Evaluations

- 110 AOCs have been sampled for arsenic
- 50/110 have received NFA approval
- 16 NFAs under review
- 30 are under further investigation
- 14 have planned or completed remedial actions
- Ongoing arsenic investigations and cleanups

NPR-1 Project Summary

- Systematic approach to AOC closure
  - Used historical information to close sites with little or no impacts
  - Comprehensive investigation strategies – Data Quality Objectives for managing sampling and site closure
- PAHs and TPH risk management
- No groundwater impacts

NPR-1 Project Summary

- Wide spread arsenic impacts due to prior use of W-41
  - Well pads
  - Disposal areas
- Triad Methodology: Systematic planning, real-time measurement, dynamic work strategies
  - Reduced costs, fast characterization, good decisions

NPR-1 Success Factors

- Partnerships
  - Regular in-person meetings
  - Consensus and trust building
- Comprehensive Planning and decision criteria
- Adapt to changing circumstances
- Dynamic risk evaluation strategies
  - What constitutes acceptable risk to future workers/landowners under a risk-based closure framework

NPR-1 Success Factors

- Innovative investigation and field techniques
- Integrated information services
  - Geographic Information System
  - Relational database
  - Collaboration Site (Share Portal)
- Document quality – speeds up review process
- Project completion dependent on available funding

Acknowledgements

- Wayne Elias, Department of Energy, Office of Petroleum Reserves

Ahtna Facility Services, Inc.

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- Mary Snow, Geologist
- Estelle Shiroma, Risk Assessor
- Nathan Unangst, Geologist
- Meghann Hurt, Geologist

Questions? Comments?

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