Arsenic, chromium, and uranium occurrence in California groundwater at the macro, well-bore, and micro scales

(Or: “More fun and interesting things than you ever cared to know about trace elements -- in 20 minutes or less”)

By: John A. Izbicki, Michael T. Wright, Bryant C., Jurgens, and Loren F. Metzger
A little chemistry and a few factoids

<table>
<thead>
<tr>
<th>Form in water</th>
<th>Arsenic</th>
<th>Chromium</th>
<th>Uranium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced</td>
<td>As III (\text{HAsO}_2^0)</td>
<td>Cr III (\text{Cr}_2\text{O}_3(s))</td>
<td>U IV (\text{U}_4\text{O}_9 (s))</td>
</tr>
<tr>
<td>Oxidized</td>
<td>As V (\text{H}_2\text{AsO}_4^{2-})</td>
<td>Cr VI (\text{CrO}_4^{2-})</td>
<td>U IV (\text{UO}_2(\text{OH})_2) (\text{UO}_2(\text{CO}_3)_2^{2-})</td>
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Abundance in rock (milligrams per kilogram)
(From Reimann and Caritat, 1998)

<table>
<thead>
<tr>
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<th>Chromium</th>
<th>Uranium</th>
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<tbody>
<tr>
<td>Continental crust</td>
<td>2</td>
<td>130</td>
<td>1.7</td>
</tr>
<tr>
<td>Ultramafic rock</td>
<td>0.7</td>
<td>2,300</td>
<td>0.02</td>
</tr>
</tbody>
</table>

MCL (\(\mu\text{g/L}\))  

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<tr>
<td>10</td>
<td>100 (\text{Cr(t)}) EPA</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>10 (\text{Cr(VI)}) CA prop.</td>
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Arsenic in California’s groundwater

About 10 percent of wells exceed US EPA Maximum Contaminant Level.

Co-occurrence in groundwater from alluvial aquifers (US)
(From Ayotte, et al., 2011)

Humid climates: B, Si
Dry climates: Al, Si, U, PO₄, K

Arsenic, in μg/L
N = 1,525
- Less than 15
- 15 to 30
- Greater than 15

USGS
science for a changing world

California WRCB/USGS GAMA data
Artsenic in California’s groundwater

About 8 percent of wells exceed US EPA Maximum Contaminant Level

“Natural arsenic pollution of groundwater and surface water affects more than 140 million people in at least 70 countries worldwide. In half the countries where arsenic pollution is now known, it was discovered within the last 10 years...”

Ravenscroft, 2007
Chromium (Cr VI) in California’s groundwater

About 9 percent of wells exceed proposed California Maximum Contaminant Level

Cr VI, in \( \mu g/L \)

- Less than 1
- 1 to 5
- 5 to 10
- Greater than 10

Co-occurrence in groundwater from alluvial aquifers (US)

(From Ayotte, et al., 2011)

- Humid climates: \( U \)
- Dry climates: \( Ni \)

California DPHS data
Uranium in California’s groundwater

About 4 percent of wells exceed the US EPA Maximum Contaminant Level.

Co-occurrence in groundwater from alluvial aquifers (US)
(From Ayotte, et al., 2011)

Humid climates: Mo, Se, Cr, Cu, TDS
Dry climates: Mo, As, NO₃, Cr, Cu, TDS

California WRCB/USGS GAMA data
Geology and selected mineralogy

1. Chromium in chromite (Coast Range)
   - Unweathered
   - Weathered

2. Arsenic in pyrite (Sierran alluvium)
   - Octahedral crystal: 4% arsenic
   - Twinned-pyritohedron crystal: 0% arsenic
Sorption on the surfaces of mineral grains

Oxide coatings on a quartz crystal

Iron oxide on the surface of a mineral grain

Iron oxide rich paleosols in unsaturated alluvium

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Sorption on the surfaces of mineral grains

Oxide coatings on a quartz crystal

Iron oxide on the surface of a mineral grain

Acid-extraction data

Chromium, in milligrams per kilogram

Apex — Toe
Position on alluvial fan
Coarser — Finer

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Sorption on the surfaces of mineral grains

Sorption of selected anions

Strongly sorbed:
- OH⁻
- H₂AsO₄⁻
- F⁻
- SO₄²⁻
- CrO₄²⁻
- HCO₃⁻
- Cl⁻
- NO₃⁻

Weakly sorbed:

(Sorptive fraction (Wentzel and others, 2001), in percent of total extractable)

Operational fraction (Wentzel and others, 2001), in percent of total extractable

Sorption is pH dependent

(From Clifford, 1999; Trussell et al., 1980)

Operational fraction (Wentzel and others, 2001), in percent of total extractable

Crystalline

Amorphous

Exchangeable

Arsenic -73

More reactive

Natural abundance

Less reactive

Natural abundance

Natural abundance

Months

(12)

(Lizbicki and others, in review)
Groundwater flow, redox, and pH

Northeastern San Joaquin Groundwater Subbasin

Changes in dissolved oxygen and redox affect spatial and depth distribution of trace elements

As, µg/L
- <5
- 10 - 15
- 5 - 10
- >15

Arsenic, in micrograms per liter

pH

Oxic groundwater

y = 0.17x + 7.2
R² = 0.56

Reduced groundwater

Arsenic V predominates

Arsenic III predominates

1:1 correlation line

All arsenic present as Arsenic V

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Groundwater flow, redox, and pH

Northeastern San Joaquin Groundwater Subbasin

Changes in dissolved oxygen and redox affect spatial and depth distribution of trace elements

Arsenic concentrations with depth

As, µg/L
- <5
- 10 - 15
- 5 - 10
- >15

Depth to bottom of deepest well screen, in feet
- Less than 330
- 330 to 500
- Greater than 500

Percent equal to or greater than
Groundwater flow, redox, and pH

Northeastern San Joaquin Groundwater Subbasin

Changes in dissolved oxygen and redox affect spatial and depth distribution of trace elements

Original well construction
Modified well construction (bottom three screens below 280 ft eliminated)

Numerical simulations at the well-bore scale to predict results
Groundwater flow, redox, and pH

Silicate Weathering
\[ \text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{H}^+ \rightarrow \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4^{\circ} \]

Surface Chemistry

X-ray spectrum of quartz mineral grain

X-ray spectrum of quartz mineral grain and surficial coatings

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Microbiology—reduction of oxidized forms

Gibbs free energy ($\Delta G^\circ$) coupled to hydrogen oxidation

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(From Ahmann, 1997; Thauer, 1977; Nordstrom and Archer, 2003)
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Isotope geochemistry

- No naturally occurring isotopes of arsenic
- Four naturally occurring-stable isotopes of chromium
  - Best suited for process-oriented work
- There is no silver-bullet that will allow you to dispense with sound hydrology and geochemistry
Isotope geochemistry

“All that glitters is not gold” and all that is radioactive is not uranium

Well 10S/5W-18M3, San Diego County, Calif., June 2011

Depth, in meters

Q = 4.7 L/s

Gross alpha

Uranium

Radium

Radon-222

Well-bore flow, in liters per second

Natural gamma, in counts per second

picoCuries per liter

Uranium progeny in red
Thorium (\(^{232}\text{Th}\)) progeny in green
Just a little more fun with trace elements

Don’t move or I’ll fill you full of 98% lead, 1% antimony, 0.75% silver, 200 ppm nickel, with trace amounts of cobalt, and other components below their respective detection limits!!!

Wait a minute! Are those values certified??

High frequency of occurrence of trace elements in California’s groundwater with respect to MCL’s and other health-based standards

U.S. EPA CCL-3
(Contaminant Candidate List)
- Cobalt
- Molybdenum
- Strontium
- Vanadium

Analytical Chemists in the Wild West