Over-pumping Leads to California Groundwater Arsenic Threat

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The Global Threat: Geogenic Groundwater Contaminants
Geogenic (indigenous) Threats
Groundwater Quality Challenge

Surface Water:Sediment Ratio, 1000:1

Groundwater:Sediment Ratio, 1:1000 ➔ Water Quality Problems
Release Pathways
Oxidation-Reduction

Oxidative (Aerobic) Release

\[
\begin{align*}
\text{Cr(III) (s)} & \rightarrow \text{Cr(VI) (aq)} \\
\text{Se(0)/S(-II) (s)} & \rightarrow \text{Se(VI) (aq)} \\
\text{U(IV) (s)} & \rightarrow \text{U(VI) (aq)}
\end{align*}
\]

Reductive (Anaerobic) Release

\[
\begin{align*}
\text{As(V) (s)} & \rightarrow \text{As(III) (aq)} \\
\text{MnO}_2 \text{ (s)} & \rightarrow \text{Mn}^{2+} \text{ (aq)}
\end{align*}
\]
A pervasive, bad actor
Potential Groundwater Arsenic Occurrence

Probability of >10 μg/L in groundwater

Geogenic (natural) Arsenic Sources

Amini et al. 2008, ES&T 42 (10) 3669-3675
Arsenic Background

- Drinking water standard: 10 µg/L
- Arsenic generally persists in two forms: As(V) (arsenate, HAsO$_4^{2-}$) and As(III) (arsenite, H$_3$AsO$_3$)
- Arsenic normally binds strongly to soils and sediments, and thus stays within the solids

Except....
Arsenic Mobilization Processes

**Known processes**

- Transition to persistent anaerobic conditions
- Alkaline pH (greater than 8.5)
- Competing anions (e.g., phosphate)

**Emerging processes**

- Change in ionic composition
- Aquifer compression with pumping
Asian Groundwater Crisis:
Contaminated Shallow Groundwater

- Indus River Delta: 12 million
- Ganges Delta: 125-143 million
- Yellow River Plain: 30-50 million
- Yangtze River Plain: 50-80 million
- Red River Delta: 17 million
- Irrawaddy and Salween River Delta: 10-15 million
- Mekong River Delta: 20-30 million
Reductive Release of Arsenic

OM Degradation

Food

CO₂

As/Fe reduction

bacteria

As (V)

Arsenic in sediment

As

Arsenic in water
How might arsenic enter groundwater within the Central Valley?
Groundwater Pumping Impacts
Arsenic in Lower Mekong Delta -- Vietnam

Erban et al. PNAS 2013
Shallow vs Deep Aquifer Arsenic
Shallow vs Deep Aquifer Arsenic

As > WHO standard

Max age (Ma)
- Holocene: 0.012
- Upper Pleistocene: 0.13
- Middle Pleistocene: 0.78
- Lower Pleistocene: 2.6
- Upper Pliocene: 3.6
- Lower Pliocene: 5.3
- Upper Miocene: 7.2

Depth (m)
- 0
- 10
- 200
- 400
- 600

As (µg/L)
- 0
- 100
- 1000
- 10000

Fraction of wells with As > 10 µg/L

Well count
- >1000
- 1000
- 100
- 10
- 1

depths of wells by aquifer in order of age

line connects aquifers

Erban et al. EST 2014
Pumping Induced Land Subsidence

InSAR-based 0
Aquifer simulation 1.4
Deep Aquifer Arsenic and Pumping

Erban et al., PNAS 2013
Arsenic Release From Clay Pore-Water with Over Pumping

Erban et al., PNAS 2013
Tulare Basin Subsidence

InSAR based
Change in subsidence rate, cm/yr

Smith, Knight, Fendorf. 2018. Nature Geoscience
Orange County Water District

Non-oxidative Release of Low-Arsenic Strata
Post-Treatment Infiltration
Monitoring Well Arsenic Concentration Over Time (Chloride and Arsenic Levels)
Cation bridging is key to arsenic retention
Destabilized Arsenic with Purified Water

Fakhreddine et al., EST 2015
Direct Injection to Confined Aquifers

2 MGD
(7,570 m³/d)

Infiltration
Injection

(30 m away)
Monitoring

(300 m away)
Monitoring

Fakhreddine, 2018
Direct injection: shifting redox environment

\[ FeAsS + 3O_2 + 4H_2O = Fe(OH)_3 + SO_4^{2-} + 2H^+ + H_3AsO_3 \]

\[ Fe(OH)_3 + H_3AsO_4 = Fe(OH)_3 \equiv H_3AsO_4 \]

Arserian pyrite

\[ Fe[As,S]_2 \]
Direct Injection to Confined Aquifers

- **FeAsS DOC**
- **As=Fe(OH)$_3$**
- **FeAsS DOC**

*Graphs showing arsenic (As) concentrations over time, with different depths indicated:*

- **161-192 m depth**
  - 17 mg/kg As
  - Oxidation of FeAsS

- **206-217 m depth**
  - 1.4 mg/kg As
  - pH-promoted release

- **344-350 m depth**
  - 4.3 mg/kg As
  - Depletion of FeAsS

*Fakhreddine, 2018*
What’s Next (or what should be next)?
**NEEDED SCIENTIFIC ADVANCEMENTS**

**Process-based predictive model:**
Coupled sedimentological, hydrological, and geochemical models

**Sentry measurements:**
Subsidence, manganese (and sulfate) concentrations

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**NEEDED MANAGEMENT ADVANCEMENTS**

**Multi-threat considerations:**
Arsenic, uranium, chromium, nitrate…

**Recharge-extraction management plans:**
Means of recharge
Recharge water chemistry
Extraction vs recharge volumes
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Groundwater Cr(VI) Concentrations
Cr(VI) Contamination of California Groundwater

Groundwater Cr(VI)

Industrial Sourced

Geogenic Cr(VI)

Kriged correlation between Cr(VI) in supply wells and proximity to ultramafic outcrops

- Significantly uncorrelated
- Not Significant
- Significantly correlated
- Major N-S rivers
- Ultramafic outcrops

Map showing distribution and correlation of Cr(VI) contamination in California groundwater.
Cr(VI) Generation from Native Cr(III) Minerals
Chromite Oxidation

\[
\text{FeCr}_2\text{O}_4(s) + \frac{7}{2}\text{MnO}_2(s) + 5\text{H}^+ = 2\text{HCrO}_4^-(aq) + \text{Fe(OH)}_3(\text{am}) + \frac{7}{2}\text{Mn}^{2+}(aq)
\]

Oze et al., PNAS 2007
Cr – Mn Separation Distance is Key to Cr(VI)

The diagram illustrates the relationship between Cr(VI) concentration and PV eluted, showing a significant increase in Cr(VI) concentration with increasing PV eluted. The distance, $d_{rxn}$, between Cr(OH)$_3$ and MnO$_2$ is highlighted with values of 0.1 um, 1 um, and 10 um, demonstrating the impact of separation distance on the reaction kinetics.
Deposition of MnO$_2$ Proximal to Cr(OH)$_3$