Using Stable Isotope Ratio Analysis to Distinguish Perchlorate Sources

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Perchlorate Contamination in the United States: Historical

**Military and Aerospace Issue**

- Rocket Testing
- Hog-Out
- Manufacturing
- Training Areas
- OB/OD Areas
- Few Commercial Sites
### Perchlorate Detections In Food (US FDA)

<table>
<thead>
<tr>
<th>Food Group</th>
<th>Number of Samples</th>
<th>Average Residue (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lettuce</td>
<td>137</td>
<td>10.3</td>
</tr>
<tr>
<td>Milk</td>
<td>125</td>
<td>5.81</td>
</tr>
<tr>
<td>Tomatoes</td>
<td>73</td>
<td>13.7</td>
</tr>
<tr>
<td>Spinach</td>
<td>36</td>
<td>115</td>
</tr>
<tr>
<td>Greens</td>
<td>14</td>
<td>92.4</td>
</tr>
<tr>
<td>Cabbage</td>
<td>13</td>
<td>8.80</td>
</tr>
<tr>
<td>Cantaloupes</td>
<td>48</td>
<td>28.6</td>
</tr>
<tr>
<td>Carrots</td>
<td>59</td>
<td>15.8</td>
</tr>
<tr>
<td>Green Beans</td>
<td>19</td>
<td>6.12</td>
</tr>
<tr>
<td>Broccoli</td>
<td>14</td>
<td>8.49</td>
</tr>
<tr>
<td>Grapes</td>
<td>12</td>
<td>8.58</td>
</tr>
</tbody>
</table>
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
Chilean Nitrate

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

- **Perchlorate Source**
  - 1910-1960
    - US imported $10^9$kg fertilizer/year
    - 0.2% ClO$_4^-$ (highly variable)
    - $10^6$kg ClO$_4^-$/year

- **Historical Impact**
  - Citrus or cotton ~50 mg/m$^2$-year
  - Possible large local Impacts

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Natural Perchlorate in the USA

- **Indigenous Perchlorate**
  - *Natural nitrate deposits*
  - *Perchlorate in soils*
  - *Perchlorate in groundwater & rainwater*
    - Atmospheric formation with O₃
    - Other mechanisms – UV, TiO₂

### Death Valley Nitrate Deposits

<table>
<thead>
<tr>
<th>Site</th>
<th>Nonsoluble Fraction</th>
<th>Concentration</th>
<th>ClO₄⁻</th>
<th>Cl⁻</th>
<th>NO₃⁻ -N</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Death Valley</td>
<td>%</td>
<td>mg kg⁻¹</td>
<td>0.25</td>
<td>320</td>
<td>1.8</td>
<td>72</td>
</tr>
<tr>
<td>Confidence Hills 1</td>
<td>NA</td>
<td>g kg⁻¹</td>
<td>0.85</td>
<td>180</td>
<td>5.5</td>
<td>100</td>
</tr>
<tr>
<td>Confidence Hills 2</td>
<td>49</td>
<td></td>
<td>0.95</td>
<td>63</td>
<td>5.9</td>
<td>23</td>
</tr>
<tr>
<td>Saratoga Hills</td>
<td>78</td>
<td></td>
<td>0.82</td>
<td>80</td>
<td>28</td>
<td>6.5</td>
</tr>
<tr>
<td>Bully Hill</td>
<td>62</td>
<td>1.7</td>
<td>80</td>
<td>28</td>
<td>6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>Zabriskie</td>
<td>64</td>
<td>1.7</td>
<td>140</td>
<td>4.4</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Atacama P1</td>
<td>42</td>
<td>243</td>
<td>80</td>
<td>12</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>Atacama P2</td>
<td>50</td>
<td>328</td>
<td>456</td>
<td>44</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>Atacama P3</td>
<td>13</td>
<td>113</td>
<td>50</td>
<td>15</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Atacama P4</td>
<td>51</td>
<td>132</td>
<td>61</td>
<td>22</td>
<td>51</td>
<td></td>
</tr>
</tbody>
</table>
Concentrations in Western US Groundwater

% Data Points

- < 0.1
- 0.1 - 1.0
- 1.0 - 10.0
- 10.0 - 100.0
- > 100

Courtesy of Dr. W. Andrew Jackson, Texas Tech
West Texas – Southern High Plains

- Study area >59,000 mi²
- 89% > 0.1 ppb
- Estimated Mass of ClO₄⁻
  - Saturated >2 X 10⁶ Kg
\[ (\text{ClO})_x + \text{O}_3 \rightarrow \text{ClO}_4^- \]
\[ (\text{ClO})_x + \text{O}_2 \rightarrow \text{ClO}_4^- \]

Deposition
Dry & Wet
Evapotranspiration

Plant uptake
\[ \text{ClO}_4^- \text{ Accumulation} \]

\[ \text{ClO}_4^- \text{ Flushing} \]

\[ \begin{array}{c}
0 \\
50 \\
100 \\
150 \\
200 \\
\end{array} \]

Depth (M)

Perchlorate
Chloride
Nitrate

Perchlorate
Chloride
Nitrate
Can You Distinguish Natural from Synthetic Perchlorate?

Stable Isotope Ratio Analysis of Chlorine and Oxygen in Perchlorate

• Other Lines of Evidence
  - $^{36}$Cl Analysis
  - Groundwater Dating
  - Co-Contaminants
  - Other Geochemical Data
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”

<table>
<thead>
<tr>
<th>Element</th>
<th>Isotopes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>$^1$H, $^2$H</td>
</tr>
<tr>
<td>Oxygen</td>
<td>$^{16}$O, $^{17}$O, $^{18}$O</td>
</tr>
<tr>
<td>Carbon</td>
<td>$^{12}$C, $^{13}$C</td>
</tr>
<tr>
<td>Chlorine</td>
<td>$^{35}$Cl, $^{37}$Cl</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>$^{14}$N, $^{15}$N</td>
</tr>
<tr>
<td>Sulfur</td>
<td>$^{32}$S, $^{34}$S</td>
</tr>
</tbody>
</table>
Stable Isotope Analysis: Perchlorate

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

IRMS – $\delta^{37}$Cl

Weigh crystal
Combust to Cl salt
Convert to CH$_3$Cl
IRMS
Determine Cl isotope ratio

IRMS – $\delta^{18}$O/$\delta^{17}$O

Weigh crystal
$\delta^{18}$O: Combust to CO ($\delta^{18}$O & $\Delta^{17}$O): decompose to O$_2$
IRMS (CO & O$_2$)
Measure yields
Determine O isotope ratios

Verification of Purity

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

Impurity detected
Terminology:
Stable Isotope Ratio Analysis

*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. \( \delta \) (in ‰) = \( (R_x/R_s-1) \times 1000 \)

- \( R \) = 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: \( \delta^{37}\text{Cl} = + 30 \%_o \)

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

\(^{18}\text{O} = \text{SMOW}\)
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).

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

$\delta^{18}\text{O} : -6.7 \pm 2.2$
Forensic Isotopic Analysis: Chilean vs. Synthetic $\Delta^{17}O$ and $\delta^{18}O$

$\delta^{17}O = \sim 0.52 \times \delta^{18}O$

$\Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{18}O \ (= O)$

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

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

Can You Differentiate Synthetic Sources?

1. There are some isotopic differences between manufacturers - but only in $^{18}\text{O}$.

2. $\text{H}_2\text{O}$ is the source of oxygen in synthetic perchlorate and $^{18}\text{O}$ in $\text{H}_2\text{O}$ varies globally.

3. Small dataset
   - batch to batch variation?
   - variation with time?
   - different “sources” in products (e.g., flares)?
Groundwater: Long Island Case Study

- Perchlorate isotopes
- Nitrate isotopes
- Major ions, trace elements
- Dissolved gases
- Groundwater dating

Locations:
- North Fork (Depot Lane)
- Westhampton (BOMARC)
- Northport (SCWA)

Preliminary data (2007) **not for distribution**

Analytical: 7 Wells

SCWA
Case Study: Long Island, NY

- Synthetic Bomarc
- Chilean SCWA/DL
- North Fork (Depot Lane)
- Westhampton (BOMARC)
- Northport (SCWA)

**δ³⁷Cl (per mil)**

**Δ¹⁷O (per mil)**

**Δ¹⁸O (per mil)**

mass-dependent fractionation

Map of Long Island with locations marked.
Long Island, NY
Depot Lane Transect

NO$_3^-$-N  ClO$_4^-$
(mg/L)  (µg/L)

GW flow

Northwest

DL6

13.6  0.9

1.0  0.1

1.1  0.3

9.1  0.8

Water table

Near recharge basin

DL1

6.3  9.9

8.0  4.6

DL4

8.0  0.6

Age (yrs)

1

18

40

Elevation (m)

Distance from DL6 (m)

Pleistocene clay confining layer

Upper glacial aquifer

Northwest

Southeast

0

10

20

-10

-20

-30

-40
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**
Indigenous Natural Perchlorate

Death Valley Caliche

Rio Grande Basin Groundwater (Ancient)

SHP Groundwater and Vadose Soil
Indigenous Perchlorate: $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$

1. There are multiple signatures for natural perchlorate but all are readily distinguished from synthetic sources via $^{37}\text{Cl}$ and $^{18}\text{O}$.

2. West Texas vadose (soil) perchlorate has a similar isotope signature to that in West Texas & NM groundwater.

Comparison of $\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$ in perchlorate from indigenous US sources with Chilean and synthetic perchlorate.
Indigenous Perchlorate: $\Delta^{17}O$ and $\delta^{18}O$

Comparison of $\Delta^{17}O$ and $\delta^{18}O$ 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 $\delta^{17}O$ 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.
Perchlorate Origin - Why different signatures?

Understanding of Natural Perchlorate Origin:

Why is $\Delta^{17}O$ 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?

$\begin{align*}
\text{(ClO)}_x + \text{O}_3 &\rightarrow \text{ClO}_4^- \\
\text{(ClO)}_x + \text{O}_3 &\rightarrow \text{ClO}_4^-
\end{align*}$

$\begin{align*}
\delta^{18}O \text{ (per mil)} &\text{ Synthesis solids} \\
\delta^{18}O \text{ (per mil)} &\text{ Atacama caliche/fertilizer} \\
\delta^{18}O \text{ (per mil)} &\text{ Death Valley caliche} \\
\delta^{18}O \text{ (per mil)} &\text{ West Texas}
\end{align*}$
Long-lived radioisotope produced in the stratosphere from $^{40}$Ar ($T^{1/2} \approx 301,000$ yrs)

$^{36}$Cl/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 $\delta^{17}$O.

2. Suggests significant component of “young” atmospheric perchlorate.

3. Atacama most likely “old” atmospheric perchlorate

When perchlorate is detected at low concentrations (< 10 μg/L) in groundwater, natural sources should be considered.

Isotope analyses ($\delta^{37}Cl$, $\delta^{18}O$, $\delta^{17}O$ and $^{36}Cl/Cl$) 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.
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