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.
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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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

BUT ITS A BIT CRUDE
THAT WAS SODIUM FUNNY

I SLAPPED MY NEON THAT ONE
Ahtna Facility Services Inc. 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
1910 – Nearby Lakeview Gusher: 18 month eruption released 9 million barrels of crude oil
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)
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)
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
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
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
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.
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
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EPA’s Triad Methodology Applied

Systematic Planning

Managing Uncertainty

Dynamic Work Strategies

Real-Time Measurement Technologies
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
Nature of soil and contaminant interactions

Contaminant Heterogeneity

Sampling Errors

Data Variability

Decision Errors

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

ITRC, ISM-1, Section 2.5.2
Sampling Size Induced Error

Particle with bound contaminant ("nugget")

representative ratio

under-estimates the ratio

over-estimates the ratio
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
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
Sample Processing
Sample Processing
Sample Analysis
Thermo Scientific Niton XL3-950
Sample Analysis
Field Data Processing
**Legend**
- SAMPLE LOCATION O:
- XRF Arsenic Result (mg/kg)
- Active Well
- XRF Arsenic Result: Non-detect
- XRF Arsenic Result: Action Level (20 mg/kg)
- XRF Arsenic Result: Action Level (25 mg/kg)
- Preliminary AOC 150 Substance Boundary
- Preliminary AOC 150 Substance - 0.5 acre
- Preceding Surf Sample Grid Spacing - 24.3 feet

**Notes:**
1. Aerial photography provided by ESRI online.
2. Well head location field located by EBL 2015.
3. Field data collected using Trimble GeoXM receiver with VRS real-time data correction.
4. Preliminary AOC 150 Substance Boundary FBS field located.
5. FBS = Field-based Screening.
6. XRF = X-ray fluorescence.
7. UCL = Upper Confidence Limit.
8. Sample location O: A map also contains the last 3 characters of the sample location O: AOC130-022-009 = 016.

**Ahtna Facility Services, Inc.**

**Former Naval Petroleum Reserve No. 1**

KERN COUNTY, CALIFORNIA

**AOC 130-022 SAMPLE LOCATIONS MAP**

**Sample Location:**
- AOC 130-022
- 301
- 022-1
Arsenic concentrations ranged from 4.3 to 3500 mg/kg.

77/764 well pads proposed for NFA due to 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.
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
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
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Questions? Comments?

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