



March 28 – April 1, 2011 • Arlington, VA



Using Stable Isotope Ratio Analysis to Distinguish Perchlorate Sources



Paul B. Hatzinger, Ph.D.
Shaw Environmental, Inc.
03/30/2011

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 30 MAR 2011		2. REPORT TYPE		3. DATES COVERED 00-00-2011 to 00-00-2011	
4. TITLE AND SUBTITLE Using Stable Isotope Ratio Analysis to Distinguish Perchlorate Sources				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Shaw Environmental, Inc,4171 Essen Lane,Baton Rouge,LA,70809				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES Presented at the 2011 DoD Environmental Monitoring & Data Quality Workshop (EMDQ 2011), 28 Mar ? 1 Apr, Arlington, VA.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 27	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			



Perchlorate Contamination in the United States: Historical

March 28 – April 1, 2011 • Arlington, VA

Military and Aerospace Issue



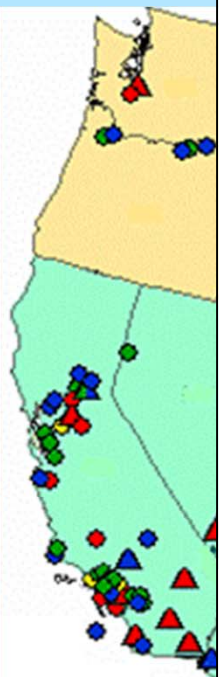
Limited Sources

- Rocket Testing
- Hog-Out
- Manufacturing
- Training Areas
- OB/OD Areas
- Few Commercial Sites





Perchlorate Detections In Food (US FDA)

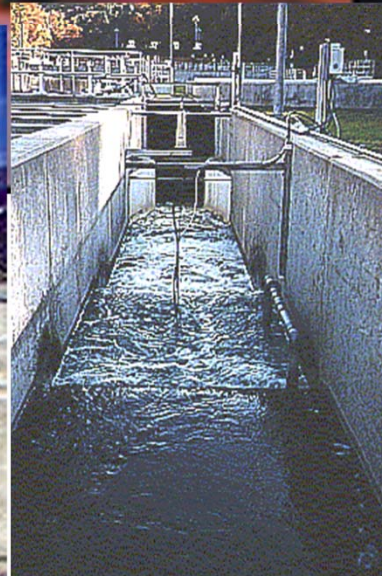


Map sou

Food Group	Number of Samples	Average Residue (ppb)
Lettuce	137	10.3
Milk	125	5.81
Tomatoes	73	13.7
Spinach	36	115
Greens	14	92.4
Cabbage	13	8.80
Cantaloupes	48	28.6
Carrots	59	15.8
Green Beans	19	6.12
Broccoli	14	8.49
Grapes	12	8.58



Other (Non-Military) Sources??



A. Natural Perchlorate

1. Chilean Caliche – Atacama Desert
- natural nitrogen fertilizer
2. Mineral deposits – Death Valley, CA
3. Southwest soils and groundwater

B. Other Anthropogenic

1. Fireworks
2. Road Flares
3. Perchloric Acid and Reagents
4. Chlorate (herbicide)
5. Chlorine Bleach



March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

Chilean Nitrate

■ Uses

- Critical N fertilizer during 19th & early 20th C (cotton, tobacco and citrus)
- Explosives manufacture

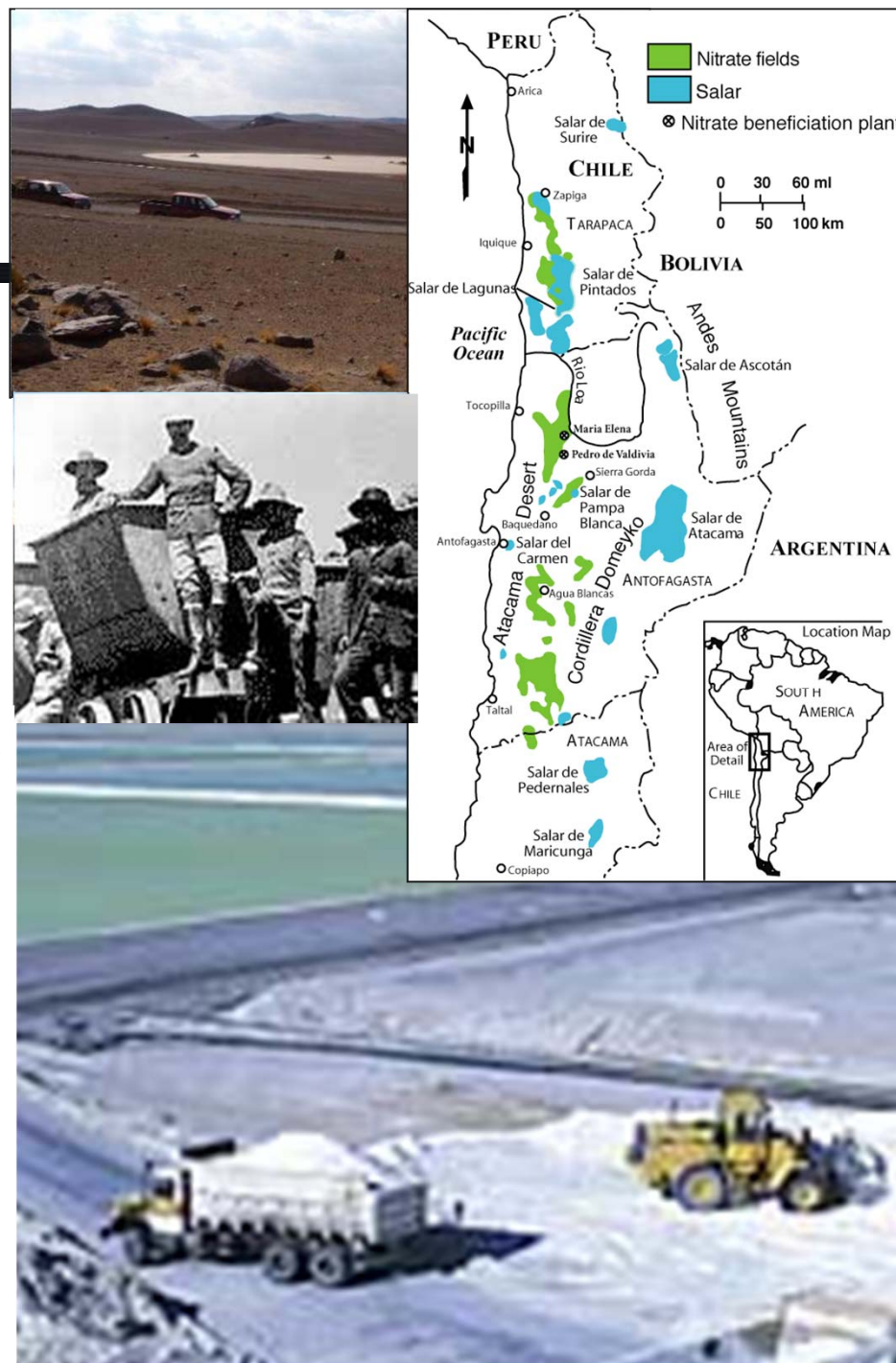
■ Perchlorate Source

- 1910-1960
 - US imported 10⁹kg fertilizer /year
 - 0.2% ClO₄⁻ (highly variable)
 - 10⁶kg ClO₄⁻ /year

■ Historical Impact

- Citrus or cotton ~50 mg/m²-year
- Possible large local Impacts

* Dasgupta, PK, et al. 2006. *Perchlorate in the United States. Analysis of Relative source contributions to the Food Chain. Environ. Sci. Technol.* 40:6608-6614



Natural Perchlorate in the USA



■ Indigenous Perchlorate

- * *Natural nitrate deposits*
- * *Perchlorate in soils*
- * *Perchlorate in groundwater & rainwater*
 - *Atmospheric formation with O_3*
 - *Other mechanisms – UV, TiO_2*

Death Valley Nitrate Deposits

site	nonsoluble fraction	concentration			
		ClO_4^-	Cl^-	$NO_3^- - N$	SO_4^{2-}
Death Valley	%	mg kg ⁻¹		g kg ⁻¹	
Confidence Hills 1	NA	0.25	320	1.8	72
Confidence Hills 2	49	0.85	180	5.5	100
Saratoga Hills	78	0.95	63	5.9	23
Bully Hill	62	0.82	80	28	6.5
Zabriskie	64	1.7	140	4.4	39
Atacama					
P1	42	243	80	12	57
P2	50	328	456	44	84
P3	13	113	50	15	51
P4	51	132	61	22	51

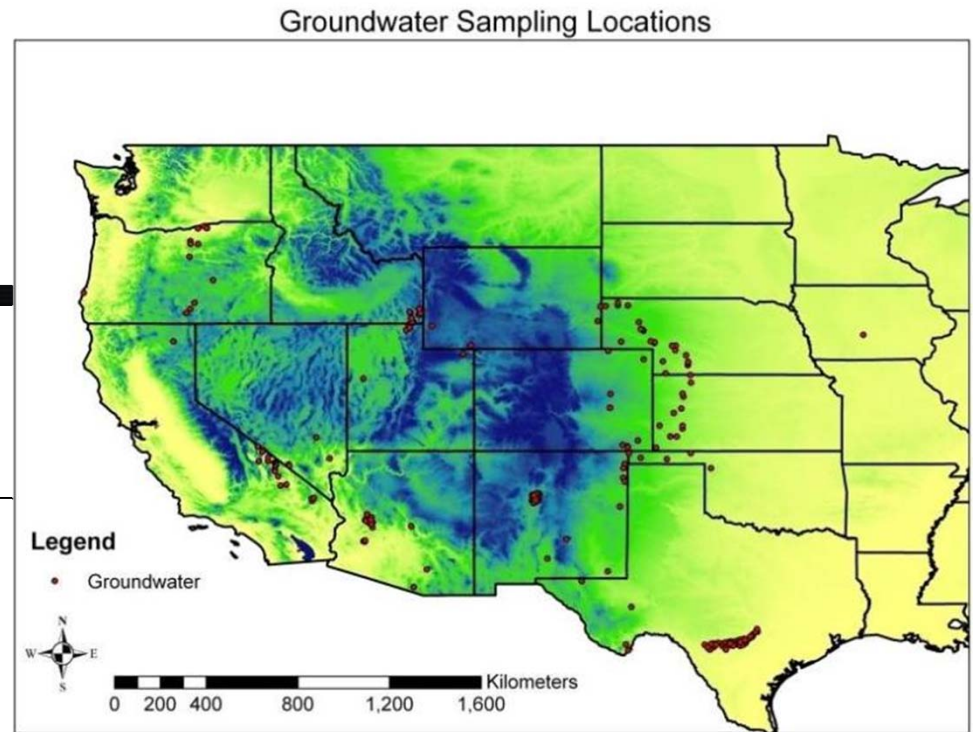
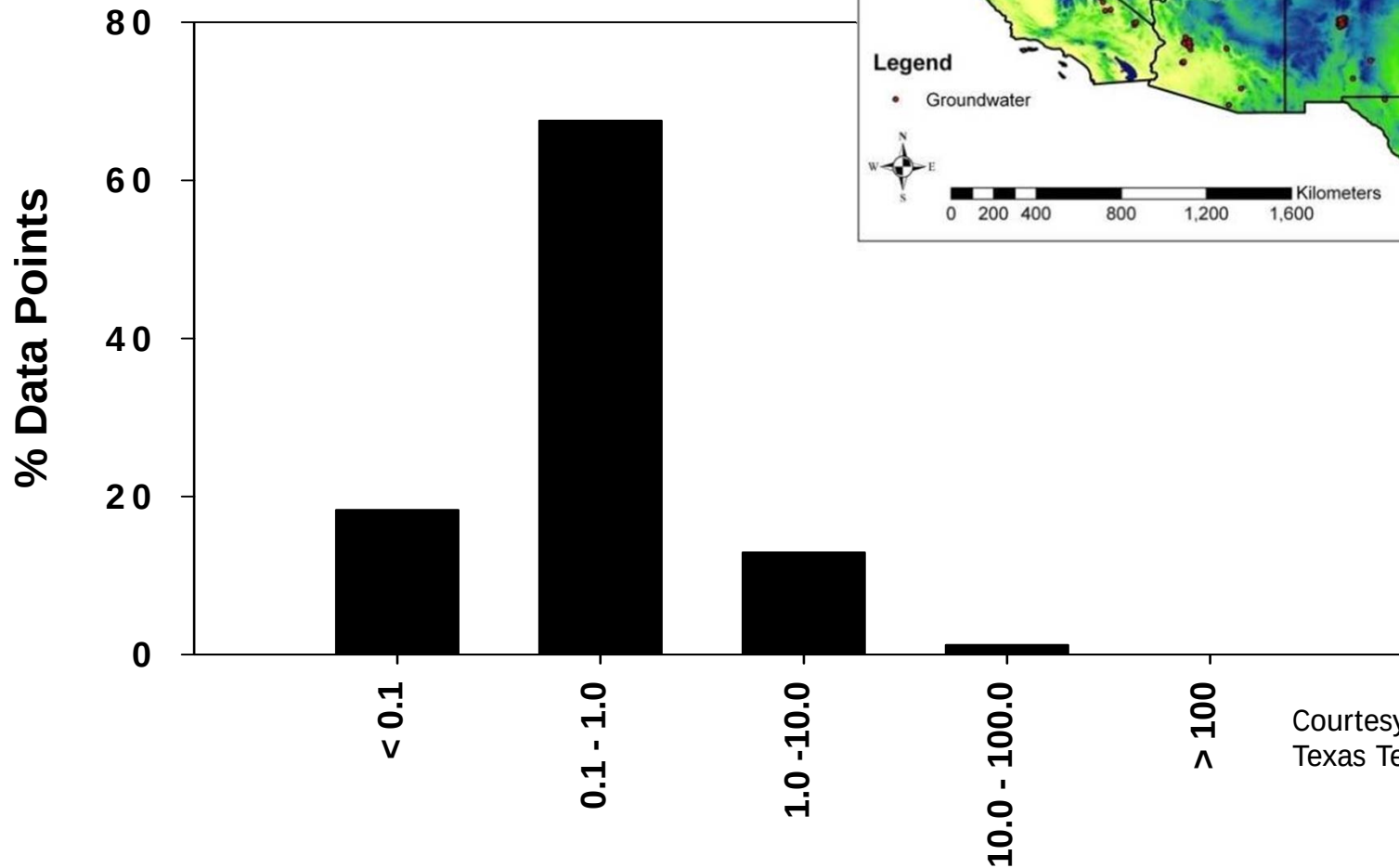




March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

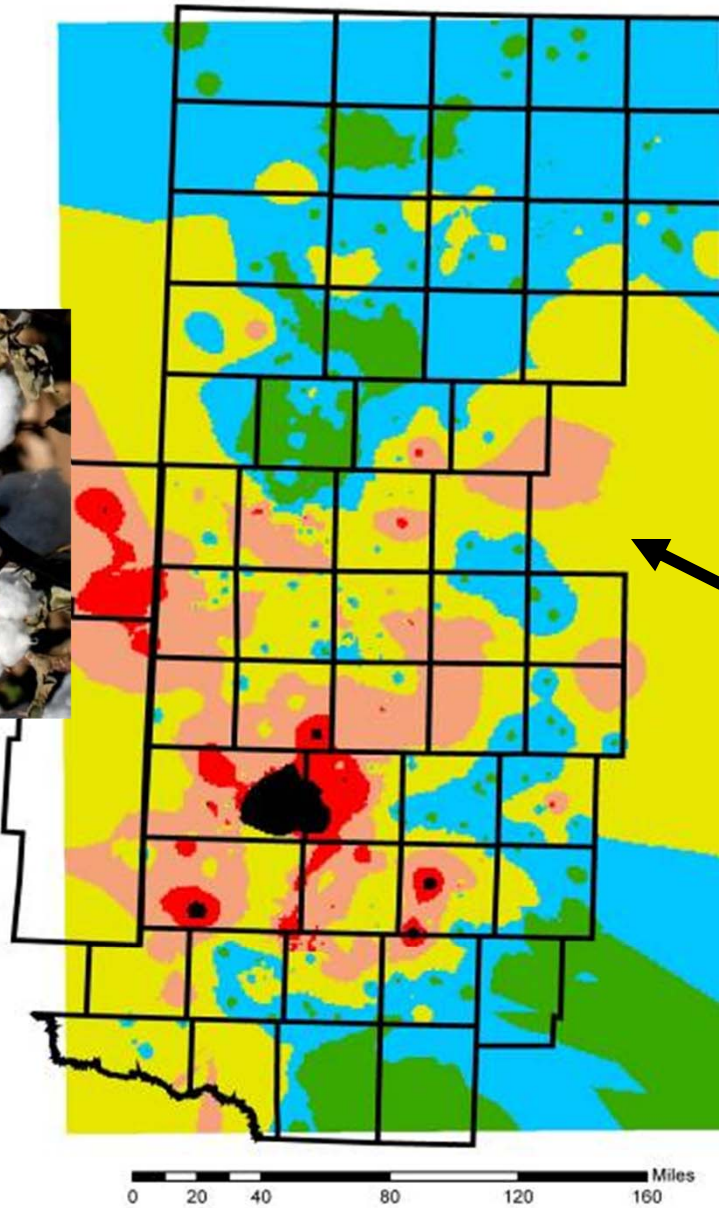
Concentrations in in Western US Groundwater



Courtesy of Dr. W. Andrew Jackson,
Texas Tech

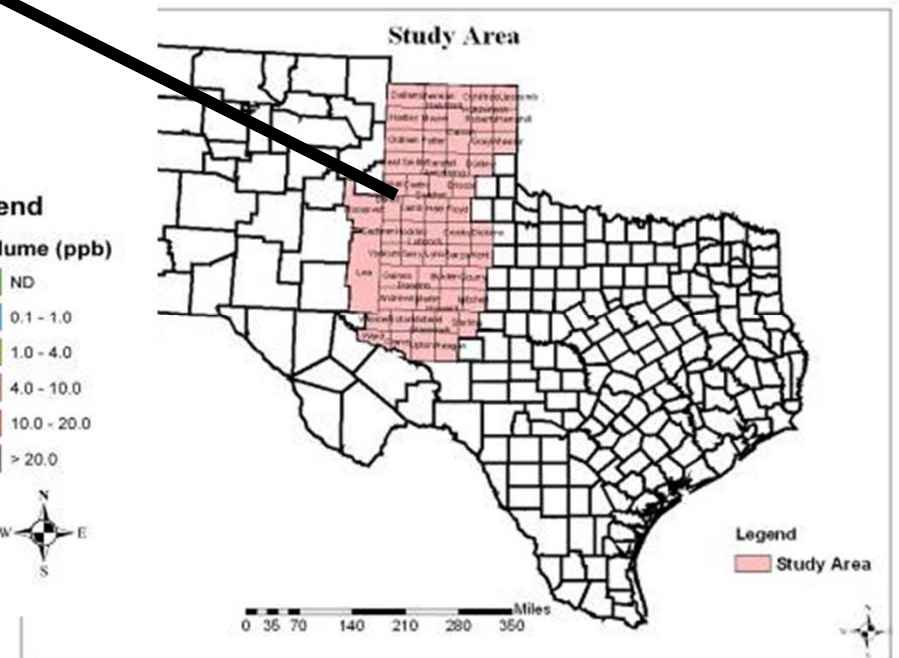


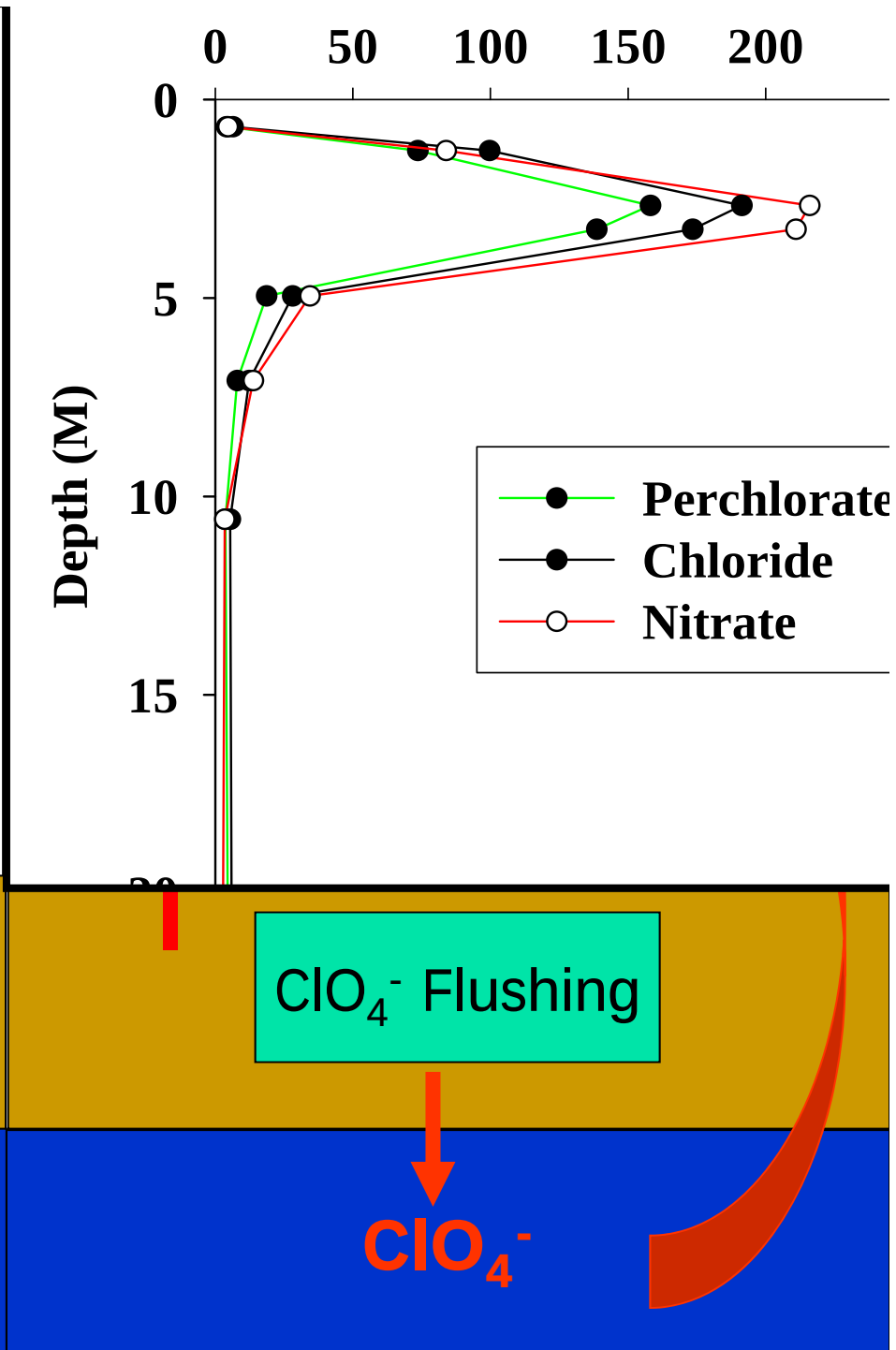
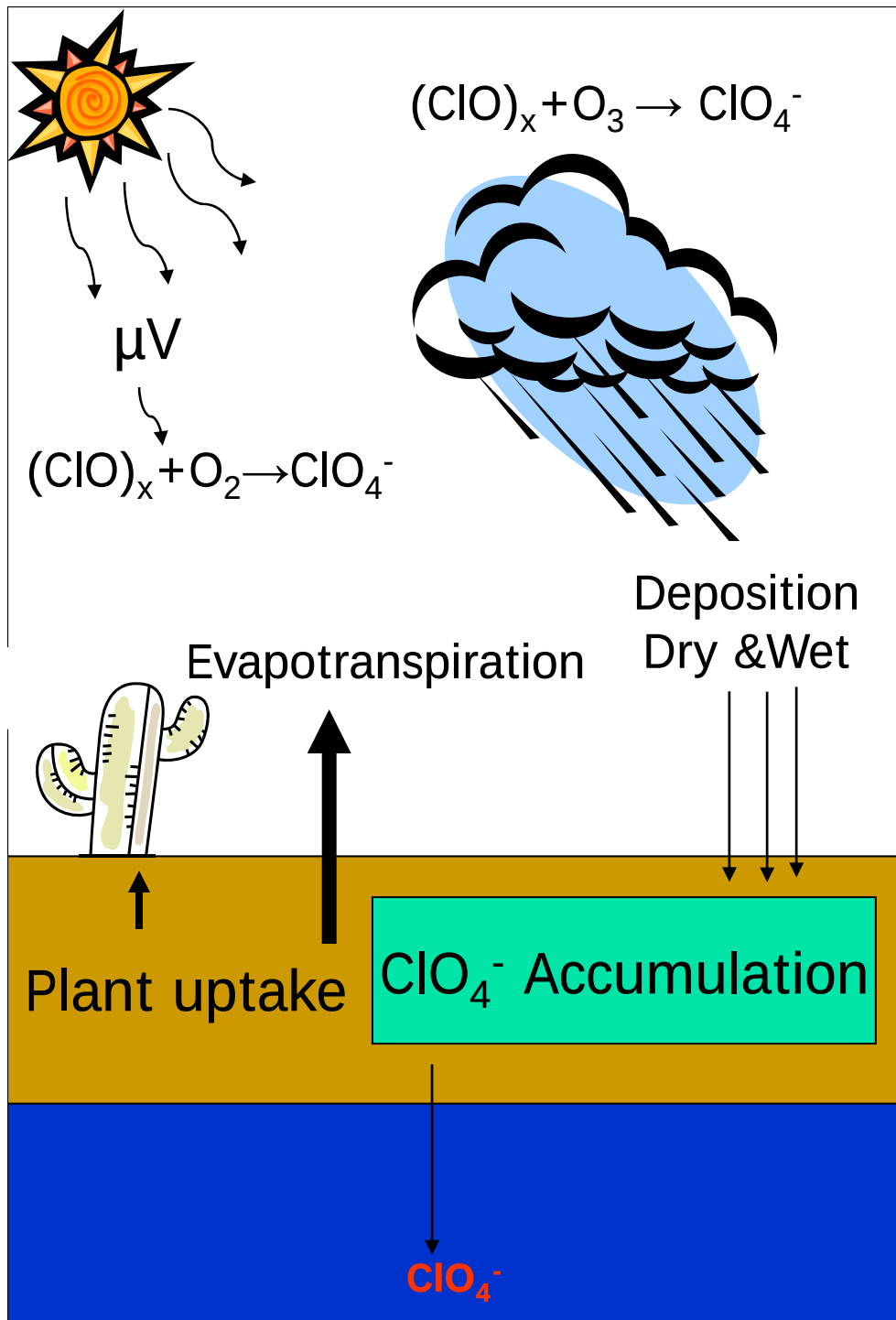
Perchlorate Plume



West Texas – Southern High Plains

- Study area >59,000 mi²
- 89% > 0.1 ppb
- Estimated Mass of ClO_4^-
 - Saturated >2 X 10⁶ Kg







Can You Distinguish Natural from Synthetic Perchlorate?



March 28 – April 1, 2011 • Arlington, VA

Stable Isotope Ratio Analysis of Chlorine and Oxygen in Perchlorate

• Other Lines of Evidence

- ^{36}Cl Analysis
- Groundwater Dating
- Co-Contaminants
- Other Geochemical Data

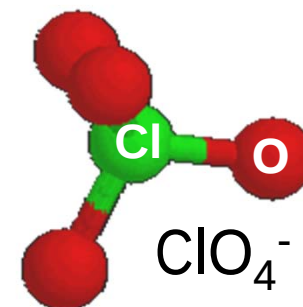




Stable Isotope Ratio Analysis: Perchlorate

March 28 – April 1, 2011 • Arlington, VA

- Methods developed for analysis of both chlorine and oxygen isotopes in perchlorate. Dual isotope comparisons possible.
- Analyzed by IRMS with a precision of about ± 0.1 to 0.4‰
- Sample preparation is critical. Methods have been developed to collect, recover, and purify perchlorate.



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 can provide a unique “fingerprint”



Hydrogen	^1H , ^2H
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



Stable Isotope Analysis: Perchlorate



March 28 – April 1, 2011 • Arlington, VA

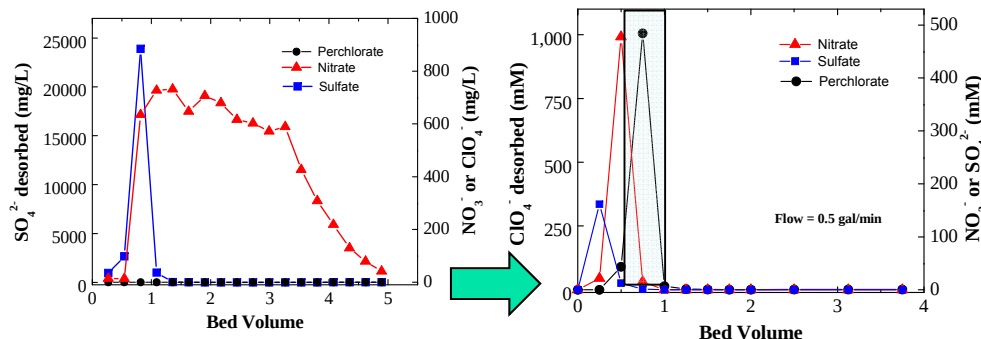
Sample Collection (5-10 mg)



ClO_4^- on IX resin (NO_3^- , SO_4^{2-} , ReO_4^-)

Preserved with HCl and 4°C

Sample Extraction & Purification



Leach with 4M HCl to remove NO_3^- & SO_4^{2-} , CO_3^- & some humics

Leach with 1M FeCl_3 + 4MHCl (FeCl_4) -collect fractions

IRMS – $\delta^{37}\text{Cl}$



Weigh crystal
Combust to Cl salt
Convert to CH_3Cl
Purify via GC
IRMS
Determine Cl isotope ratio

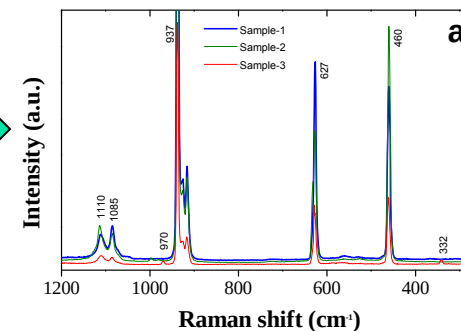
IRMS – $\delta^{18}\text{O}/\delta^{17}\text{O}$



Weigh crystal
 $\delta^{18}\text{O}$: Combust to CO
($\delta^{18}\text{O}$ & $\Delta^{17}\text{O}$): decompose to O_2
IRMS (CO & O_2)
Measure yields
Determine O isotope ratios

Cl^-

Verification of Purity



- * Neutralize -Remove FeO_3
- * Concentrate ClO_4 supernatant
- * Filter unwanted precipitates
- * Crystallize ClO_4 as CsClO_4 or KClO_4
- * Wash crystals with MeOH

Crystal morphology
Ion chromatography (lg sample)
Micro-Raman spectroscopy

Impurity detected



March 28 – April 1, 2011 • Arlington, VA

Terminology:

Stable Isotope Ratio Analysis

Terminology:

*Isotopic compositions of light elements are generally reported as “delta” (δ) values in parts-per-thousand (denoted “‰” = per mil) deviations (enrichments or depletions) relative to a known standard

Equation 1. δ (in ‰) = $(R_x/R_s - 1) * 1000$

R = ratio heavy/light isotope (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$)

R_x = sample (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$ in environmental sample)

R_s = standard (e.g., $^{37}\text{Cl}/^{35}\text{Cl}$ in chlorine standard “SMOC”)

*** Example: $\delta^{37}\text{Cl} = + 30$ ‰**

30 parts-per-thousand (3 %) more ^{37}Cl in sample relative to a known standard (Standard Mean Ocean Chloride; SMOC).

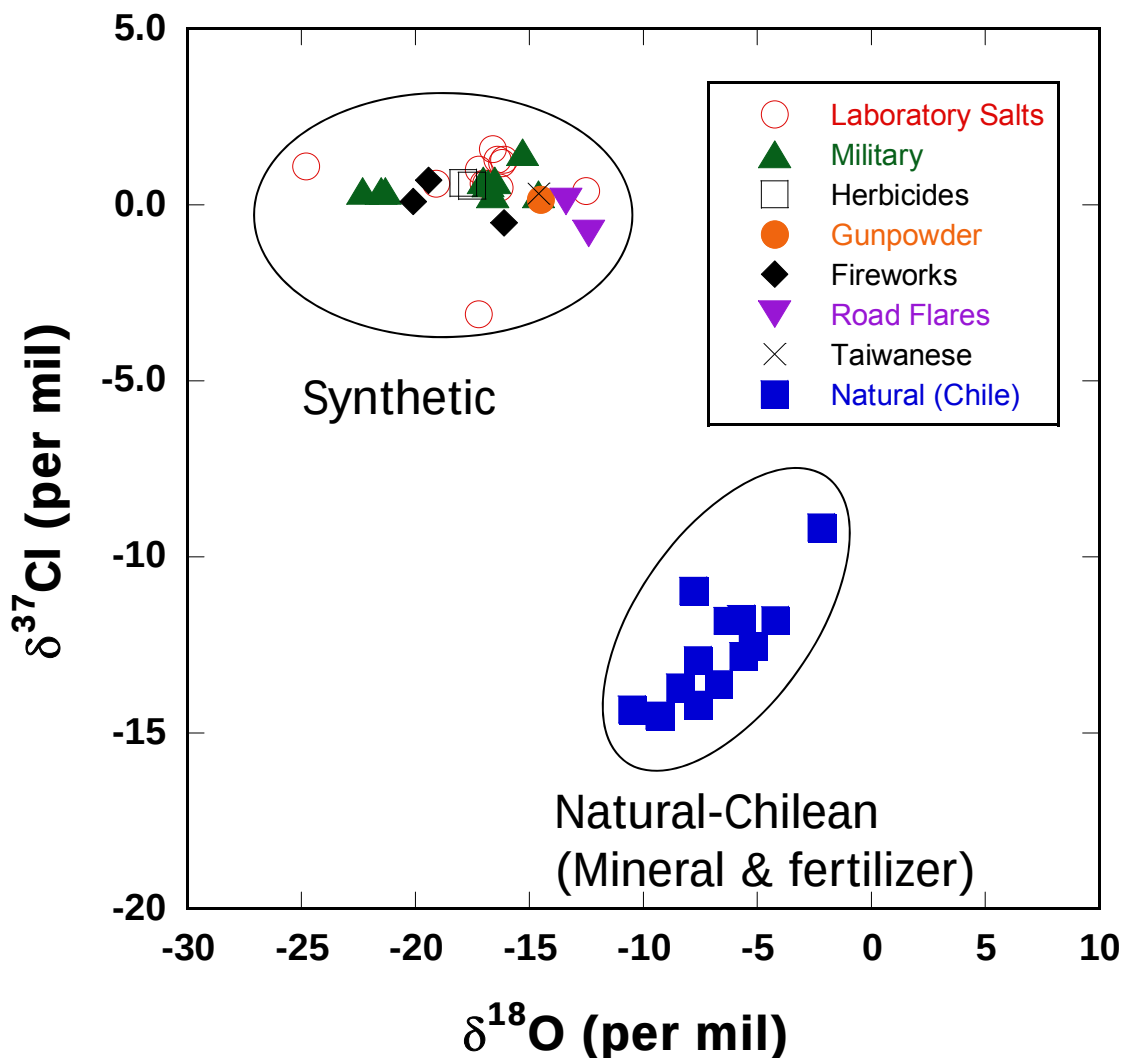
(^{18}O = SMOW)



March 28 - April 1, 2011
Arlington, VA

March 28 - April 1, 2011 - Arlington, VA

Forensic Isotopic Analysis: Chilean vs. Synthetic $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$



Chlorine markedly
“heavier” in synthetic
perchlorate (n = 43).

$$\delta^{37}\text{Cl}: 0.5 \pm 1.0$$

$$\delta^{18}\text{O}: -17.5 \pm 2.7$$

Oxygen consistently
“heavier” in natural
(Chilean) perchlorate
(n = 13).

$$\delta^{37}\text{Cl}: -12.6 \pm 1.5$$

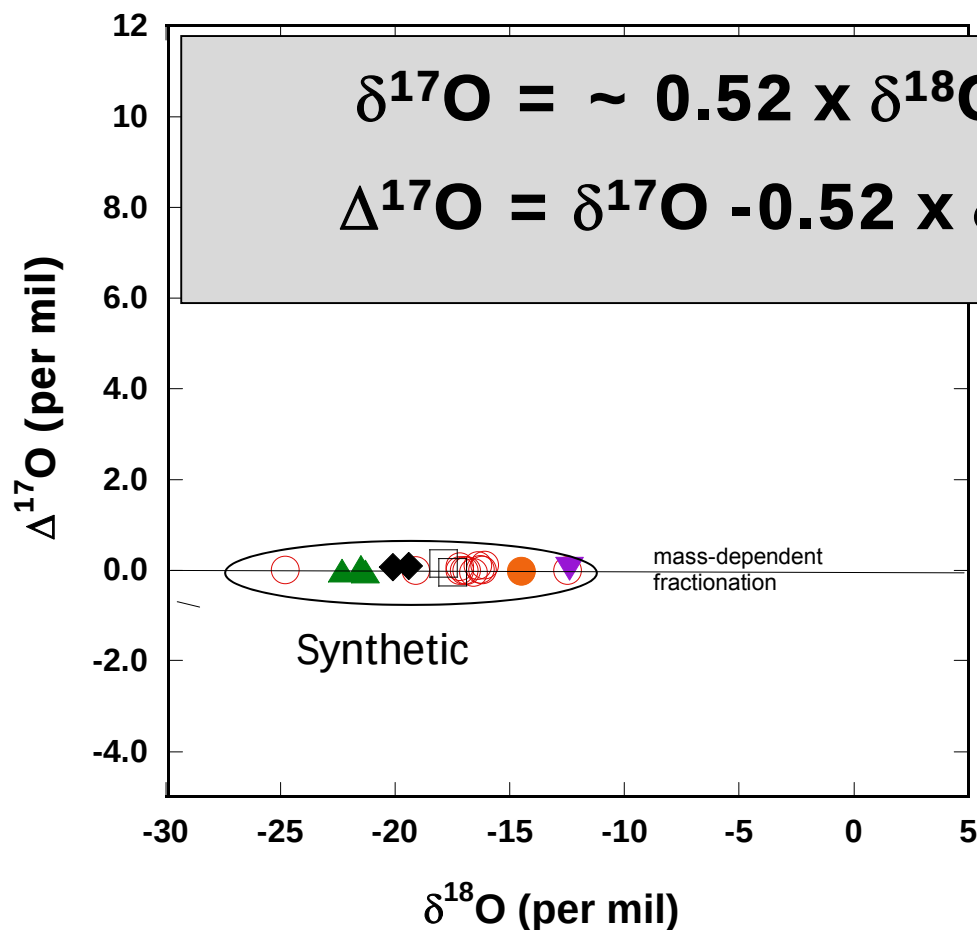
$$\delta^{18}\text{O}: -6.7 \pm 2.2$$



March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

Forensic Isotopic Analysis: Chilean vs. Synthetic $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$



Synthetic perchlorate
“mass dependent”
fractionation (n = 43)

$\Delta^{17}\text{O}$: **0.01 ± 0.06**
Range: - 0.24 to 0.11

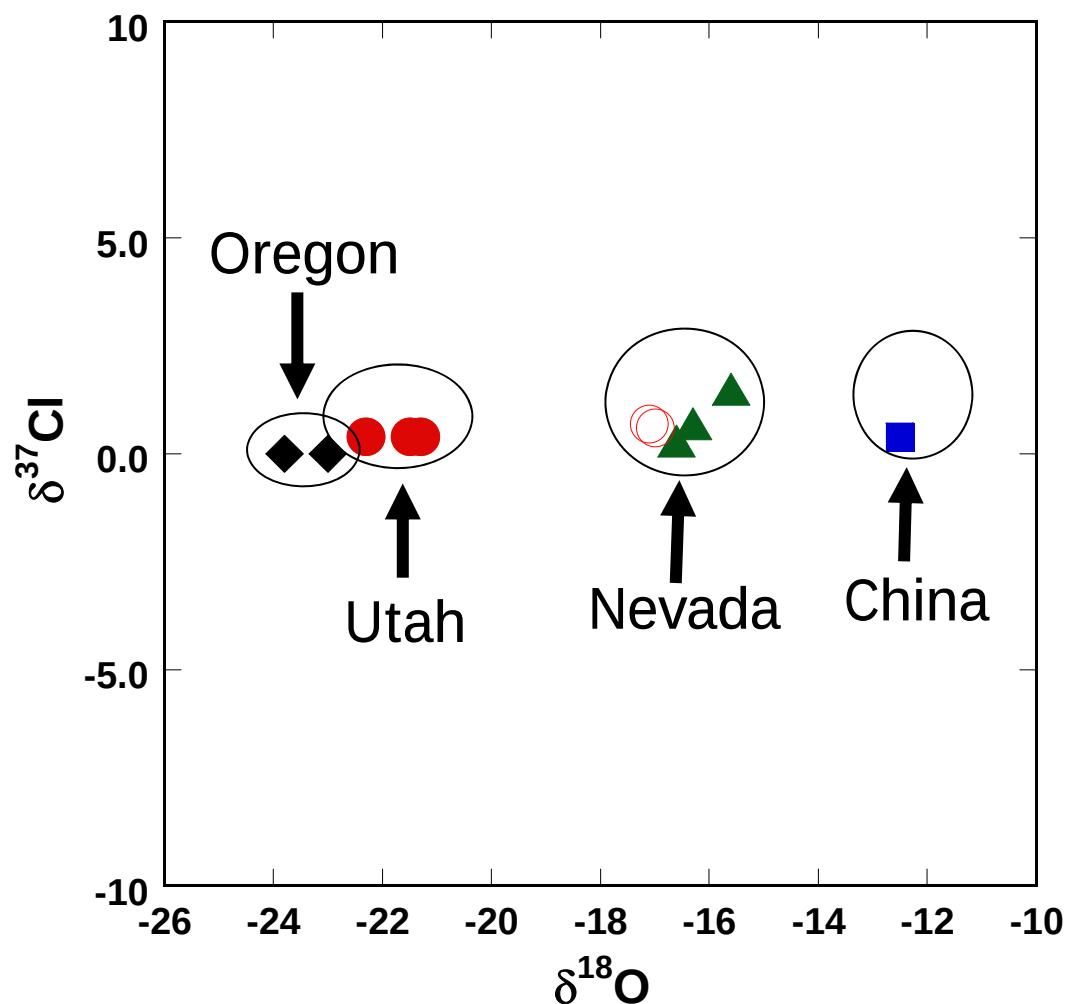
Bohlke, J.K., N.C. Sturchio, B. Gu, G.M. Brown, J. Horita, W. A. Jackson, J. Batista, and P. B. Hatzinger. 2005. Perchlorate isotope forensics. Analytical Chemistry, 77; 7838-7842.



March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

Can You Differentiate Synthetic Sources?

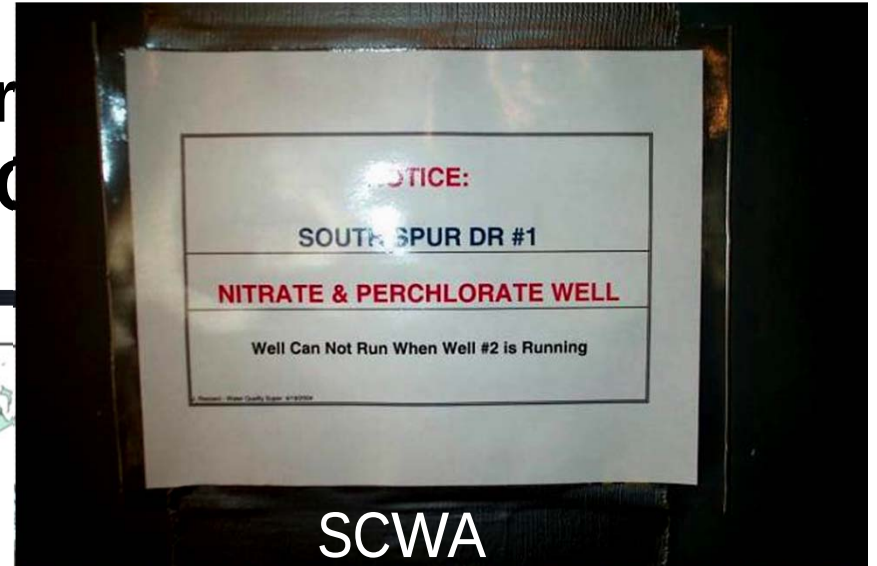


1. There are some isotopic differences between manufacturers – but only in ^{18}O .
2. H_2O is the source of oxygen in synthetic perchlorate and ^{18}O in H_2O varies globally.
3. **Small dataset**
 - batch to batch variation?
 - variation with time?
 - different “sources” in products (e.g., flares)?

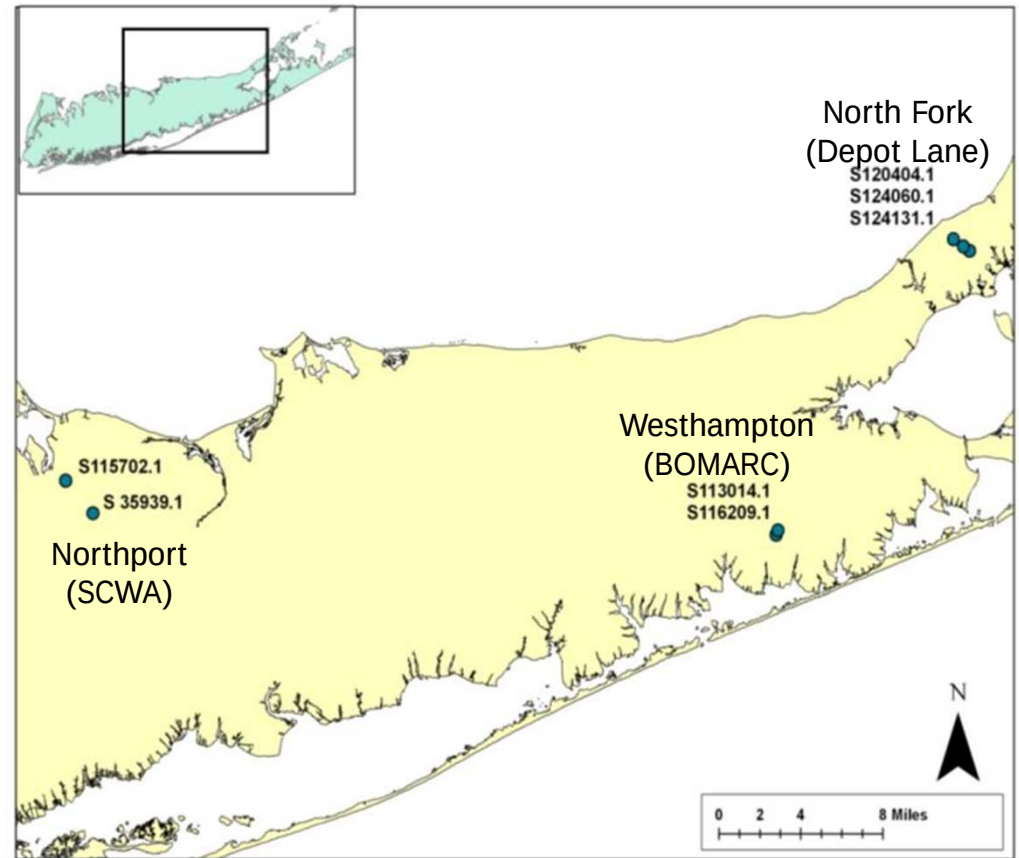
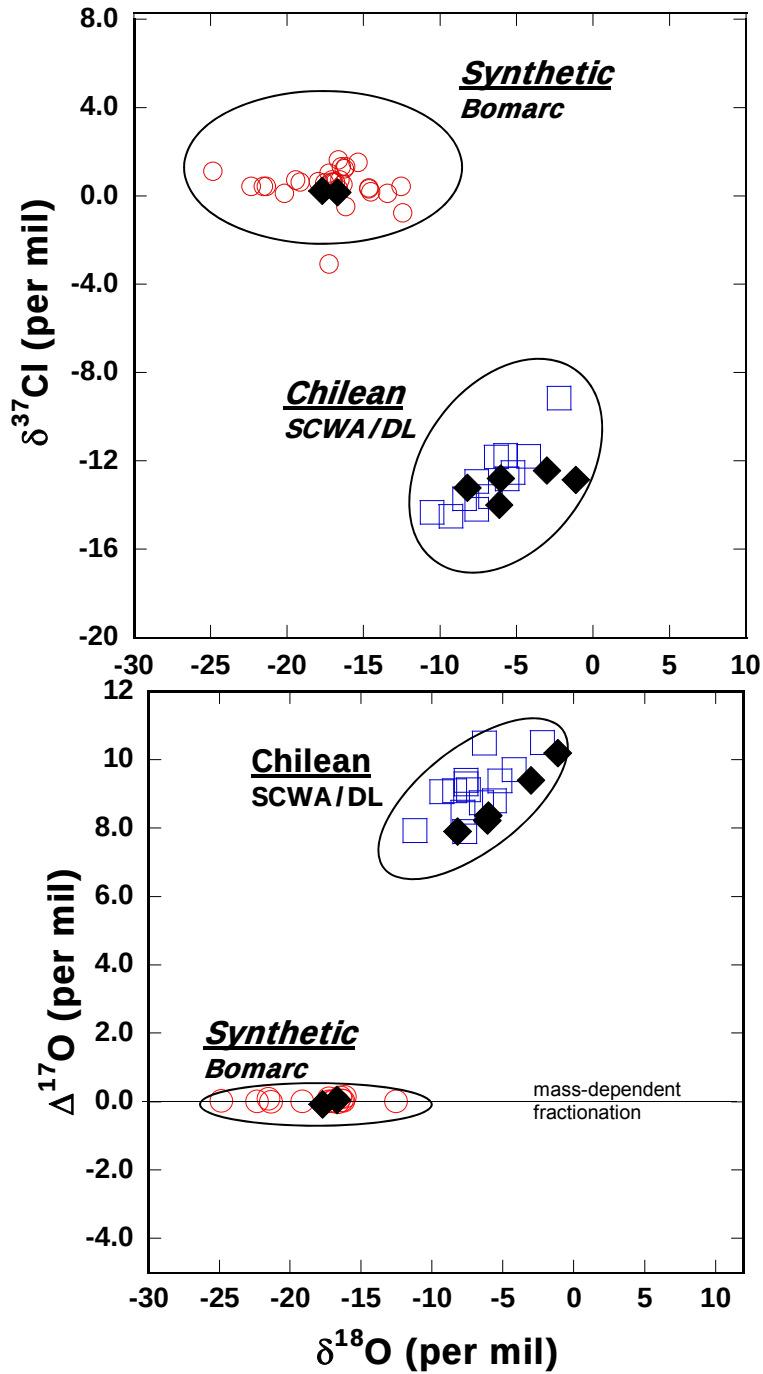
Depot Lane



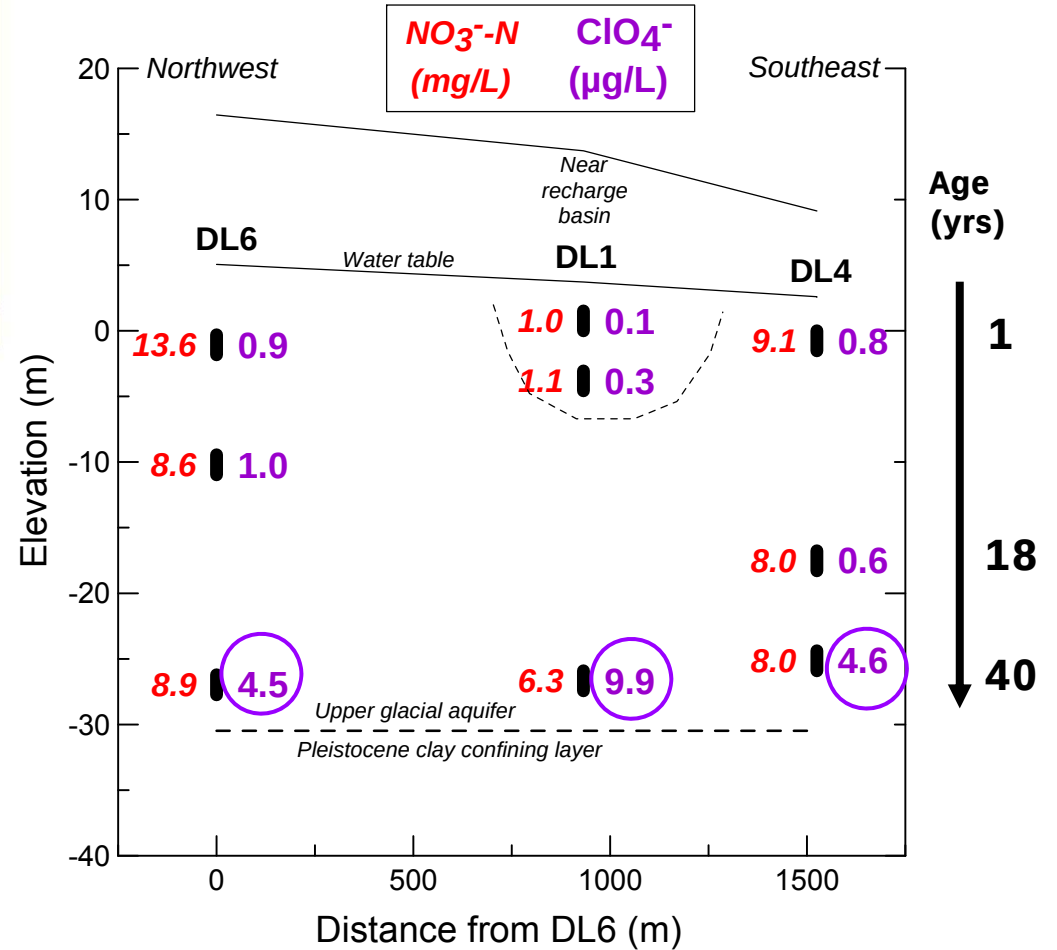
BOMARC



Case Study: Long Island, NY



Long Island, NY Depot Lane Transect





March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

Isotope Results: Groundwater Data from Various Sites Compared to Chilean and Synthetic Sources

Anthropogenic

Long Island, NY

Amherst, MA

Edwards AFB, CA

Henderson, NV

Southern California (2)

Elkton, MD

Dahlgren, VA

Israel

Chilean Fertilizer

Long Island

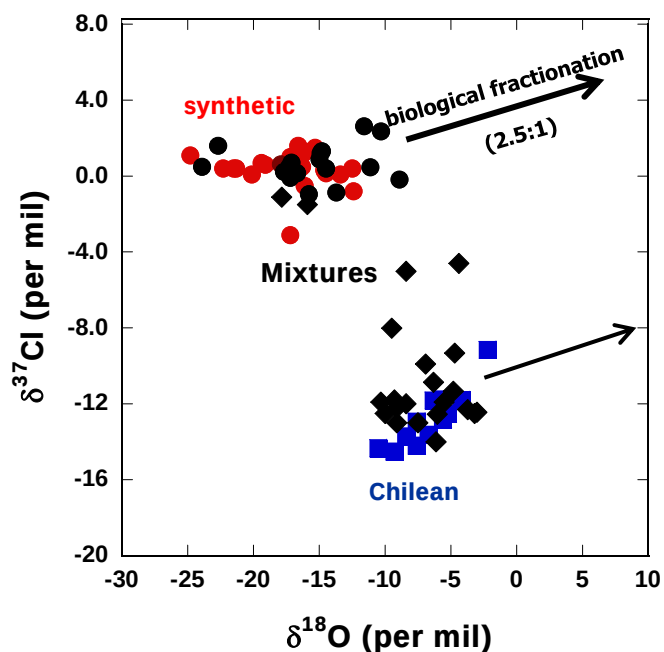
Southern California (3)

New Jersey

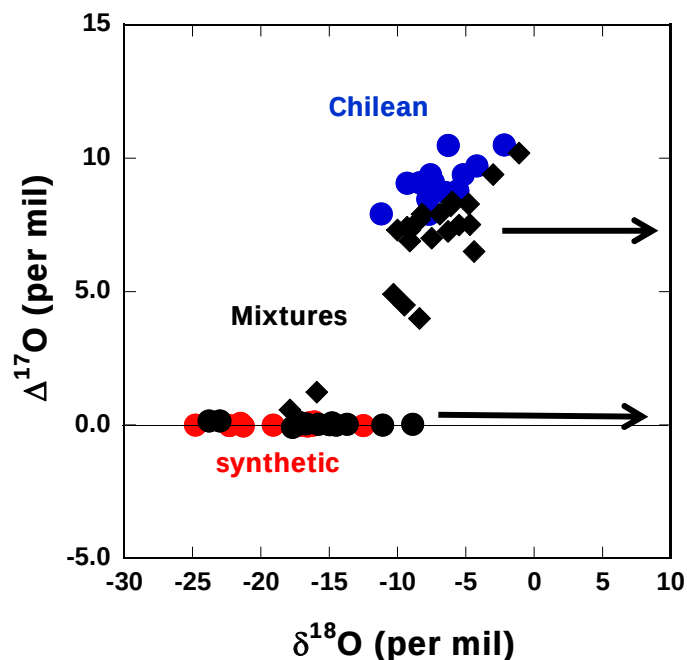
Mixtures:

Southern California (2)

Comparison of $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ of perchlorate in groundwater from to synthetic solids and natural Chilean sources



Comparison of $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$ of perchlorate in groundwater to various synthetic solids and natural Chilean sources





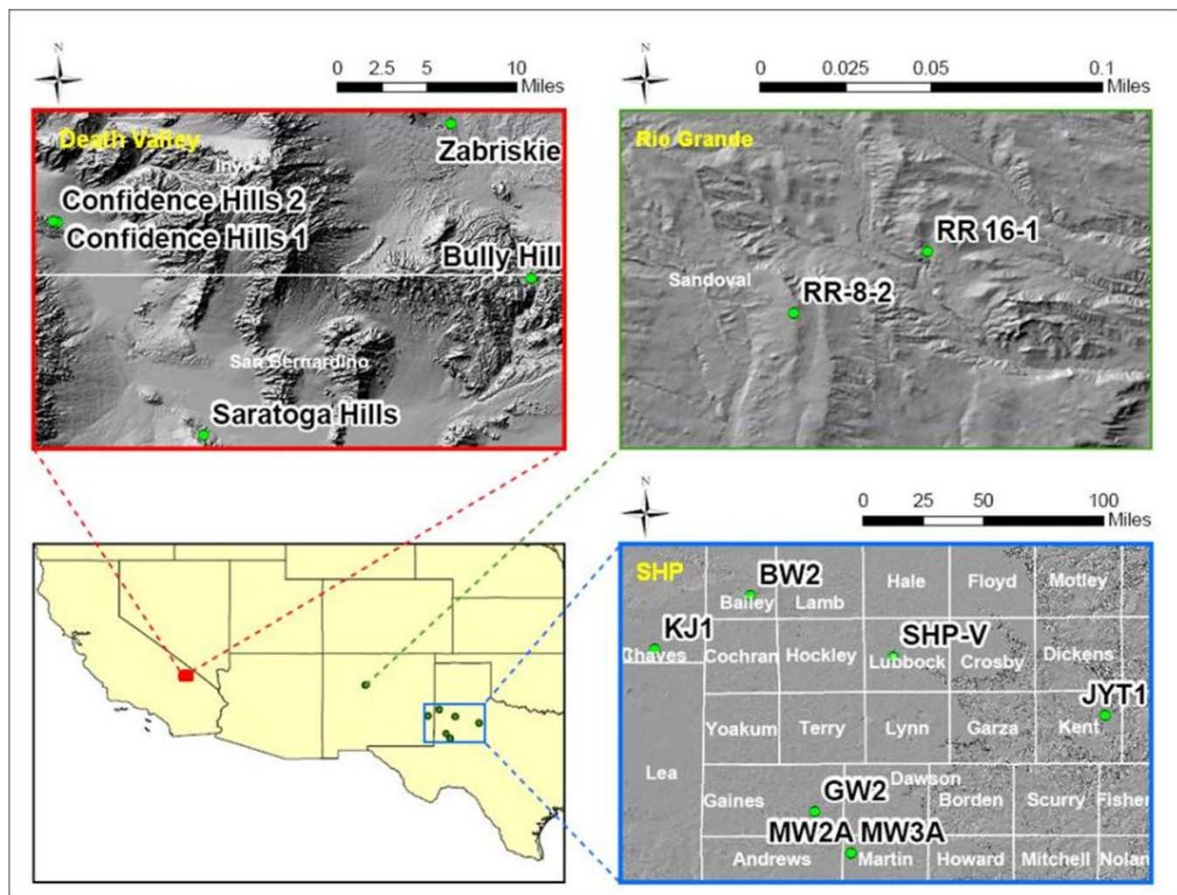
March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

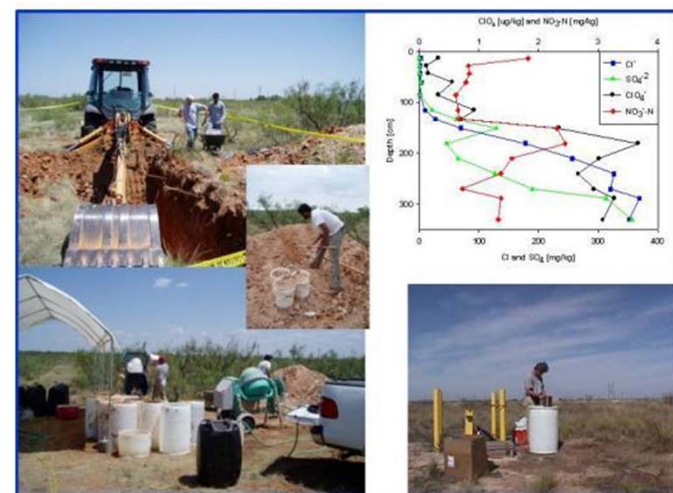
Indigenous Natural Perchlorate



Death Valley Caliche



Rio Grande Basin Groundwater (Ancient)



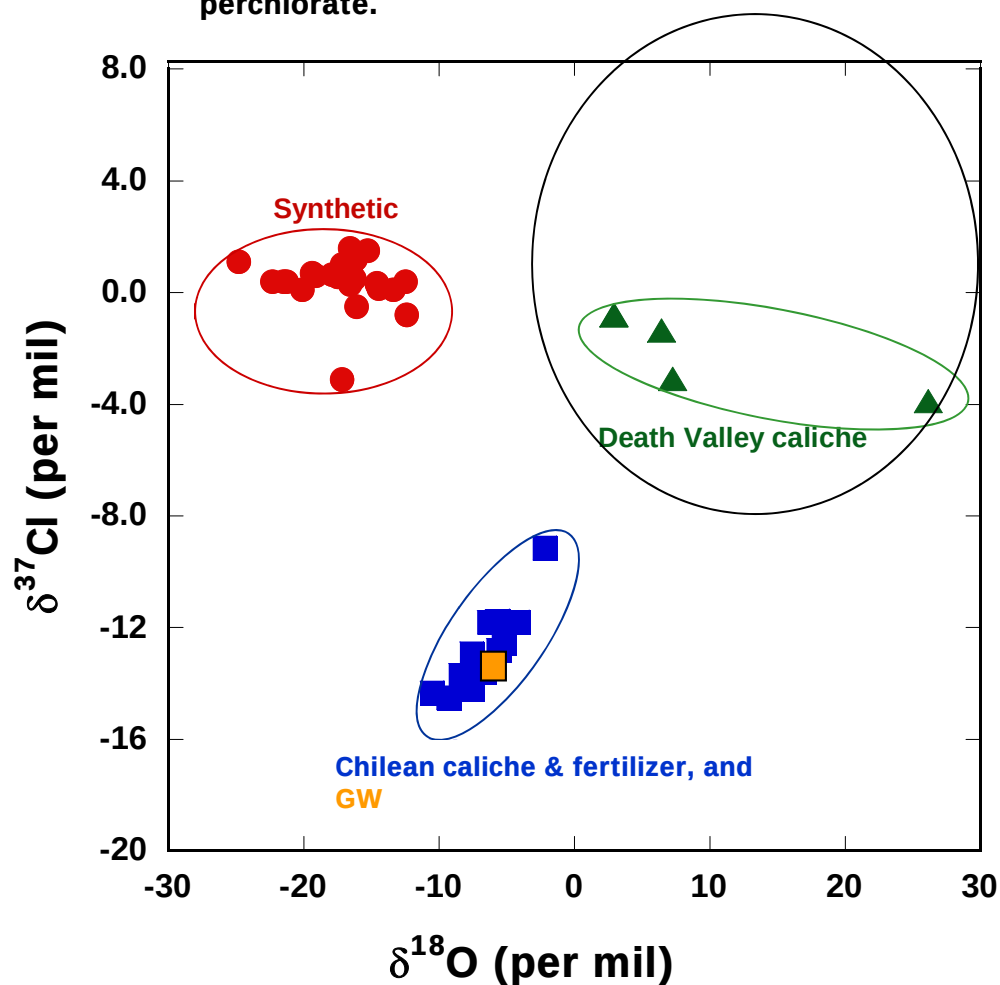
SHP Groundwater and Vadose Soil



Indigenous Perchlorate: $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$

March 28 – April 1, 2011 • Arlington, VA

Comparison of $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ in perchlorate from indigenous US sources with Chilean and synthetic perchlorate.



1. There are multiple signatures for natural perchlorate but all are readily distinguished from synthetic sources via ^{37}Cl and ^{18}O .
2. West Texas vadose (soil) perchlorate has a similar isotope signature to that in West Texas & NM groundwater.

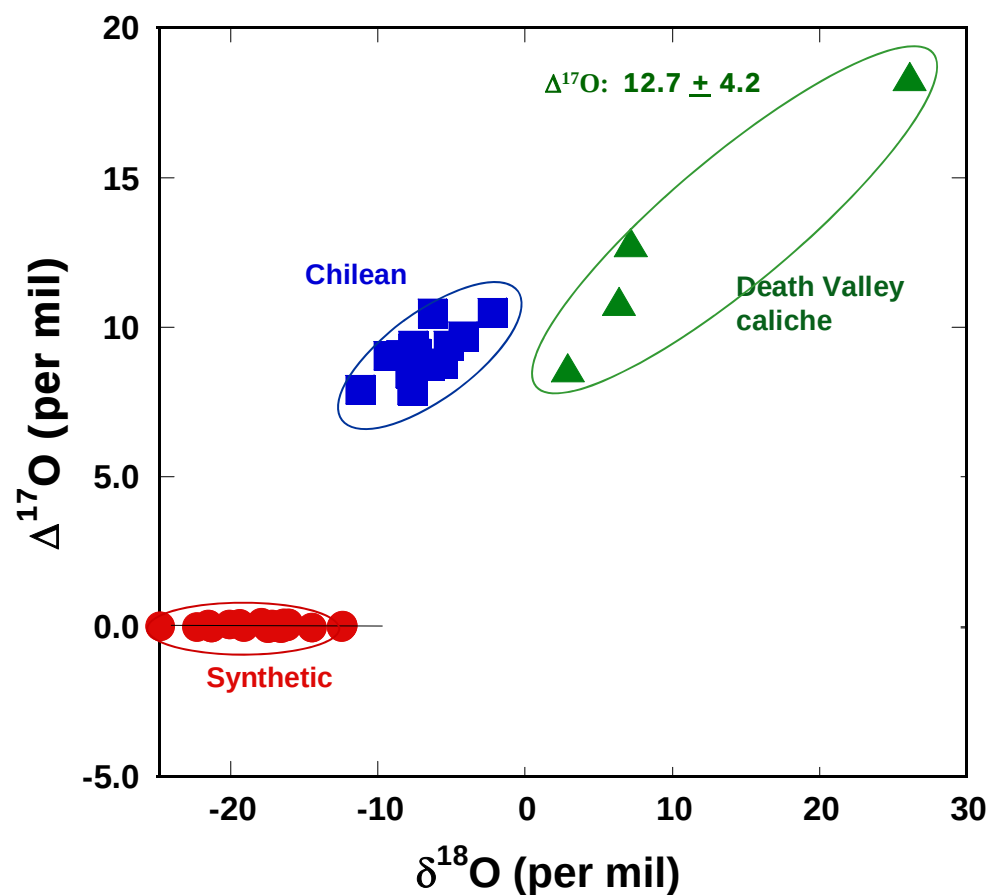




Indigenous Perchlorate: $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$

March 28 – April 1, 2011 • Arlington, VA

Comparison of $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$ in perchlorate from indigenous US sources with Chilean and synthetic perchlorate.



1. Like Chilean samples, Death Valley deposits have significant excess ^{17}O in perchlorate.

2. SHP soil and groundwater has only slight $\delta^{17}\text{O}$ excess – no difference between saturated and unsaturated zone??

3. Understanding the origin of natural perchlorate (and the resulting isotope values) is currently the subject of significant research.



March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

Perchlorate Origin - Why

Understanding of Natural Perchlorate Origin:

Why is $\Delta^{17}\text{O}$ so low in SHP Perchlorate ?

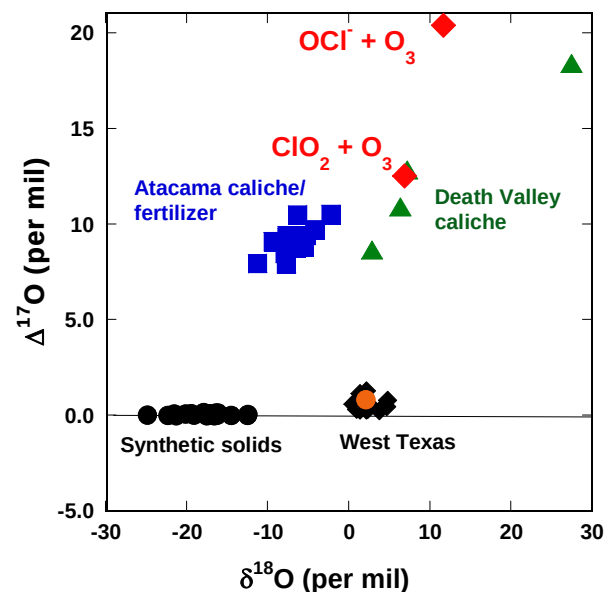
(1) Different reaction mechanism and/or location.

- Ozone vs. UV reaction?
- Atmosphere vs. surface catalyzed?
- What does ^{36}Cl tell us?

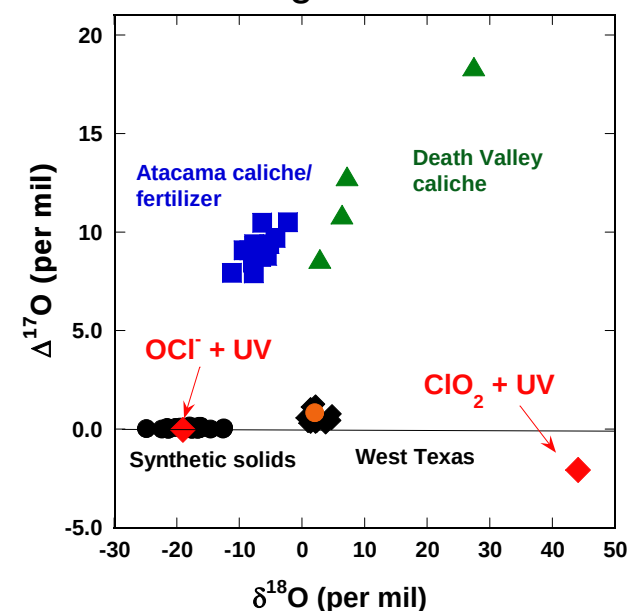
(2) Post-depositional modification.

- Does oxygen in perchlorate exchange with water?
- Role of plants or microorganisms?

Perchlorate generated with O_3



Perchlorate generated with UV





March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

^{36}Cl Analysis

^{35}Cl 34.96885 75.77% Stable	^{36}Cl $t_{1/2} = 301,000$ yrs Cosmogenic/ anthropogenic	^{37}Cl 36.96590 24.23% Stable
--	---	--

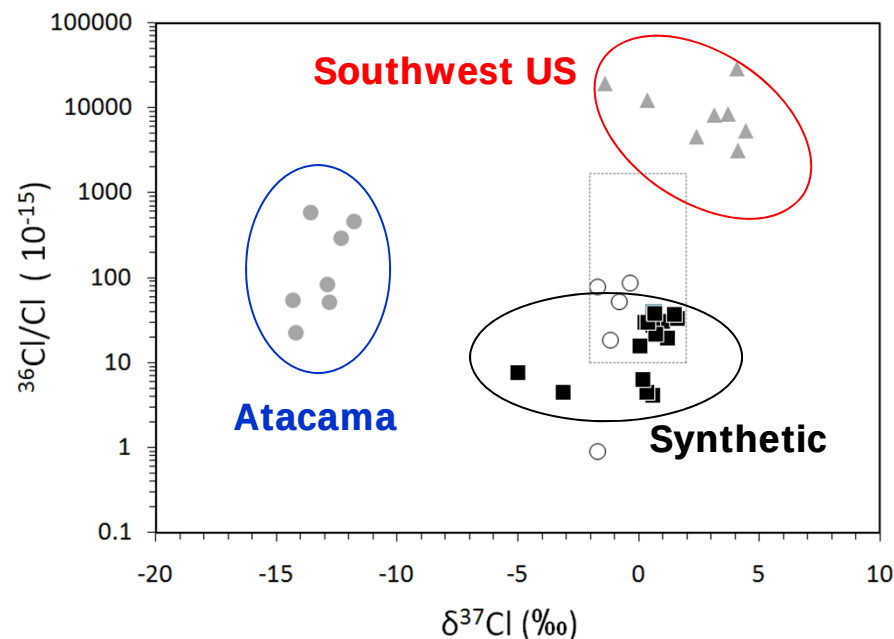
Long-lived radioisotope produced in the stratosphere from ^{40}Ar ($T^{1/2} = \sim 301,000$ yrs)

$$^{36}\text{Cl}/\text{Cl} = \sim 700 \times 10^{-15}$$

Analyzed by *Accelerator Mass Spectrometry (AMS)*

Analyzed purified perchlorate samples

- Southwest US
- Atacama
- Synthetic



1. Southwest perchlorate (SHP and DV) significantly enriched in ^{36}Cl – Irrespective of $\delta^{17}\text{O}$.
2. Suggests significant component of “young” atmospheric perchlorate.
3. Atacama most likely “old” atmospheric perchlorate

Sturchio N.C., Caffee M.R., Beloso A. D., Heraty L.J., Böhlke J.K., Gu B., Jackson W.A., Hatzinger P.B., Heikoop J.R., and Dale M., 2009. Chlorine-36 as a tracer of perchlorate origin. *Environmental Science & Technology* 43, 6934–6938.



March 28 – April 1, 2011
Arlington, VA

March 28 – April 1, 2011 - Arlington, VA

Perchlorate Forensic Analysis: Summary

- ▶ When perchlorate is detected at low concentrations ($< 10 \mu\text{g/L}$) in groundwater, natural sources should be considered.
- ▶ Isotope analyses ($\delta^{37}\text{Cl}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$ and $^{36}\text{Cl}/\text{Cl}$) can be used to distinguish between synthetic and natural sources – Four independent measurements.
- ▶ Natural perchlorate (from Chilean fertilizer and from “indigenous” sources) has been detected in numerous wells in the US via isotope analysis.
- ▶ A “Guidance Manual” for perchlorate isotope sampling is presently under development by SERDP/ESTCP.





March 28 – April 1, 2011 • Arlington, VA

Contact Information

Paul Hatzinger, Ph.D.
Shaw Environmental Inc
Paul.hatzinger@shawgrp.com
1-609-895-5356

ER-0509 Project Team

Neil C. Sturchio, Ph.D.
University of Illinois at Chicago
Chicago, IL
Tel. (312) 355-1182
sturchio@uic.edu

John Karl Bohlke, Ph.D.
US Geological Survey
Reston, VA
(703) 648-6325
jkbohlke@usgs.gov

Baohua Gu, Ph.D.
Oak Ridge National Lab
Oak Ridge, TN
(865)-574-7286
gub1@ornl.gov

We gratefully acknowledge SERDP and ESTCP for supporting this work

