SERDP & ESTCP Perchlorate Sources

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DoD's Environmental Technology Programs

ESTCP

DoD EPA DOE SERDP
Strategic Environmental Research and Development Program

Demonstration/Validation

Basic and Applied Research

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Perchlorate RDT&E Issues

- Treatment
  - In-situ Cleanup
  - Ex situ : waste water and drinking water
- Alternatives
- Eco-toxicology
- Sources
  - Understanding DoD's Responsibility
    - Alternate sources
    - Natural sources
    - Identification

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Evaluation of Alternative Causes of Wide-Spread, Low Concentration Perchlorate Impacts to Groundwater

- Objectives
  - Estimate the potential for perchlorate impacts to surface water & groundwater from:
    - Road flares and pyrotechnics
    - Explosives for construction, quarrying & mining
    - Past and ongoing fertilizer practices (Chilean nitrate)
    - Electrochemically-prepared (ECP) chlorine products
- Project Team: GeoSyntec, University of Rhode Island, American Pacific Corporation

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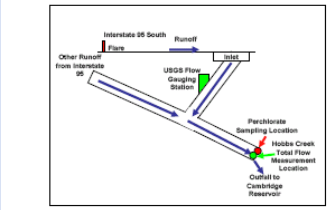
Road Flares

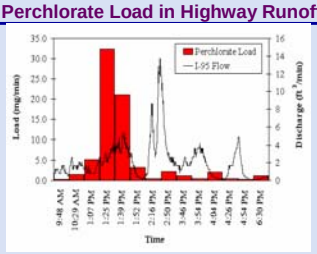
- Background
  - 20-40 million flares sold annually
- Laboratory
  - Lab studies showed 5-6% potassium perchlorate in unburned flares
  - Complete burning reduced perchlorate by 99% - still have up to 66 mg perchlorate in flare residue
- Field
  - Monitoring of background levels of perchlorate in highway runoff
  - Monitored highway run-off near a road flare deployed by State Police at an accident scene (I-95 MA)

Perchlorate in Highway Runoff

Perchlorate Sampling in Highway Runoff



Perchlorate Load in Highway Runoff



- Max ClO4- concentration leaving highway :~ 314 mg/L.
- Peak load of ClO4- leaving highway : 32.4 mg/min.
- Total ClO4- load to receiving waters :1,294 mg
- Flares can be a significant point source of perchlorate

Fireworks

- Background
  - 221 million pounds of fireworks consumed in U.S. in 2003
  - Fireworks charge may contain up to 70 wt% potassium perchlorate
  - Case studies in the literature discussing extent of soil and water contamination at firework display sites are limited
- Approach
  - Measure the perchlorate content in firework charges
  - Quantify impacts on groundwater and soil from commercial fireworks display
    - Two study sites
  - University of Massachusetts Dartmouth (UMD)
    - 40 soil samples were collected before and after fireworks display at UMD campus
    - Analyzed for perchlorate (Method 332.0) and metals (Method 6010B: Aluminum, Antimony, Barium, Calcium, Magnesium, Potassium, Sodium and Strontium) in pre and post display soil samples
    - Analyzed un-detonated firework charges for perchlorate (Method 314.0) and metals (Method 6020A)

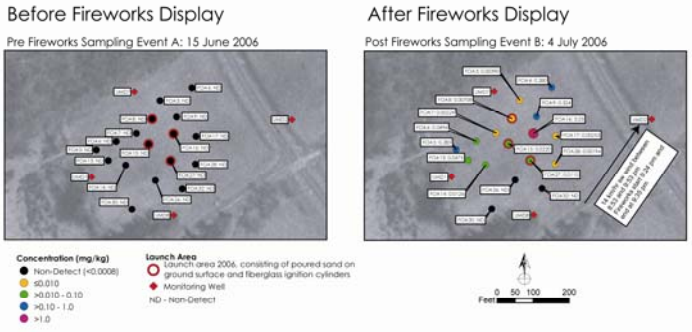
Perchlorate & Metals in Fireworks Charges

Perchlorate and Metals Concentrations in Firework Charges

Parameter (mg/kg)	Charge 1	Charge 2
Perchlorate	389,000,000	355,000,000
Aluminum	77,000	120,000
Antimony	ND	ND
Barium	440	190
Calcium	1,700	720
Magnesium	80,000	120,000
Potassium	160,000	160,000
Sodium	ND	150
Strontium	18	22

- Perchlorate concentration in fireworks charge was 389 g/kg. Aluminum, magnesium and potassium were also present at high concentrations

Perchlorate in Soil



- Concentration of perchlorate in soil increased from ND to maximum of 5 mg/kg after the fireworks display

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Evaluation of Alternative Causes of Wide-Spread, Low Concentration Perchlorate Impacts to Groundwater

Identification and Characterization of Natural Sources of Perchlorate

- Objectives
  - Combine theoretical, laboratory, and field investigations to address the natural production and occurrence of perchlorate
  - Describe and confirm natural mechanisms of perchlorate production
  - Determine hydrologic and geochemical processes for selective geographic concentration of perchlorate
  - Supply field evidence of atmospheric and geochemical processes involved in the formation of natural perchlorate in geologically young environments
- Project Team
  - U.S. Air Force (Greg Harvey, project lead), Texas Tech University, U.S. Geological Survey

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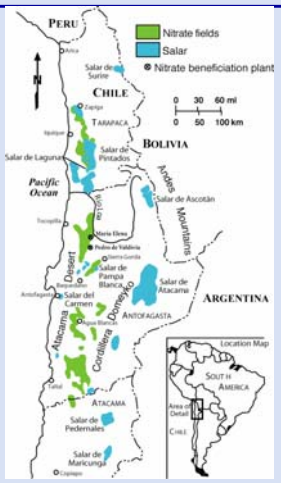
Identification and Characterization of Natural Sources of Perchlorate

Where it all started



- Chilean NO_3^- Deposits (Atacama Desert)
  - Desert for at least last 1 MY
  - ClO_4^- (>.1%) identified over 100 years ago
  - Deposits also contain IO_3, CrO_7 (mg/kg in some strata)

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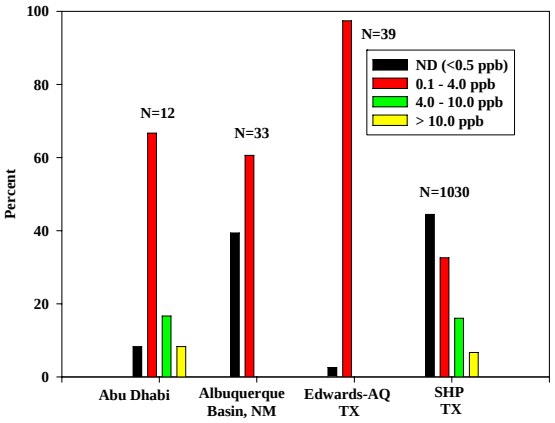
Identification and Characterization of Natural Sources of Perchlorate

Does Natural Perchlorate Impact other Areas?



Concentration Distribution of Perchlorate in Groundwater from Selected Locations

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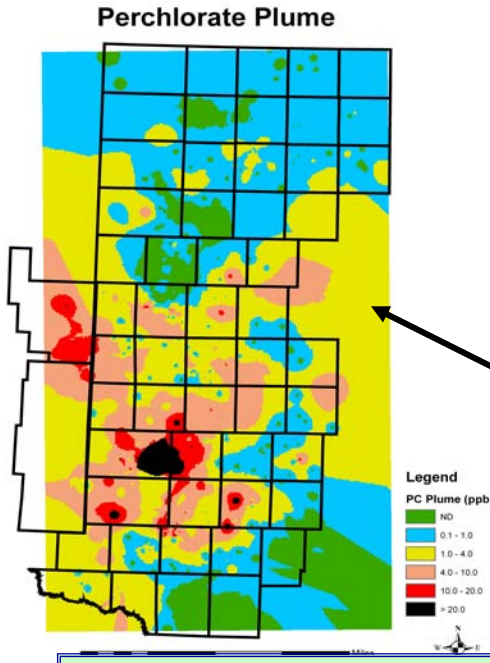
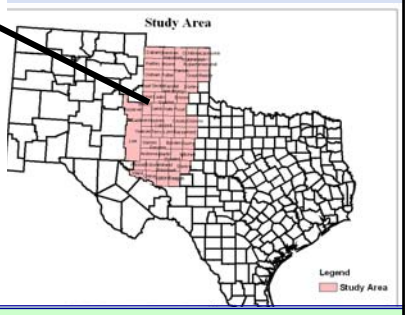
Identification and Characterization of Natural Sources of Perchlorate

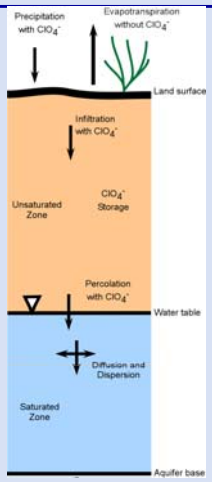


Other Suspected Natural Occurrences

- Study area >59,000 mi^2
- 89% > 0.1 ppb
- Estimated Mass of PC
  - Saturated >2 X 10^6 Kg



Proposed Perchlorate Accumulation Mechanisms



- Atmospheric Production and Deposition
- Partial Transport in Undisturbed Arid Areas
- Accumulation over long Periods
- Flushing Possible from Irrigation or Climate Shifts
- Not Stable in Anaerobic Environments and Some Plant Uptake

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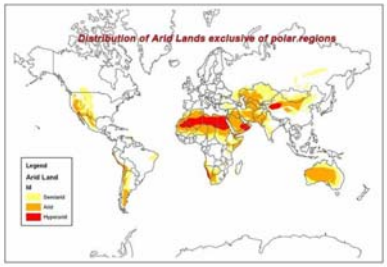
What's the overall significance?



- Exposure
  - Plants?
  - Milk?
  - GW?
- Future GW impacts
  - Dessert Urbanization
  - Climate Change
  - Irrigation
- Site Assessment
  - Establish Background
  - Isotopic Differentiation

Natural vs. Anthropogenic Perchlorate

Key Question: Can You Distinguish Natural from Man-Made Perchlorate?

Isotope Ratio Analysis to Differentiate Perchlorate Sources

- Objectives
  - Analyze Isotope Ratios in Commercial, Military, and Natural Perchlorate Sources.
    - Develop broad database quantifying difference between natural and anthropogenic perchlorate.
  - Analyze Isotope Ratios of Perchlorate in Groundwater Plumes with Anthropogenic Origin and Suspected Natural Sources.
    - Demonstrate/validate isotopic procedure for forensic analysis.
- Project Team
  - Shaw, USGS, ORNL, Univ. Illinois

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Stable Isotope Analysis

Isotopes: same number of protons & electrons, different number of neutrons

Hydrogen	^{1}H, ^{2}H
Oxygen	^{16}O, ^{17}O, ^{18}O
Carbon	^{12}C, ^{13}C
Chlorine	^{35}Cl, ^{37}Cl
Nitrogen	^{14}N, ^{15}N
Sulfur	^{32}S, ^{34}S

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Stable Isotope Analysis

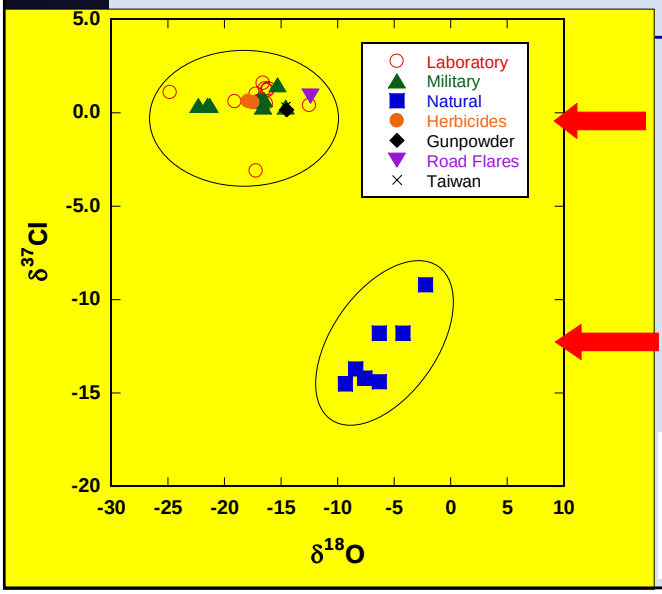
- Elements in a compound can have widely different isotopic ratios based on mode of formation (e.g.,^{18}O in NO_3 from nitrification vs. atmospheric).

- Stable isotope ratios provide a unique "fingerprint" of a chemical compound, another dimension of information invisible from dissolved concentrations

First Objective: Analyze Isotope Ratios in Commercial, Military, & Natural Perchlorate Sources

- 3 military sources
  - Propellant-grade perchlorate
  - Demilitarization activities
- 9 commercial sources
  - Reagent grade perchlorate
  - Fireworks
  - Emergency flares
  - Cotton defoliants
- 6 natural sources
  - Chilean caliche
  - Natural fertilizers with Chilean nitrate
  - Southwest US: Evaporites
  - Potash salt

Results:
Forensic Isotopic Analysis of Perchlorate
$\delta^{37}Cl$ and $\delta^{18}O$



Chlorine markedly "heavier" in anthropogenic Perchlorate (n = 25).

$\delta^{37}Cl$: 0.6 ± 0.9
Range: - 3.1 to 1.6

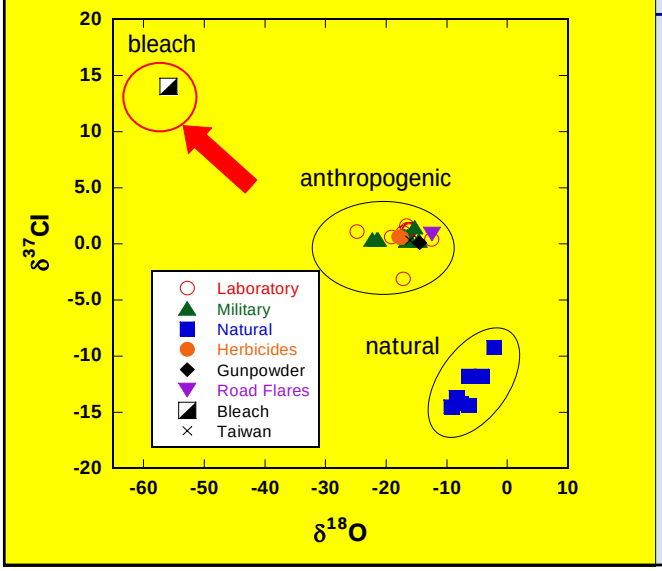
$\delta^{18}O$: -17.2 ± 2.8
Range: -24.8 to -12.5

Oxygen consistently "heavier" in natural Perchlorate (n = 7).

$\delta^{37}Cl$: -12.8 ± 2.0
Range: -14.5 to -9.2

$\delta^{18}O$: -6.3 ± 2.5
Range: -9.3 to -2.2

Perchlorate in Bleach
$\delta^{37}Cl$ and $\delta^{18}O$



Perchlorate forms
Slowly in bleach
~ 8 ppm/yr

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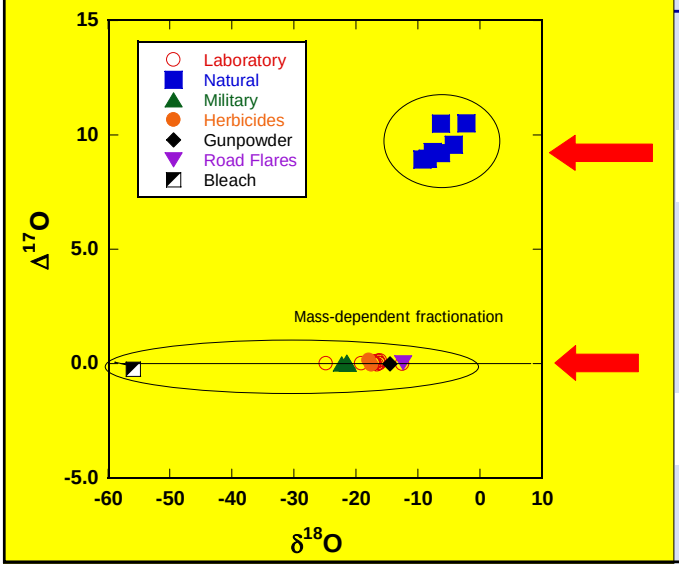
Results:
Forensic Isotopic Analysis of Perchlorate
$\Delta^{17}O$ and $\delta^{18}O$



Natural perchlorate Excess $\Delta^{17}O$ (n = 7)

$\Delta^{17}O$: 9.6 ± 0.7

Range: 8.9 to 10.5

Anthropogenic perchlorate "mass dependent" fractionation (n = 20)

$\Delta^{17}O$: 0.01 ± 0.08

Range: - 0.24 to 0.11

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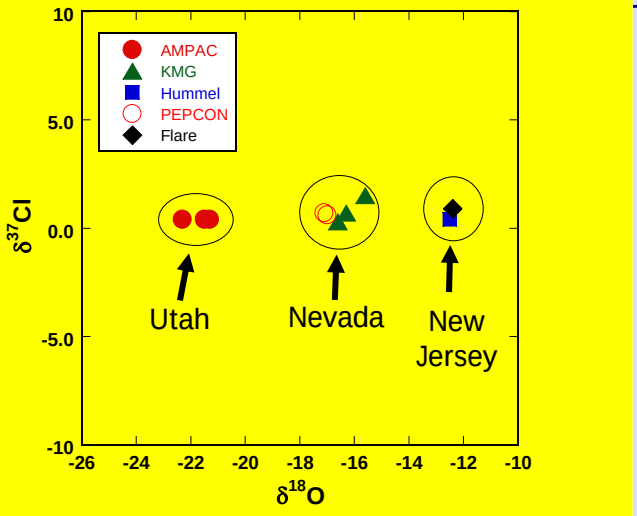
Results: Can You Differentiate Anthropogenic Sources?



Manufacturer?

Geographical Origin ?

Partially fractionated signature of $\delta^{18}O$ in source water

More data necessary

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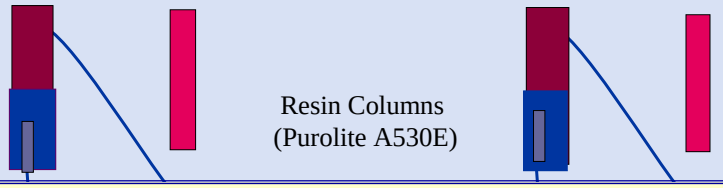
Isotope Ratio Analysis to Differentiate Perchlorate Sources

Second Objective:

Analyze Isotope Ratios of Perchlorate in Groundwater Plumes with Anthropogenic Origin & Suspected Natural Sources

- Site Selection and Groundwater Sampling
  - Site Selection: 6 - 9 locations.
    - Include military, natural, fertilizer, fireworks sources
  - Select wells for sampling
    - Geology, geochemistry, perchlorate levels, suspected source (1 – 6 wells)
  - Developed resin columns for field collection of perchlorate.
  - Collect perchlorate (~10 mg) from dilute groundwater.
  - Collect additional groundwater for dating and geochemical data



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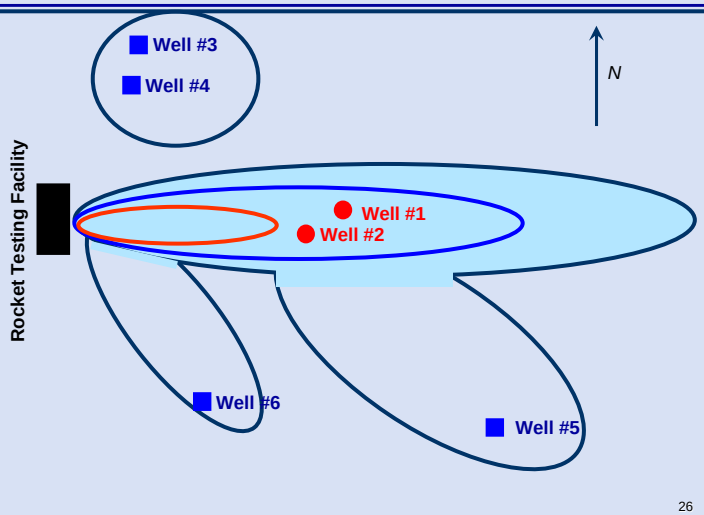
Isotope Ratio Analysis to Differentiate Perchlorate Sources

Results: Southern California Site



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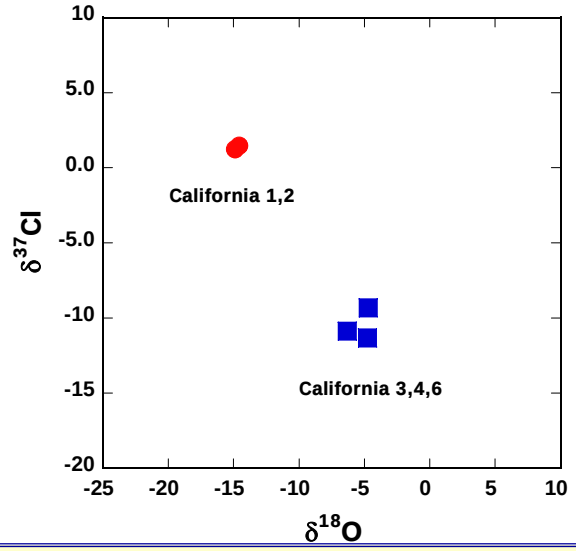
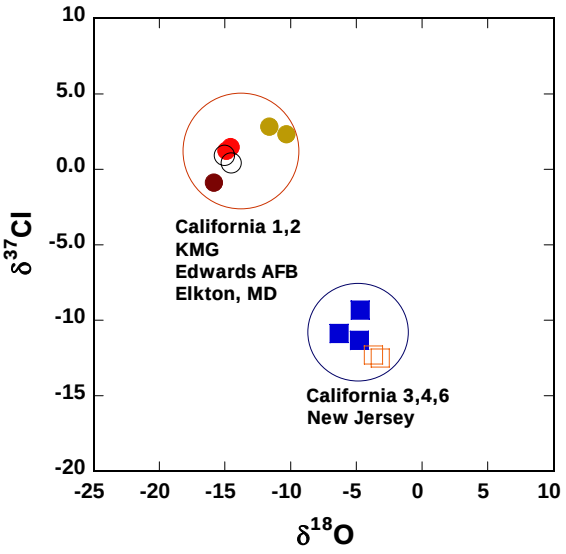
Isotope Ratio Analysis to Differentiate Perchlorate Sources

Results: Groundwater $\delta^{37}Cl$ and $\delta^{18}O$



Isotope Ratio Analysis to Differentiate Perchlorate Sources

Results: Groundwater $\delta^{37}Cl$ and $\delta^{18}O$



Statistics

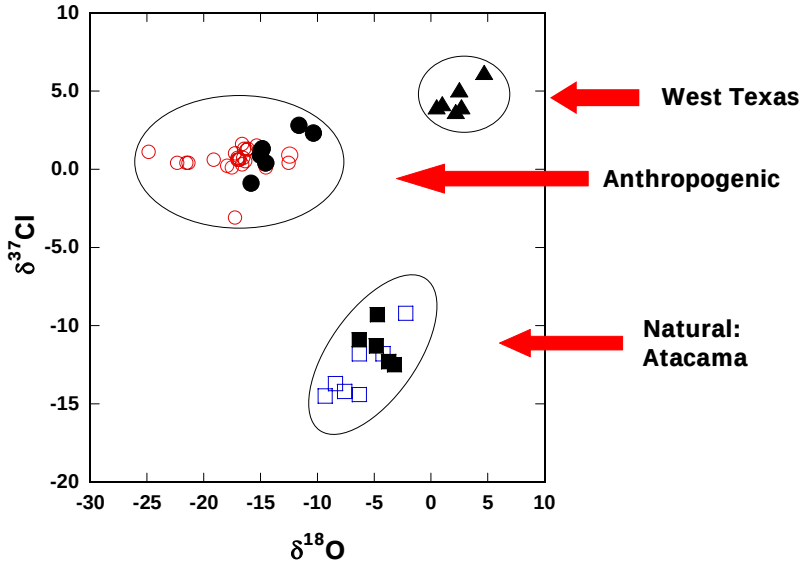
$\delta^{37}Cl$: 1.1 ± 1.2

$\delta^{18}O$: -13.8 ± 2.0

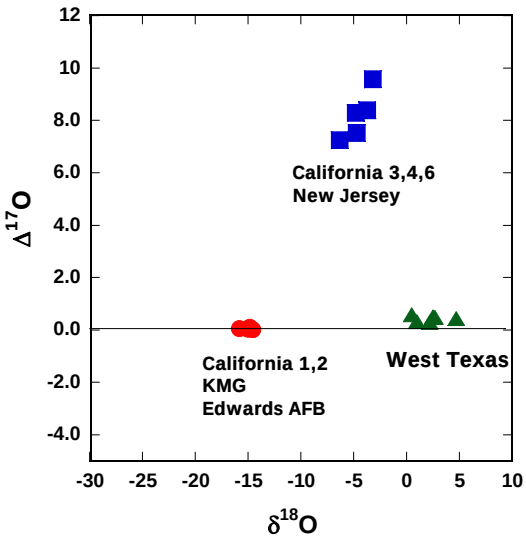
$\delta^{37}Cl$: -11.3 ± 1.3

$\delta^{18}O$: - 4.5 ± 1.2

Results:
Groundwater: Comparison to Solids
$\delta^{37}Cl$ and $\delta^{18}O$



Results:
Groundwater
$\Delta^{17}O$ and $\delta^{18}O$



Statistics

▲ $\Delta^{17}O$: 0.4 ± 0.1
$\delta^{18}O$: 2.2 ± 1.3

● $\Delta^{17}O$: 0.03 ± 0.03
$\delta^{18}O$: -15.0 ± 0.5

■ $\Delta^{17}O$: 8.2 ± 0.9
$\delta^{18}O$: - 4.5 ± 1.2

Isotope Ratio Analysis to Differentiate Perchlorate Sources

Summary

- **Management of Perchlorate Requires Understanding the Source**
  - Multiple Non-Military Sources
  - Significant Natural Sources
- **Tools are Available to Identify Sources**
  - Stable isotope can distinguish natural from anthropogenic

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http://www.serdp.org

ESTCP Environmental Security Technology Certification Program

http://www.estcp.org

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