Distribution of Naturally-Occurring Perchlorate in Groundwater in California and the Southwest US

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U.S. Geological Survey
Acknowledgements

- ~ 1500 well owners and water purveyors allowed USGS to sample their wells
- 30 members of USGS GAMA team in 2004-2009
- Funding from California state bonds, administered by California State Water Resources Control Board
Outline

- Background on perchlorate
- California Groundwater Ambient Monitoring and Assessment (GAMA) Program
- Data analysis and modeling
- Distribution of naturally-occurring perchlorate in California and Southwest US
Perchlorate Basics

- **Chemistry:**
  - Highly soluble anion, $\text{ClO}_4^-$
  - Redox behavior similar to nitrate

- **Health effects:**
  - Impairs iodine uptake and thyroid hormone production
  - Most critical for fetuses, infants, young children - thyroid hormones affect growth and neurological development

- **Regulation:**
  - USEPA interim drinking water health advisory level 15 µg/L
  - California MCL 6 µg/L (Oct 2007)
  - Other states ... 1 to 50 µg/L
Perchlorate Sources

- **Natural**
  - Atmospheric origin
  - Found in Chilean Atacama Desert nitrate deposits, some evaporites, and salts accumulated in unsaturated zones in arid/semi-arid areas

- **Anthropogenic**
  - Aerospace/military/industrial (solid rocket fuel, explosives, safety flares, fireworks, matches, etc)
  - Agricultural (fertilizer derived from Chilean nitrate deposits)
  - Disinfection byproduct (aging of hypochlorite solutions)
What is the natural background distribution of perchlorate in groundwater?

- Differentiate between perchlorate from natural and anthropogenic sources
  - Direct measures – water quality parameters
  - Indirect measures – land use, climate, etc.
- Need large dataset with lots of variability in potential source terms ... California GAMA
GAMA Priority Basin Project 2004 - 2010

- Comprehensive statewide assessment of groundwater quality in aquifers used for public drinking water supply
- Design* based on NAWQA

35 study units
~ 2,500 wells

*Belitz et al., 2003
GAMA Perchlorate 2004-2009

<table>
<thead>
<tr>
<th>Report limit (µg/L)</th>
<th>Statewide detection frequency</th>
<th>Study Unit detection frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td>0.1</td>
<td>63</td>
<td>12</td>
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<tr>
<td>0.5</td>
<td>25</td>
<td>0</td>
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<tr>
<td>1</td>
<td>14</td>
<td>0</td>
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<tr>
<td>4</td>
<td>3</td>
<td>0</td>
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</tbody>
</table>

Detections (µg/L)
- 0.1 – 0.5
- 0.5 – 1
- 1 – 4
- > 4

Nondetections (µg/L)
- <0.1
- <0.5
- <1 or higher

Perchlorate
n = 1624
Logistic Regression Model

- Probability of perchlorate detection (above a specified reporting level, RL)
- RLs: 0.1, 0.5, 1, and 4 μg/L
- Independent variables
  - Natural sources
  - Anthropogenic sources

\[
Pr = \frac{e^{(b_0 + b_{AI}AI + b_{AS}AS)}}{1 + e^{(b_0 + b_{AI}AI + b_{AS}AS)}},
\]

- Observed Detection Frequencies
- Deciles of risk test of model fit
- \(R^2 = 0.98\)
Proxy for Natural Source is Aridity Index

\[
AI = \frac{\text{Precipitation}}{\text{Potential ET}}
\]

- \(<0.05\) Hyper-arid
- \(0.05-0.2\) Arid
- \(0.2-0.5\) Semi-arid
- \(0.5-0.65\) Dry subhumid
- \(0.65-1\) Humid
- \(>1\) Wet

*PRISM, 2006
**Flint and Flint, 2007
Anthropogenic Sources Represented by a 4-Component ‘Anthropogenic Score’

- Nitrate-N greater than 3 mg/L
- Pesticides or fumigants present
- Solvents or fuel components present
- Close to known contamination sites
  - 1 site within 10 km or 2 within 25 km
  - Special case of Colorado River water
- Other variables tested
  - Land use (urban, agricultural)
  - Chloroform
Study Unit Results

> 0.1 µg/L

> 0.5 µg/L

Aridity Index

Study Unit
Average AS

- AS=0
- AS=4

Detection Frequency or Predicted Probability

0.2 - 0.7
0.9 – 1.1
1.1 – 1.5
1.6 – 3.2
Probability that Detected Perchlorate is Naturally-Occurring
Probability of Detecting Naturally-Occurring Perchlorate

- > 70%
- 60 – 70
- 50 – 60
- 40 – 50
- 20 – 40
- 10 – 20
- 5 – 10
- 1 – 5
- < 1 %

- > 0.1 µg/L
- > 0.5 µg/L
- > 1 µg/L
Summary

- Logistic regression model yields probability of detecting naturally-occurring perchlorate as a function of climate
  - Model uses direct measures – water quality – to infer presence of potential anthropogenic sources
  - Low concentrations (<0.5 µg/L) widespread
  - Probability decreases rapidly as concentration increases

- Study unit scale anthropogenic sources/processes
  - Relative importance of industrial and agricultural sources
  - Redistribution of natural perchlorate by anthropogenic process – irrigation