SERDP & ESTCP Perchlorate Sources

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16 April 2007

DoD’s Environmental Technology Programs

Demonstration/Validation    Basic and Applied Research
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

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
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

- 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

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

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

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

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)

Identification and Characterization of Natural Sources of Perchlorate

Does Natural Perchlorate Impact other Areas?

Concentration Distribution of Perchlorate in Groundwater from Selected Locations
Other Suspected Natural Occurrences

- Study area >59,000 mi²
- 89% > 0.1 ppb
- Estimated Mass of PC
  - Saturated >2 X 10⁶ 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
What’s the overall significance?

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

Identification and Characterization of Natural Sources of Perchlorate

Natural vs. Anthropogenic Perchlorate

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

Isotope Ratio Analysis to Differentiate Perchlorate Sources
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

Stable Isotope Analysis

<table>
<thead>
<tr>
<th>Isotopes: same number of protons &amp; electrons, different number of neutrons</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrogen</strong></td>
</tr>
<tr>
<td>$^1\text{H}$, $^2\text{H}$</td>
</tr>
<tr>
<td><strong>Oxygen</strong></td>
</tr>
<tr>
<td>$^{16}\text{O}$, $^{17}\text{O}$, $^{18}\text{O}$</td>
</tr>
<tr>
<td><strong>Carbon</strong></td>
</tr>
<tr>
<td>$^{12}\text{C}$, $^{13}\text{C}$</td>
</tr>
<tr>
<td><strong>Chlorine</strong></td>
</tr>
<tr>
<td>$^{35}\text{Cl}$, $^{37}\text{Cl}$</td>
</tr>
<tr>
<td><strong>Nitrogen</strong></td>
</tr>
<tr>
<td>$^{14}\text{N}$, $^{15}\text{N}$</td>
</tr>
<tr>
<td><strong>Sulfur</strong></td>
</tr>
<tr>
<td>$^{32}\text{S}$, $^{34}\text{S}$</td>
</tr>
</tbody>
</table>
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: $0.6 \pm 0.9$
Range: -3.1 to 1.6

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

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

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

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

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

Perchlorate forms Slowly in bleach ~ 8 ppm/yr
Results: Forensic Isotopic Analysis of Perchlorate Δ^{17}O and δ^{18}O

- **Natural perchlorate Excess Δ^{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

Results: Can You Differentiate Anthropogenic Sources?

- Manufacturer?
- Geographical Origin?
- Partially fractionated signature of δ^{18}O in source water
- More data necessary

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

Results: Southern California Site

Isotope Ratio Analysis to Differentiate Perchlorate Sources
Results:

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

Isotope Ratio Analysis to Differentiate Perchlorate Sources

Statistics

- $\delta^{37}Cl$: $1.1 \pm 1.2$
- $\delta^{18}O$: $-13.8 \pm 2.0$

- $\delta^{37}Cl$: $-11.3 \pm 1.3$
- $\delta^{18}O$: $-4.5 \pm 1.2$
Results:
Groundwater: Comparison to Solids
$\delta^{37}\text{Cl}$ and $\delta^{18}\text{O}$

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

Statistics

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

Home Pages

- [http://www.serdp.org](http://www.serdp.org)
- [http://www.estcp.org](http://www.estcp.org)