Science and Regulation of Arsenic in Groundwater

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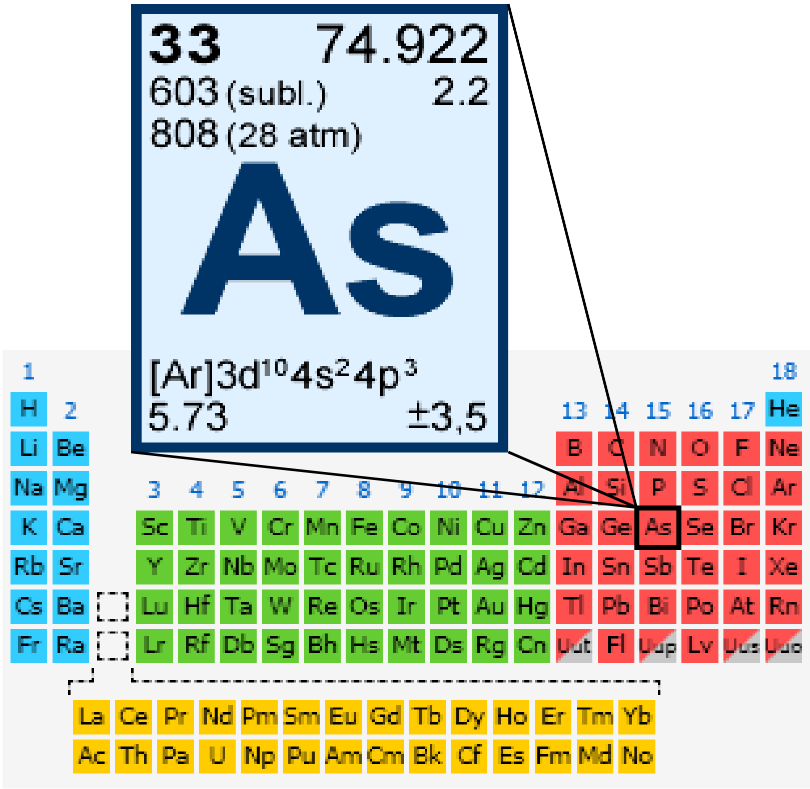
Arsenic

- **Metalloid**

- **Ubiquitous**
  - Elemental
  - Minerals
  - Soil
  - Rivers
  - Oceans
  - Groundwater
  - Food

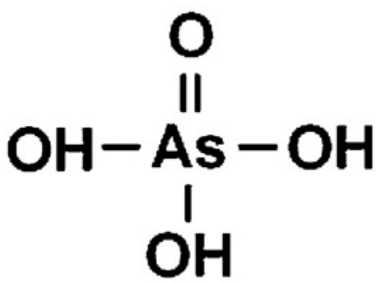


http://www.knowledgedoor.com http://www.inorganicventures.com

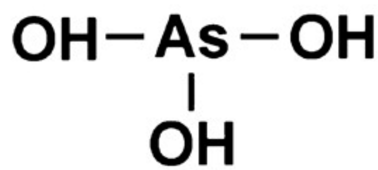
- **Most abundant in rocks, *commonly associated with <u>shales</u>, <u>deep-sea clays</u>, <u>iron oxides</u>, <u>sulfur minerals</u>, <u>volcanic sediments</u>***

- **Redox Active Species**
  - **3+, 5+** are most common
  - 1+, 2+, 3- are less common

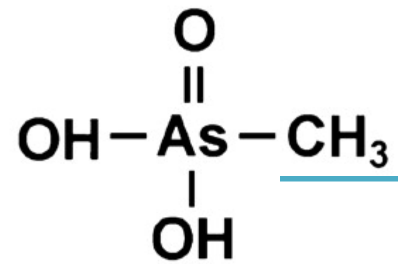
Arsenic Compounds



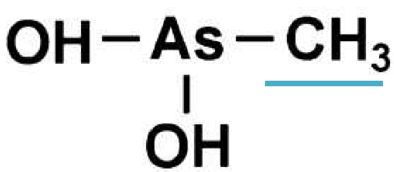
Arsenate (5+)



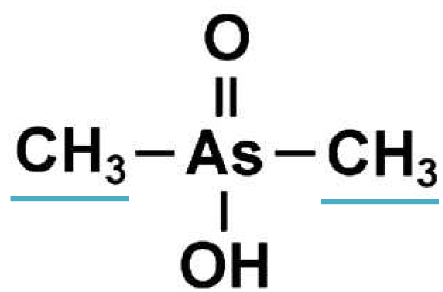
Arsenite (3+)



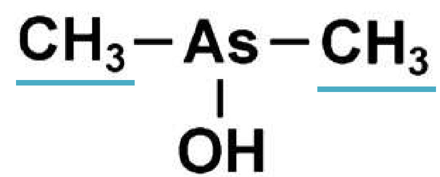
Monomethyl-
arsonic acid



Monomethyl-
arsonous acid



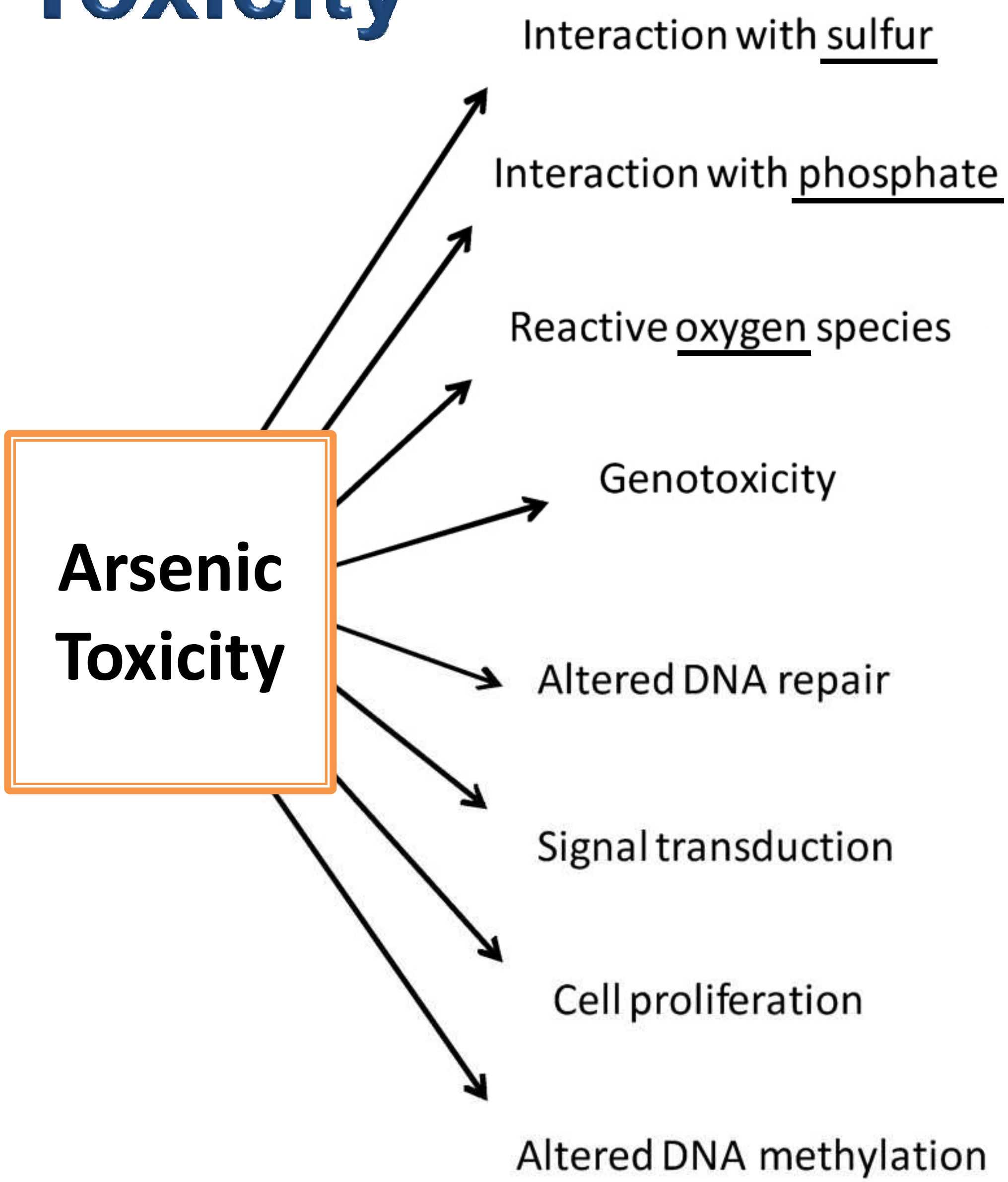
Dimethylarsinic
acid



Dimethylarinous
acid

Hughes M F et al. Toxicol. Sci. 2011;123:305-332.
Published by Oxford University Press on behalf of the Society of Toxicology 2011.

Toxicity



http://www.mineraltest.ca/wp-content/uploads/2012/11/arsenic-skin-lesion-300x300.jpg

Hughes M F et al. Toxicol. Sci. 2011;123:305-332.

Arsenic Uses

- **Poison -** Poison of Kings
- **Medicinal -** Fowler's Solution
- **Hardening alloys**
- **Glass manufacturing**
- **Electrical device component**
- **Semiconductor**
- **Pesticides**
- **Pigments**
- **Wood preservation**

Forwler's Solution, Dave Ward/Flickr


Dusting cotton, 1934/USDAgov/Flickr


CCA wood preservatives, 2011/npic.orst.edu

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Arsenic in the Oilfield

- **Production tubing <u>corrosion inhibitor</u>** (Frenier et al., 1989)
- **<u>Produced water</u>** (Gallup et al., 1996)
- **Crude oils** (Magaw et al., 2001)
  - ~60 ug/L (average of 26 crude samples)
- **Gas condensate** (Krupp et al., 2007)
  - 33-122 ug/L

- **Released hydrocarbons can liberate arsenic from soils**

http://www.cjstech.com/wp-content/uploads/2013/07/Truck-and-Spool.jpg

Naturally Occurring Arsenic

Quiruvilca Mine (La Libertad Mine; ASARCO Mine), Quiruvilca District, Santiago de Chuco Province, La Libertad Department, Peru © Christian Bracke

As_2S_3

Panasqueira Mine (Couto Mineiro da Panasqueira), Panasqueira, Covilhã, Castelo Branco District, Portugal © Kristalle and Crys

FeAsS

http://www.minfind.com

As_4S_4

- **More than <u>150</u> arsenic-bearing minerals**
- **Arsenic has an affinity for <u>iron</u> and <u>sulfur</u>**

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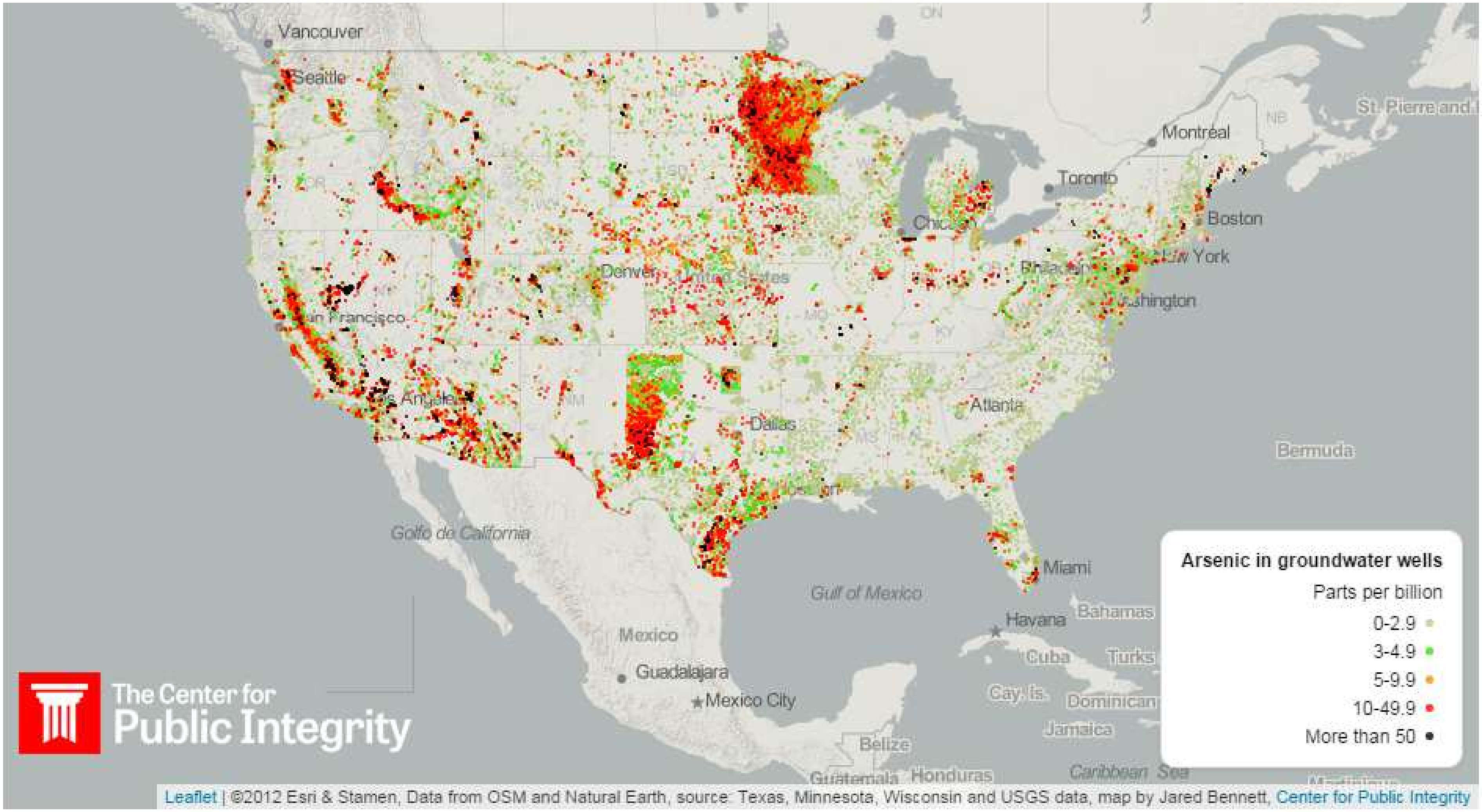
Arsenic in Groundwater



Arsenic in Groundwater

FeAsS

Dissolution

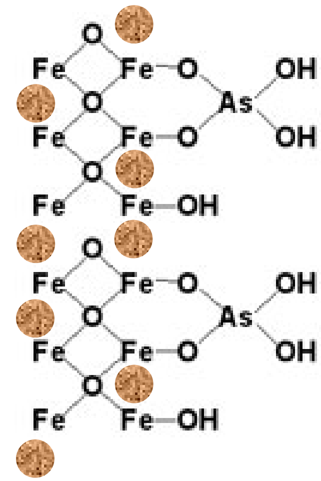
Precipitation

$As^{3+}_{(aq)}$

$As^{5+}_{(aq)}$

Adsorption

Desorption



Immobile

Mobile in Groundwater

Immobile

pH

Iron Oxides

Redox

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Mobility : pH

- $pKa_1 = 2.2$

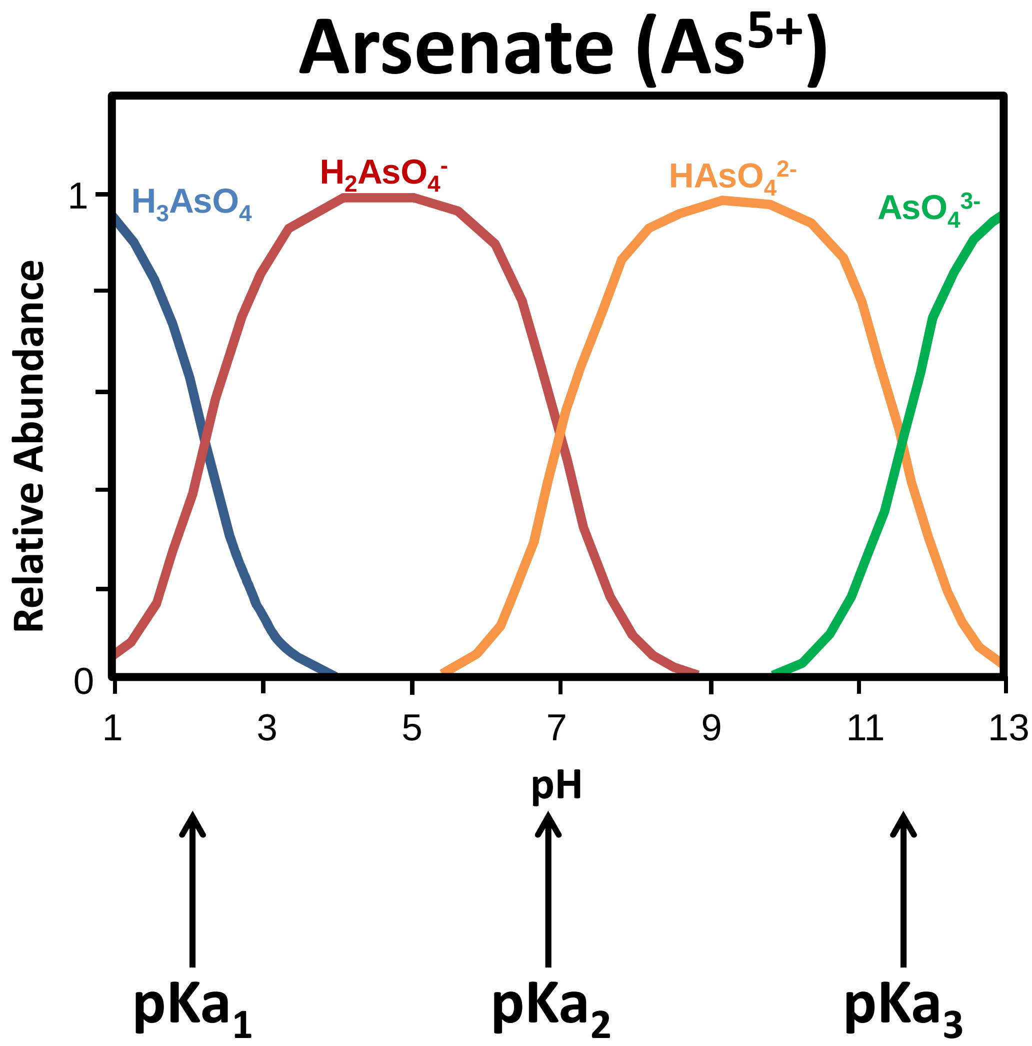
$H_3AsO_4^{\circ} \rightarrow H^+ + H_2AsO_4^-$

- $pKa_2 = 6.97$

$H_2AsO_4^- \rightarrow H^+ + HAsO_4^{2-}$

- $pKa_3 = 11.53$

$HAsO_4^{2-} \rightarrow H^+ + AsO_4^{3-}$



Mobility : pH

- $pKa_1 = 9.22$

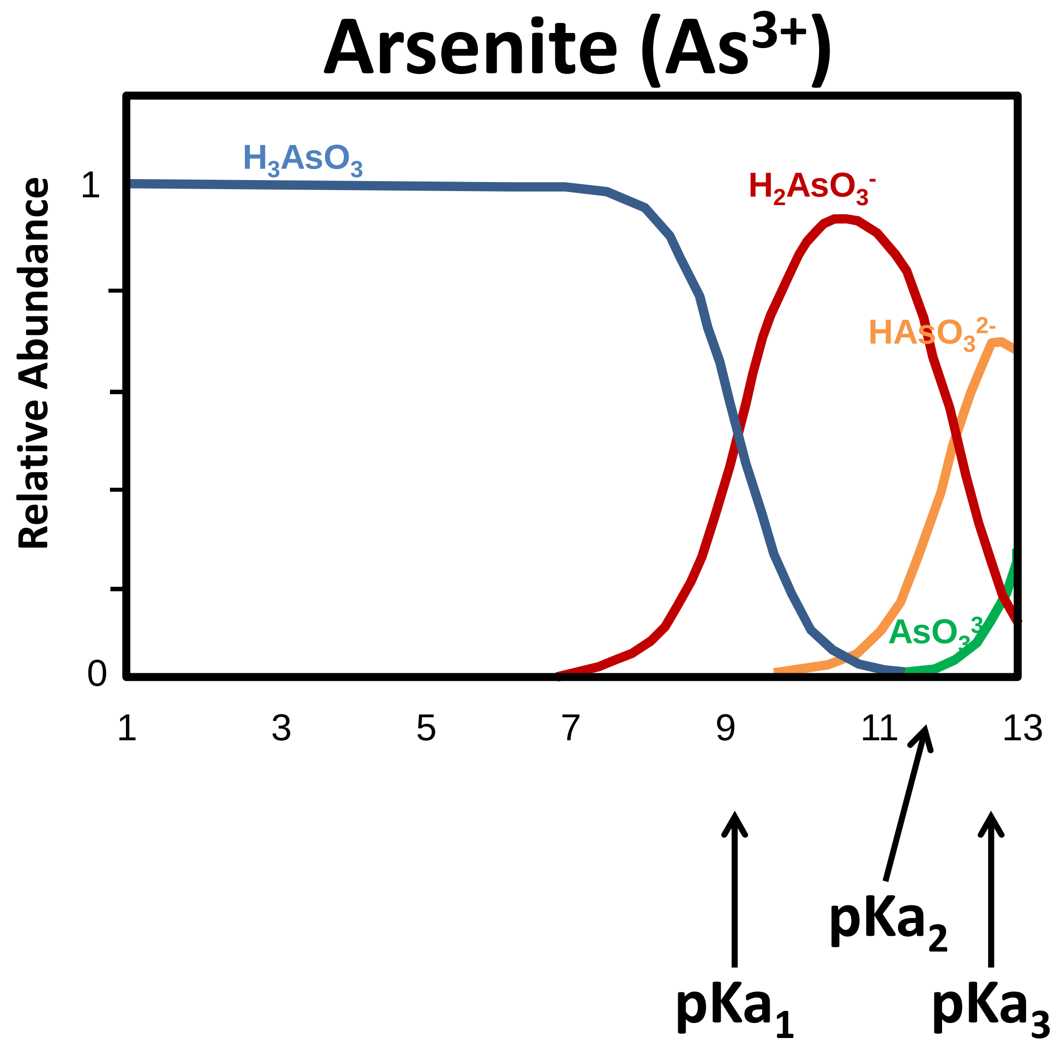
$H_3AsO_3^{\circ} \rightarrow H^+ + H_2AsO_3^-$

- $pKa_2 = 12.13$

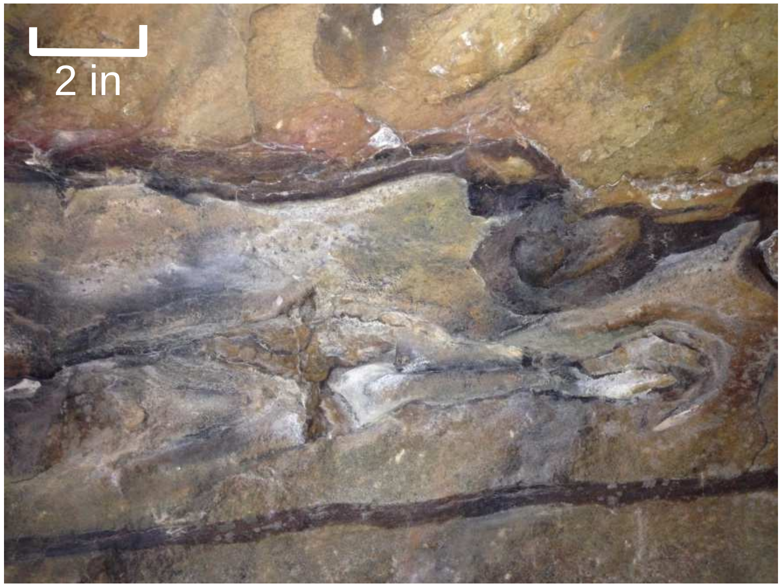
$H_2AsO_3^- \rightarrow H^+ + HAsO_3^{2-}$

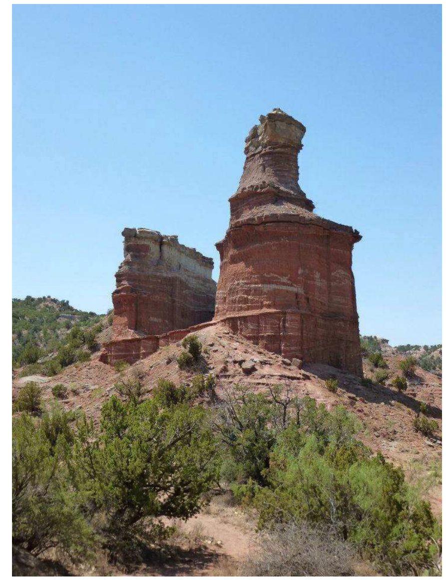
- $pKa_3 = 13.4$

$HAsO_3^{2-} \rightarrow H^+ + AsO_3^{3-}$

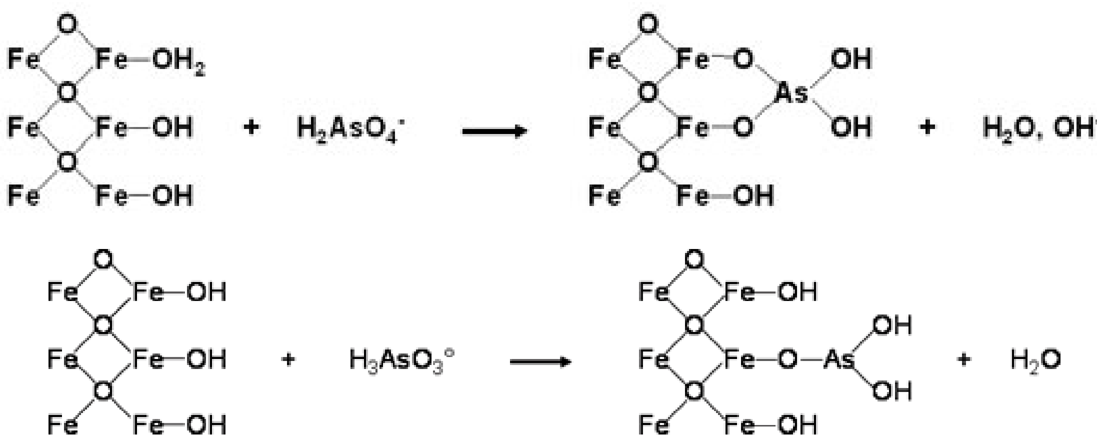


Mobility – Iron (III) Oxides





- Metal oxyhydroxides can act as a sink and source of arsenic



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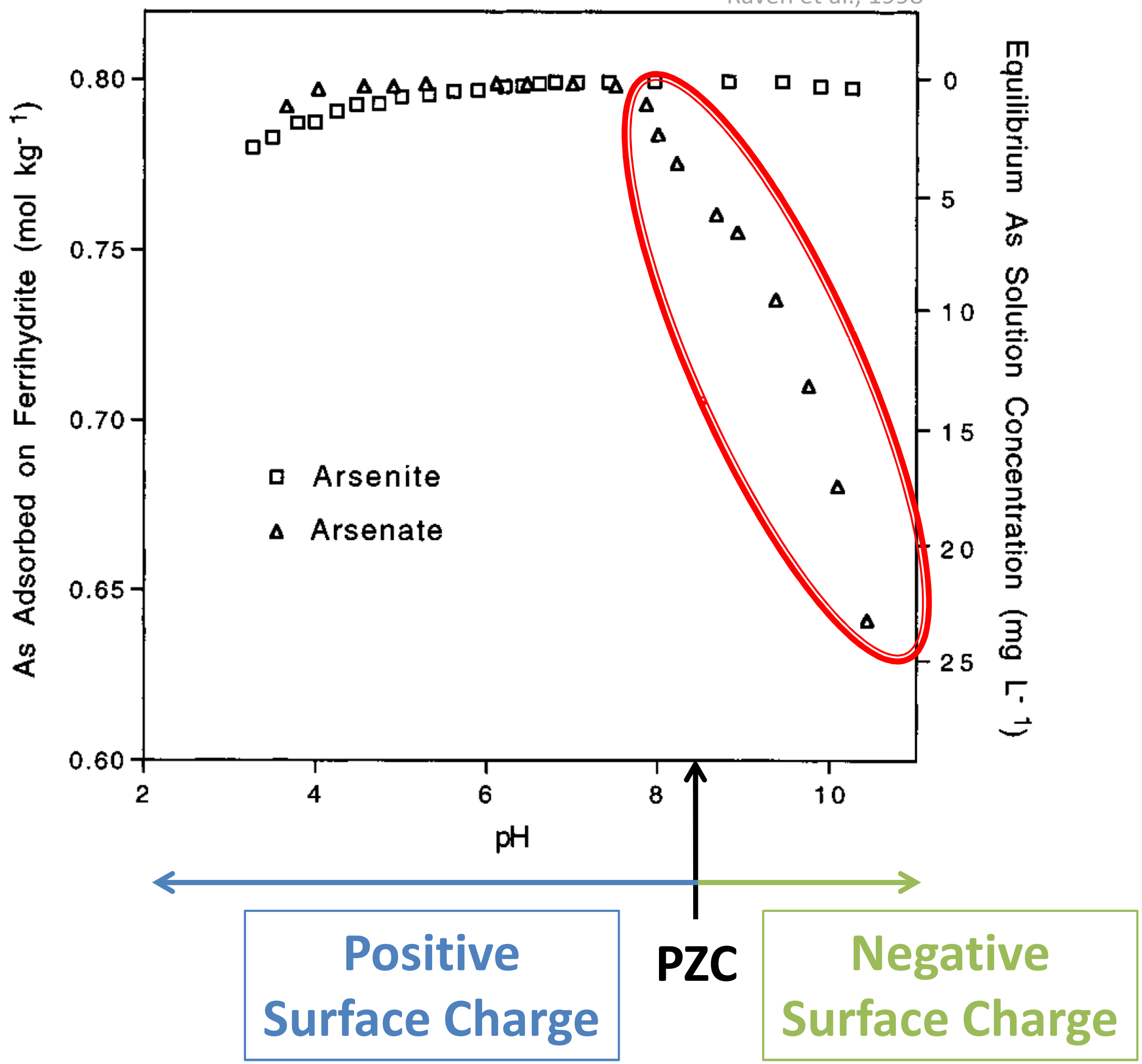
Adsorption to Iron (III) Oxides

Raven et al., 1998

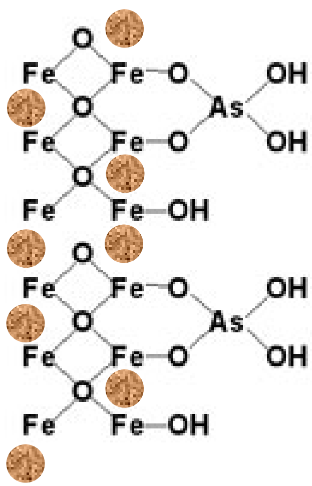


Mobility – Iron (III) Oxides

- Ligand Exchange Reactions (phosphate, sulfate, carbonate, silicate)

Fe oxide–As(V) + phosphate → Fe oxide–PO_4 + As(V)

- Reductive Dissolution



Dissolution →

$Fe^{2+}_{(aq)}$ + $As^{3+}_{(aq)}$ $As^{5+}_{(aq)}$

$[As]_{GW}$ ↑

Mobile

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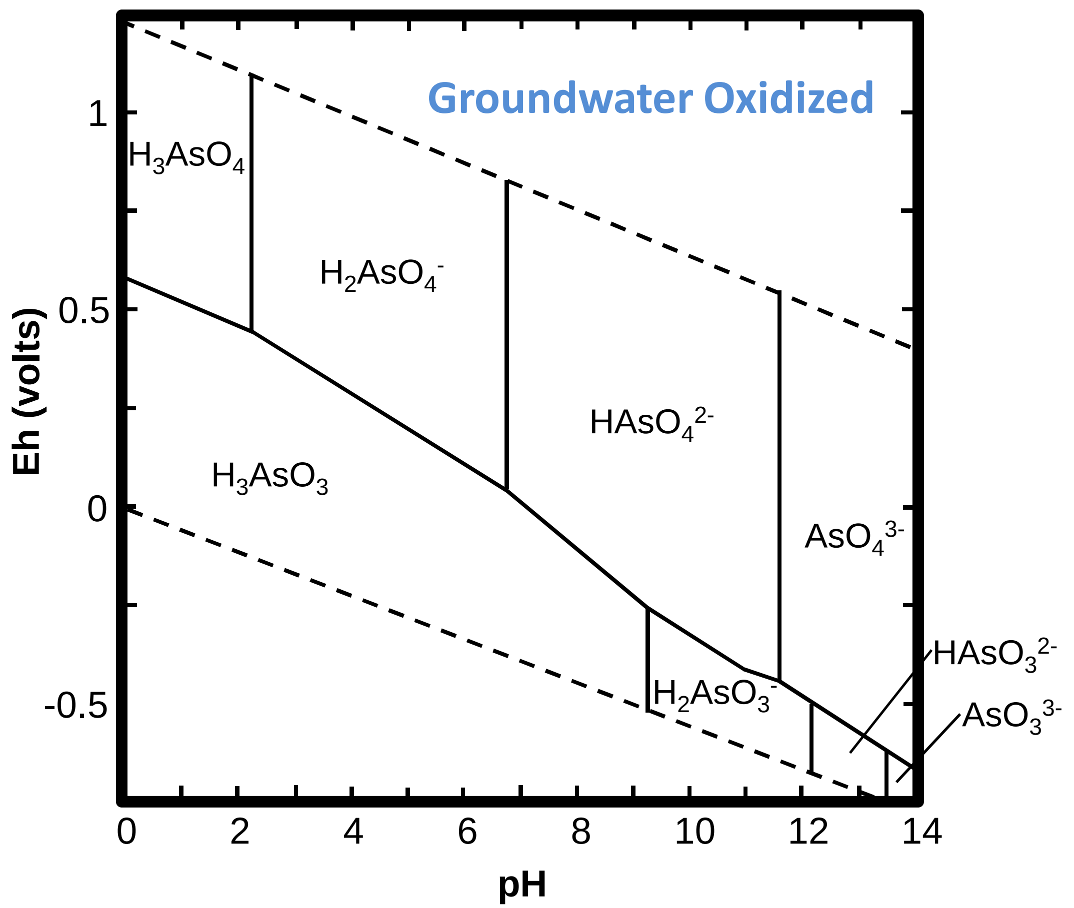
Oxygenated Redox Conditions

- Arsenate more prevalent
- Arsenic will be predominantly immobile

[As]$_{GW}$ ↓



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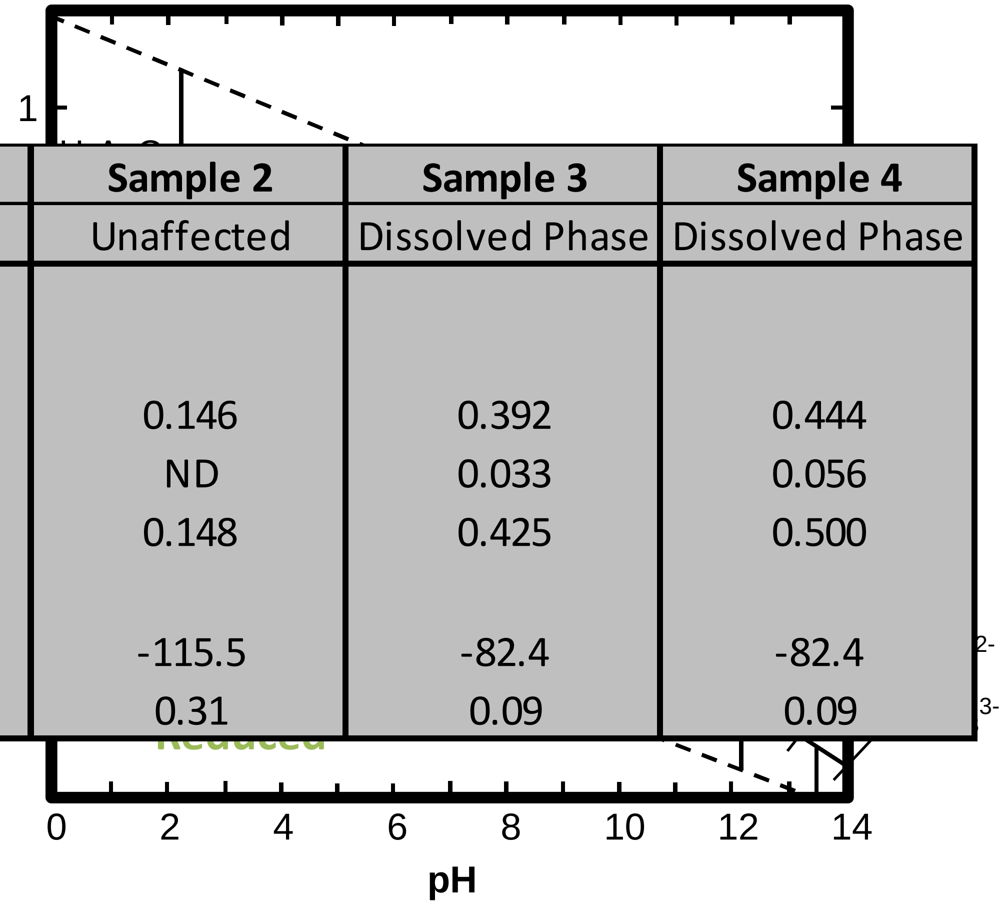
Post-Oxic Redox Conditions

- Arsenic more likely to be mobile

Sample Identification	Sample 1	Sample 2	Sample 3	Sample 4
Hydrocarbon Status	LNAPL	Unaffected	Dissolved Phase	Dissolved Phase
<u>Arsenic Speciation (1362A)</u>				
Arsenic (III), mg/L	0.164	0.146	0.392	0.444
Arsenic (V), mg/L	ND	ND	0.033	0.056
Inorganic Arsenic, mg/L	0.164	0.148	0.425	0.500
Oxidation Reduction Potential	-154.2	-115.5	-82.4	-82.4
Dissolved Oxygen, mg/L	0.10	0.31	0.09	0.09

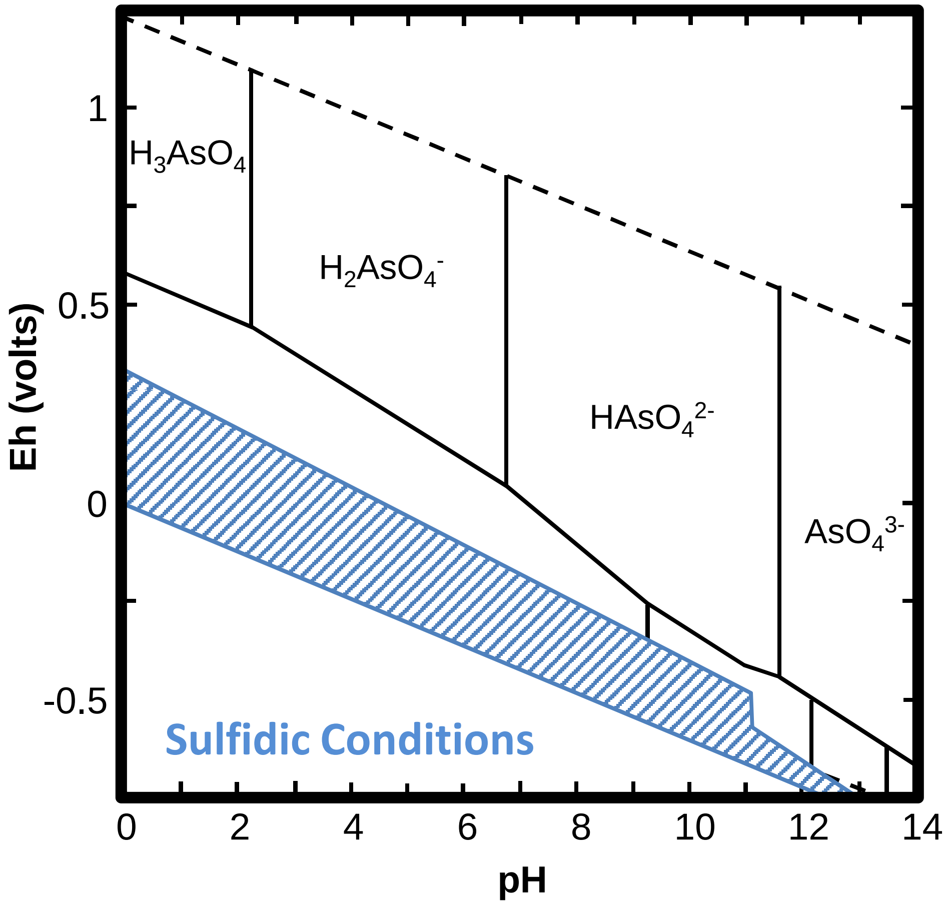
$[As]_{GW}$ ↑



Sulfidic Redox Conditions

- Arsenic will be predominantly <u>immobile</u>
- Orpiment, arsenopyrite, pyrite precipitate (bind arsenic)

$[As]_{GW} \downarrow$



Reeder et al., 2006

US Arsenic Regulatory History

EPA adopts standard of 50 ug/L
1975

1988
EPA declares As a carcinogen

Congress passed Safe Drinking Water Act
08-06-1996

10-22-2001
EPA sets new drinking water standard (10 ug/L)

Arsenic rule became effective
03-25-2002

EPA affirms standard (0.010 mg/L)
03-25-2003

10-23-2006
Compliance date for new standard

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National Arsenic Rule

- "National Primary Drinking Water Regulations; Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring" published in Federal Register (66 FR 6976)

- Maximum Contaminant Level (MCL) = 0.010 mg/L
  - Enforceable

- Maximum Contaminant Level Goal (MCLG) = 0 mg/L
  - Non-enforceable

- Applies to public water systems

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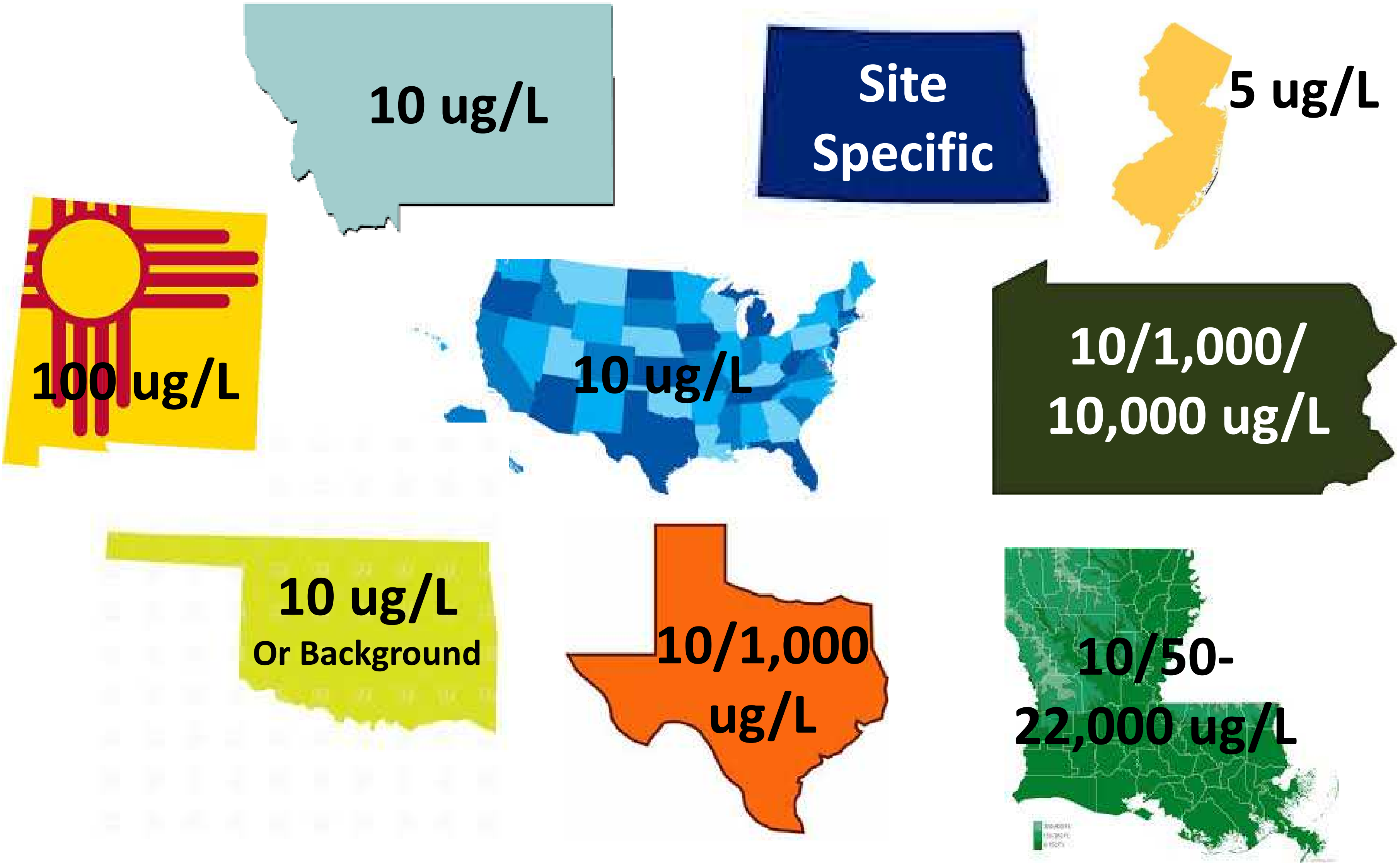
Cleanup Standards by State



Cleanup Standards by State

State	Agency	Standard (ug/L)	Guidance
National	EPA	10	https://federalregister.gov/a/01-1668
Louisiana	Louisiana Department of Environmental Quality	10/50-22,000	http://www.deq.louisiana.gov/portal/Portals/0/technology/recap/2003/RECAP%202003%20Text%20Table%201.pdf
Montana	Montana Department of Environmental Quality	10	http://www.deq.mt.gov/StateSuperfund/PDFs/DEQ7_2012.pdf
New Jersey	NJ Department of Environmental Protection	5	http://www.nj.gov/dep/rules/rules/njac7_9c.pdf
New Mexico	New Mexico Environmental Department	100	http://www.nmenv.state.nm.us/gwb/documents/2062NMAC-Amended2014.pdf
North Dakota	North Dakota Department of Health Waste Management	Site Specific	Chapter 33-16-02.1 Standards of Water Quality of the State
Oklahoma	Oklahoma Department of Environmental Quality	10/Background	http://www.deq.state.ok.us/rules/690.pdf
Pennsylvania	PA Department of Environmental Protection	10/1000/10,000	http://www.pacode.com/secure/data/025/chapter250/chap250toc.html
Texas	Texas Commission on Environmental Quality	10/1000	http://www.tceq.state.tx.us/remediation/trrp/trrppcls.html

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Conclusions

- Arsenic is present in groundwater due to natural and anthropogenic sources
- The two major valence states of arsenic in groundwater are 3+ (arsenite) and 5+ (arsenate) – mobility and toxicity differences
- Arsenic concentrations increase as pH increases, under post-oxic conditions
- Arsenic immobilized under oxidizing conditions, sulfidic conditions
- Regulation of arsenic varies by state
  - No valence state standards

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Sources

- Hughes et al. 2011. Arsenic Exposure and Toxicology: A Historical Perspective. Toxicol. Sci. 123 (2): 305-332.
- Raven et al. 1998. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. Environ. Sci. Technol. 32:344–349.
- Reeder et al. 2006. Reviews in Mineralogy and Geochemistry . 64 (1): 59-113.