Understanding and Minimizing the Potential for Arsenic Mobilization during Aquifer Storage and Recovery

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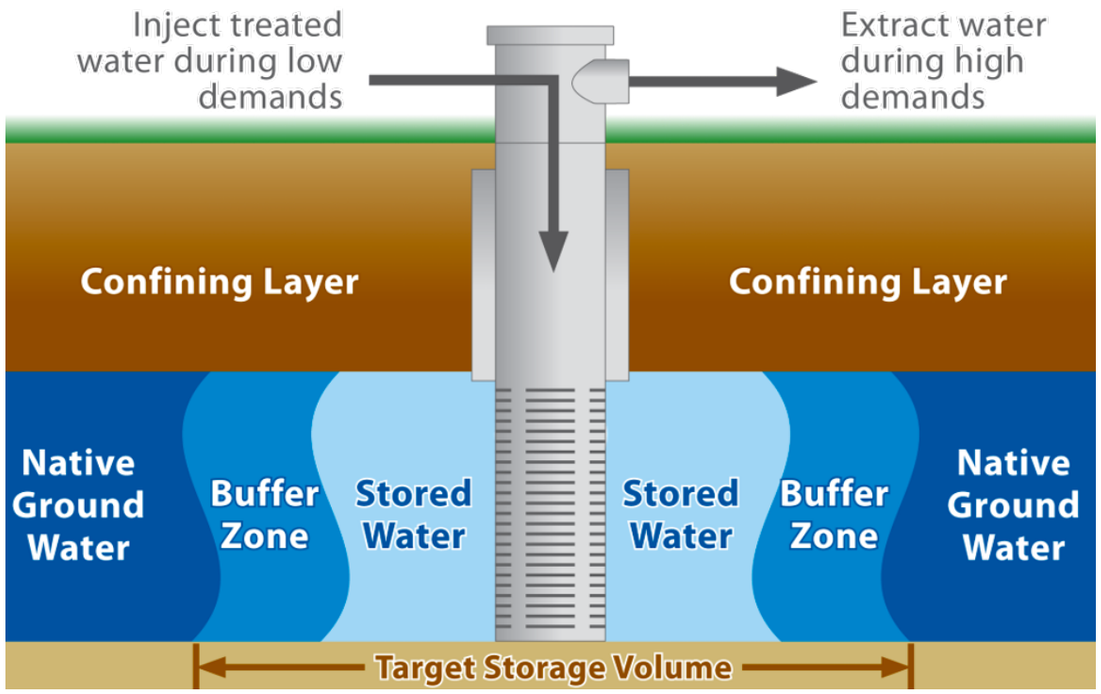
Ground Water Protection Council
ASR-MAR Workgroup

December 2nd, 2021

Aquifer storage and recovery:
an increasingly applied water enhancement strategy

Schematic of an ASR well



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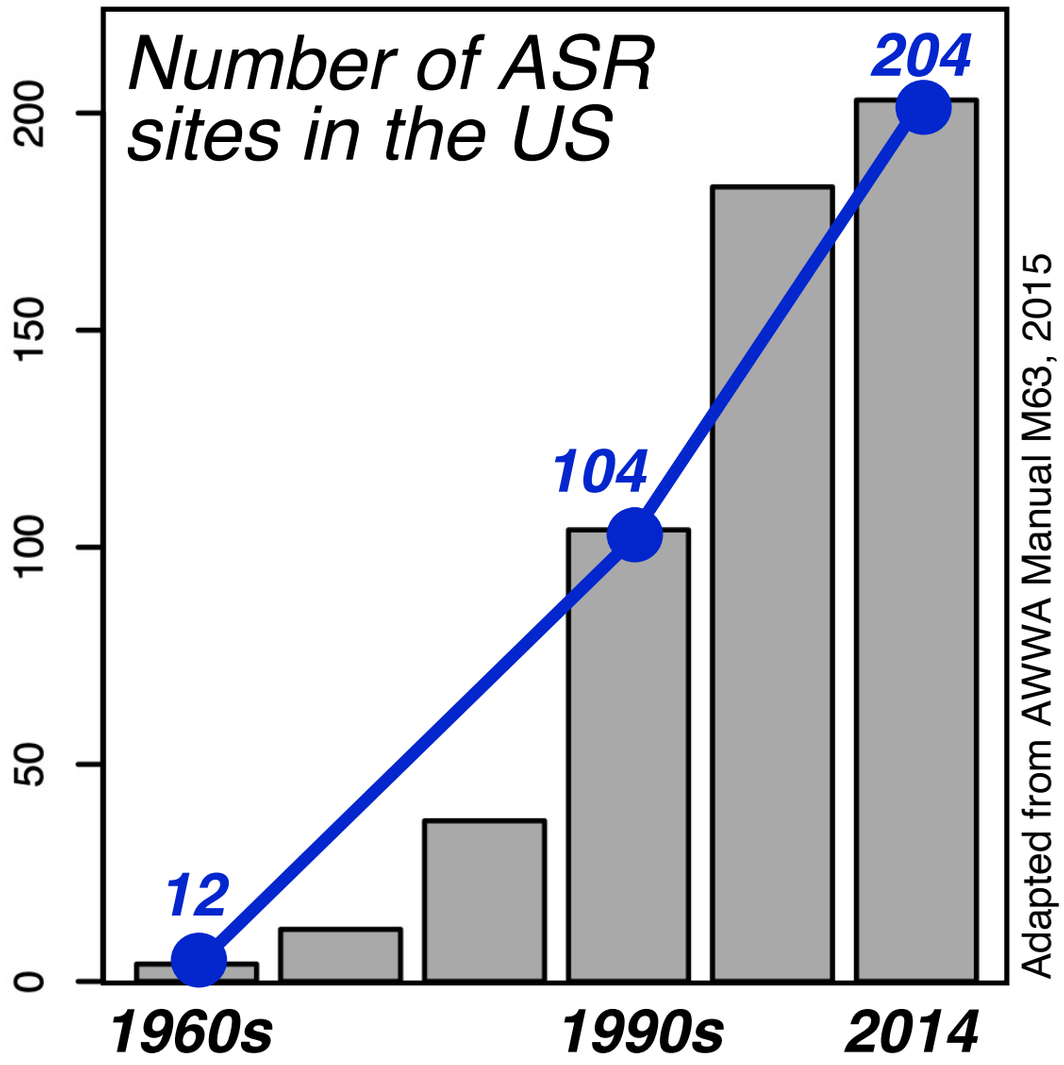
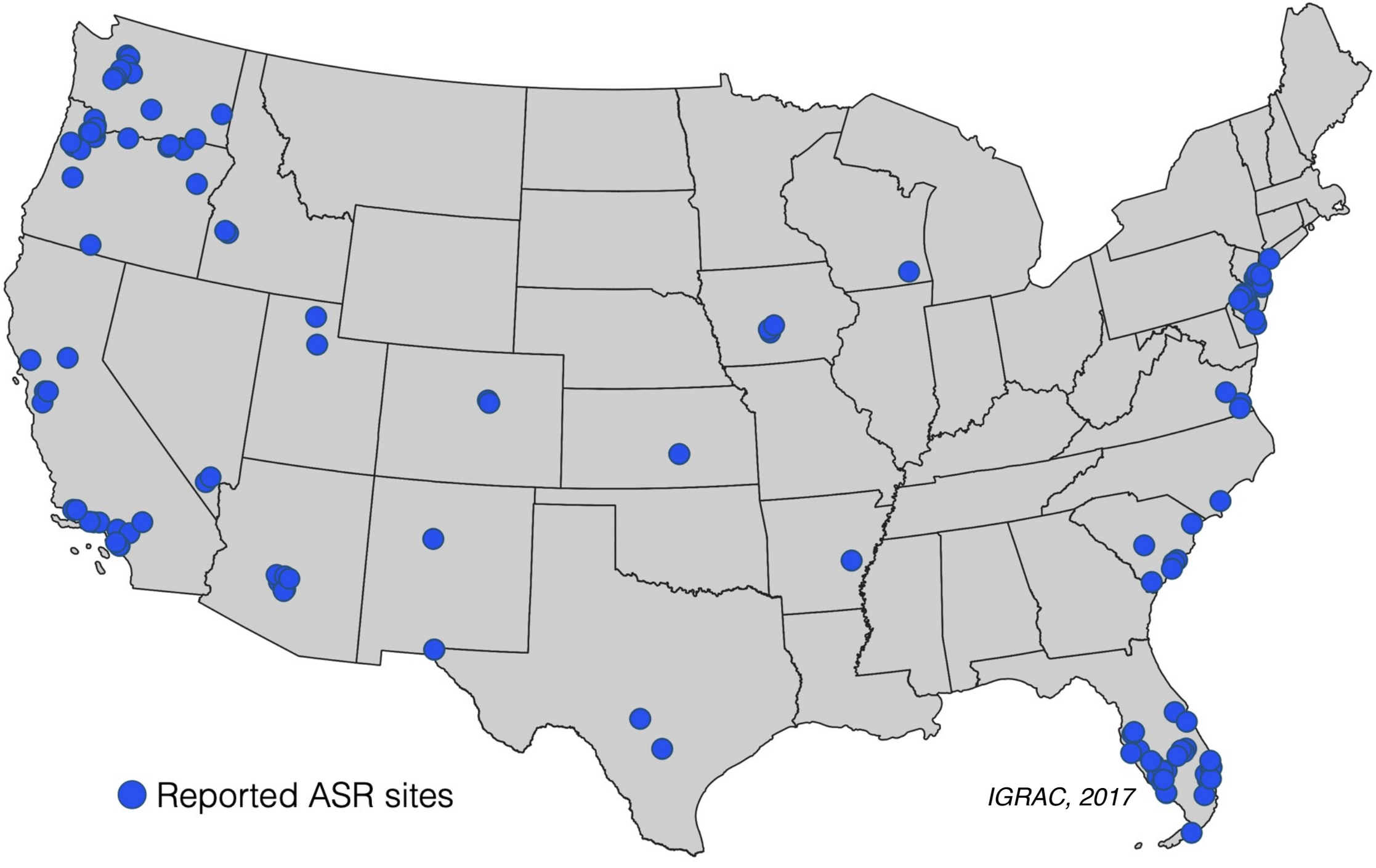
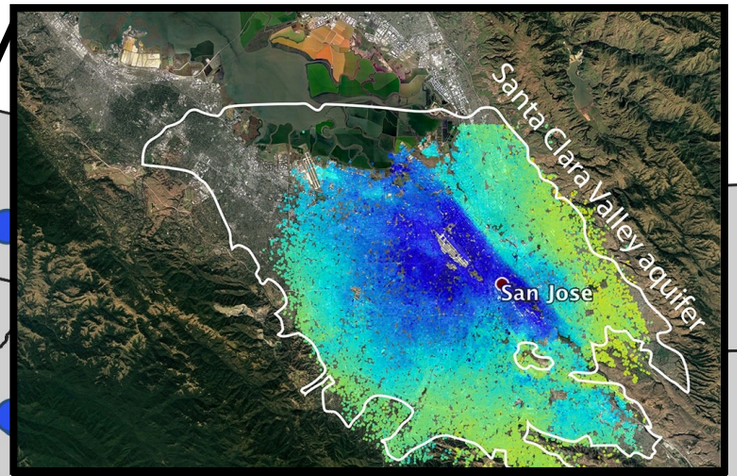


- Federal agencies are encouraging MAR to **mitigate climate risks and ensure water security** (FEMA, 2017; USACE, 2020)
- States, including Texas, Colorado, Oklahoma, and California have **reformed laws and permitting structures** to promote the adoption of ASR (Bray, 2020)

Aquifer storage and recovery:
an increasingly applied water enhancement strategy

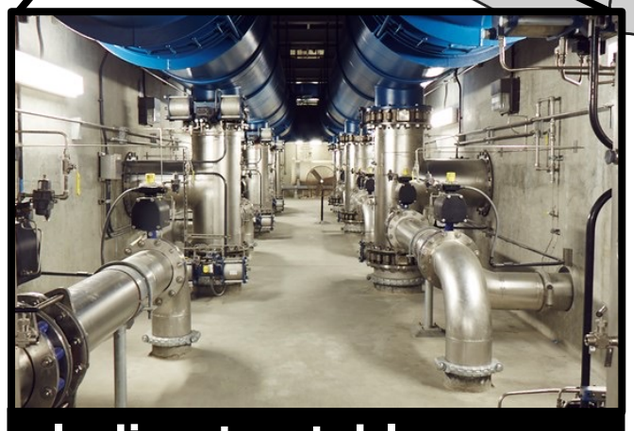


Aquifer storage and recovery:
an increasingly applied water enhancement strategy



Mitigating land subsidence

Ecosystem restoration

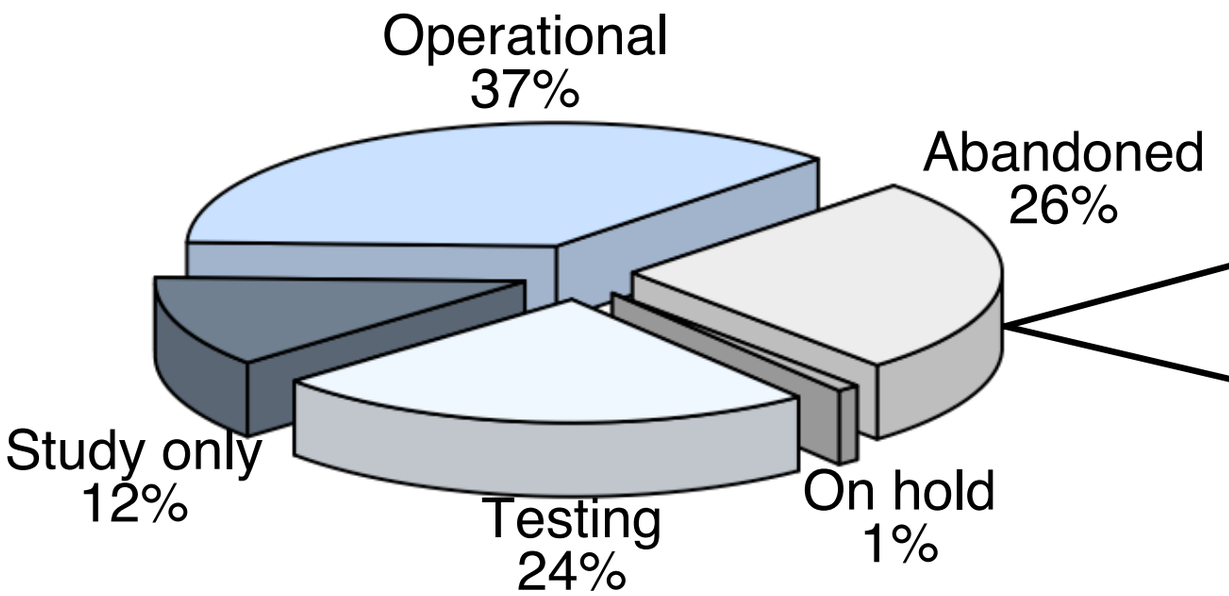


Indirect potable reuse

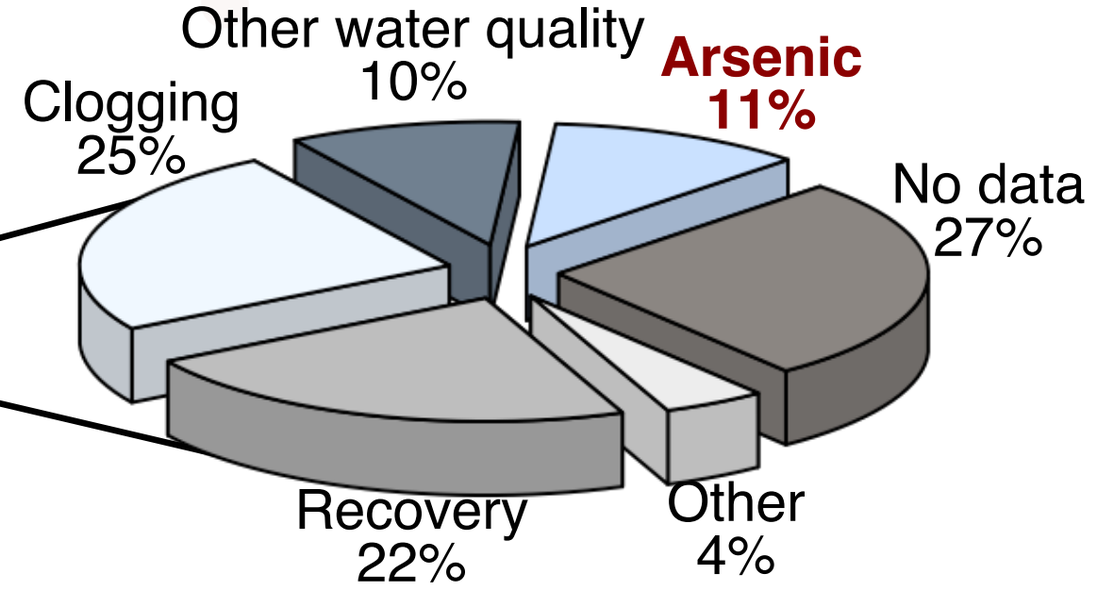
Drought resilience

Naturally-occurring contaminants threaten the viability of aquifer storage and recovery

Status of ASR wells in the US



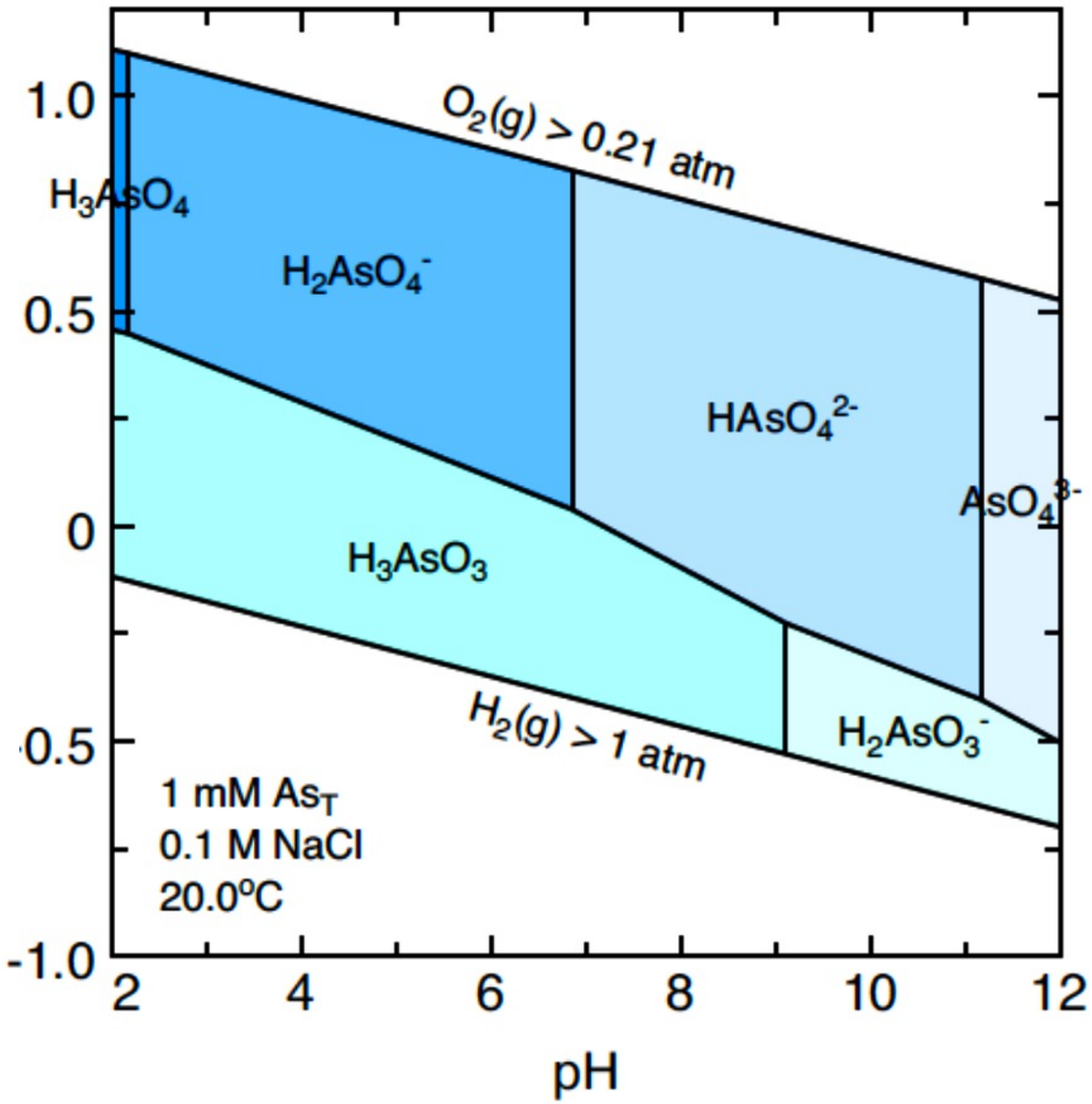
Reasons for abandoning wells



Adapted from Bloetscher et al., 2014

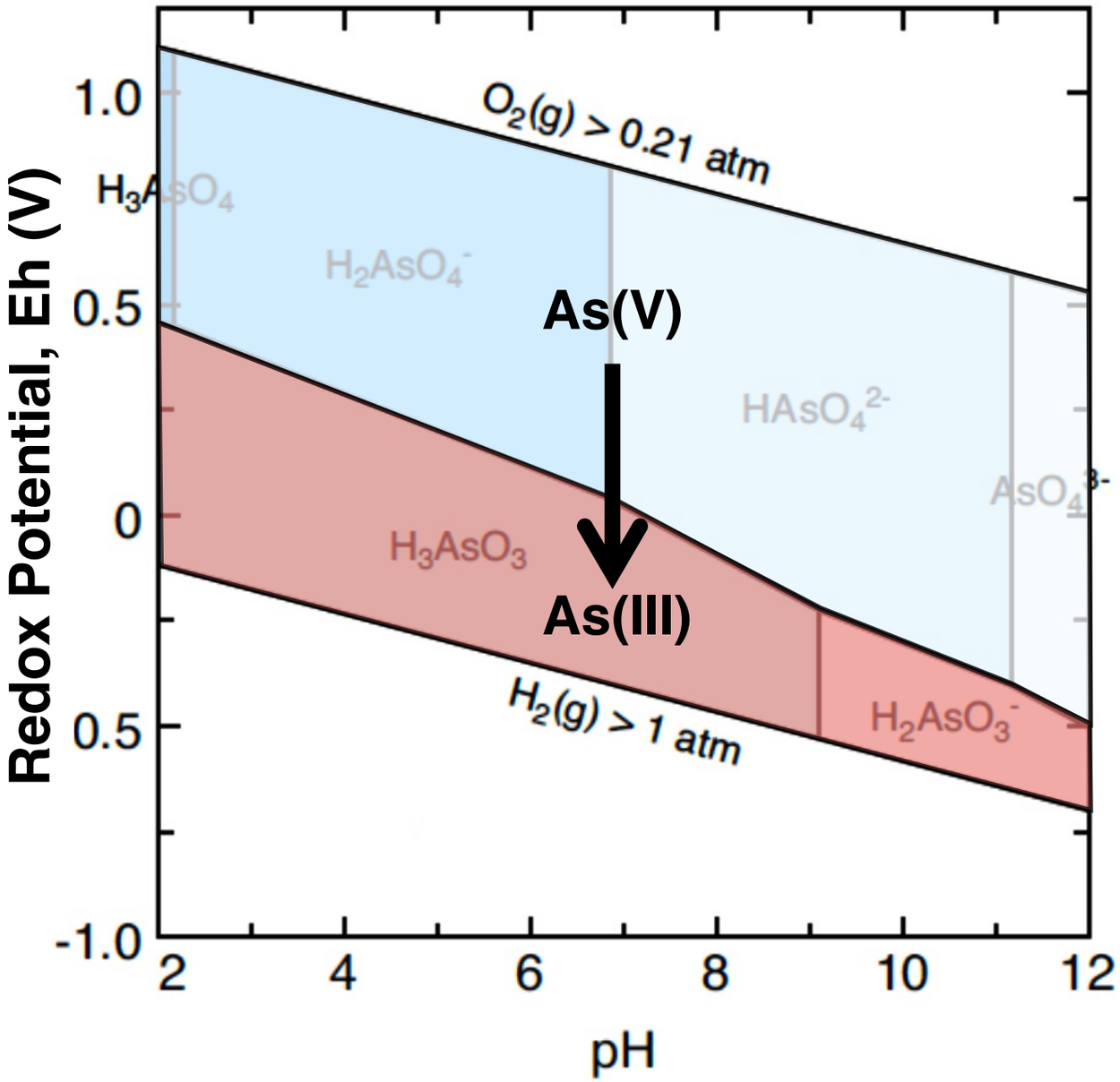
Arsenic poses a particular threat to aquifer storage and recovery

Challenges to addressing potential arsenic mobilization during ASR



- Toxic, naturally occurring contaminant
- Native to sediments around the world (3-10 mg/kg average concentration globally)
- 10 µg/L drinking water limit but no lower limit for health
- Mobility and toxicity depend on redox state
  - As(V) → less mobile, less toxic
  - As(III) → more mobile, more toxic

Naturally-occurring arsenic mobilization during managed aquifer recharge



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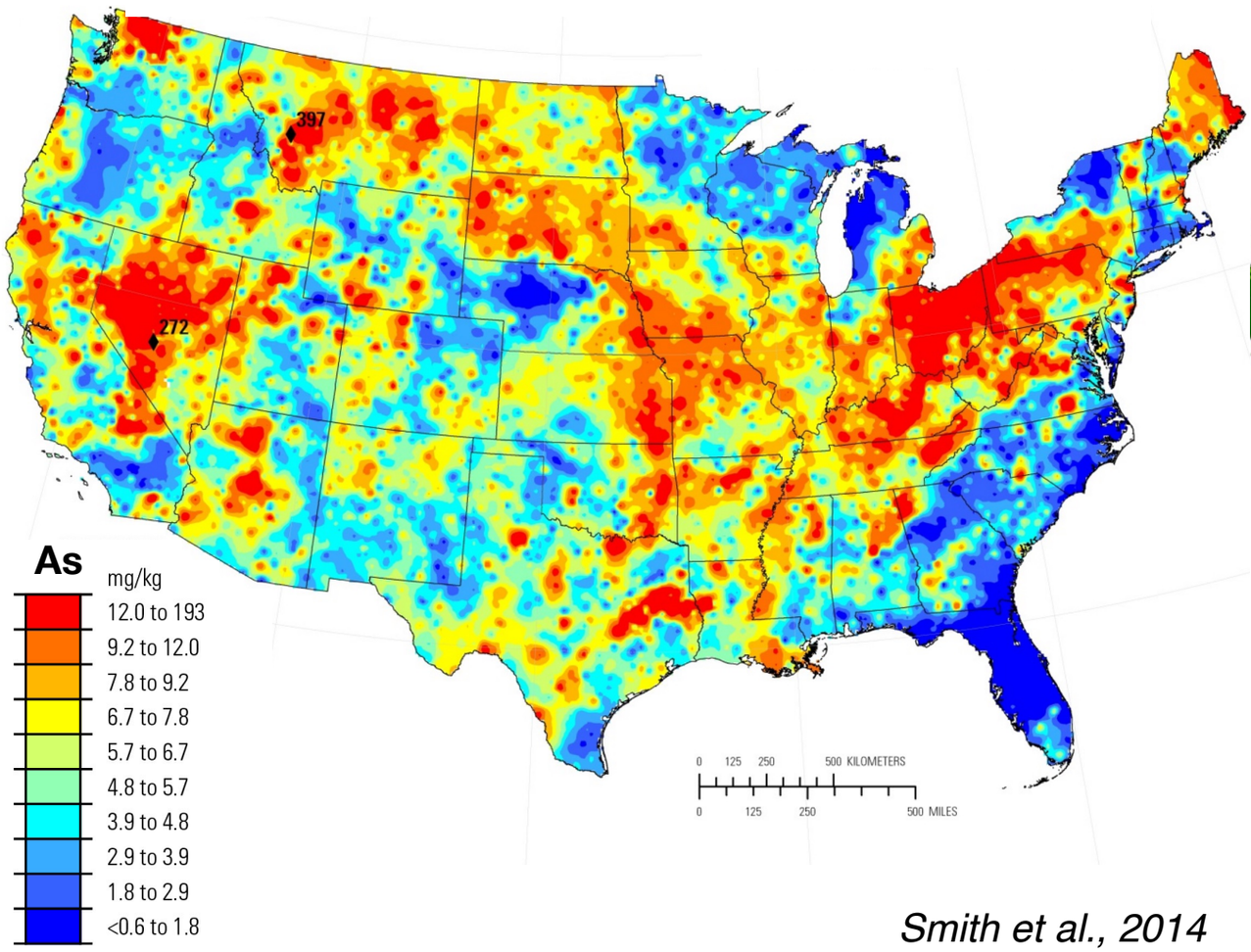
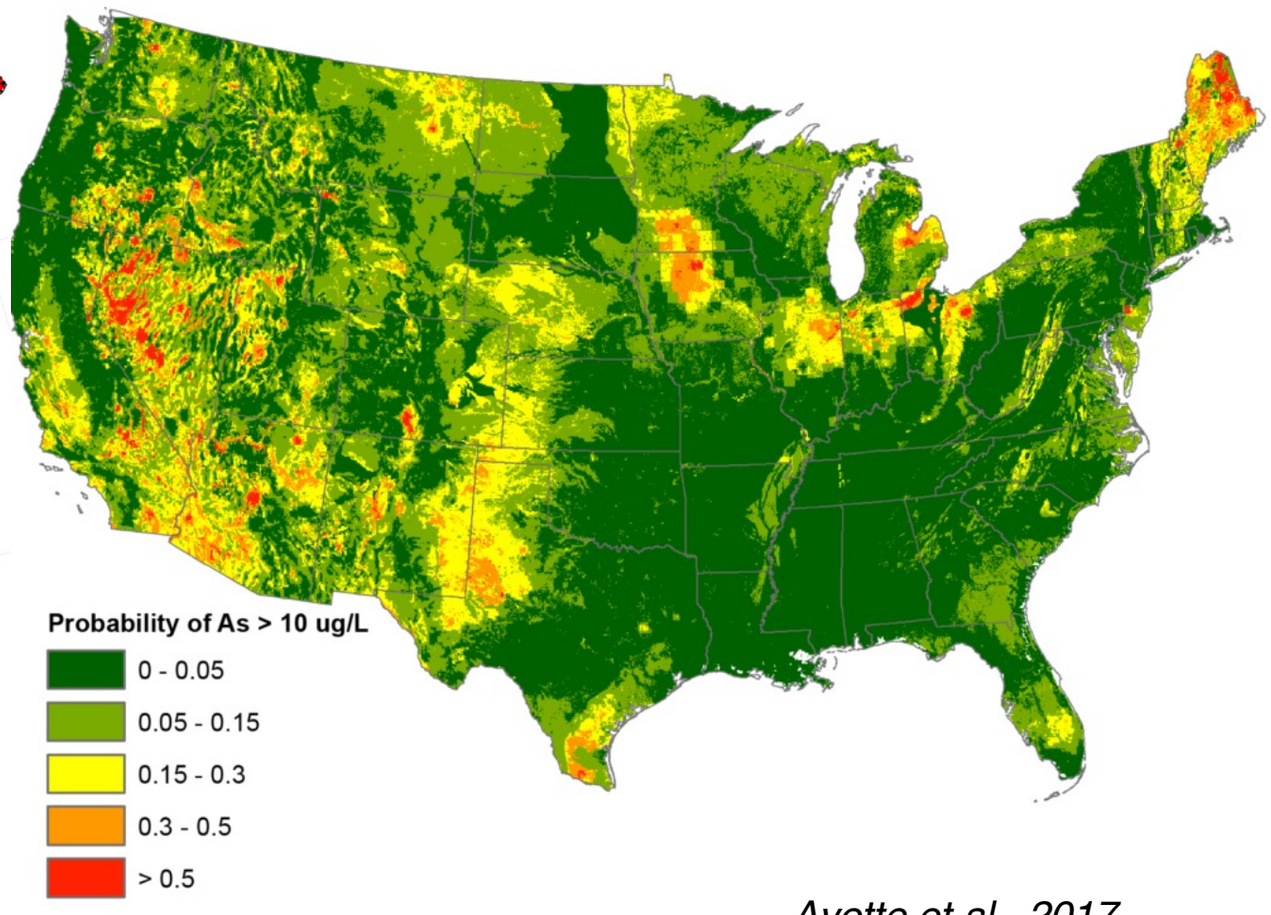
Site-specific biogeochemical conditions

Arsenic in soils



Smith et al., 2014

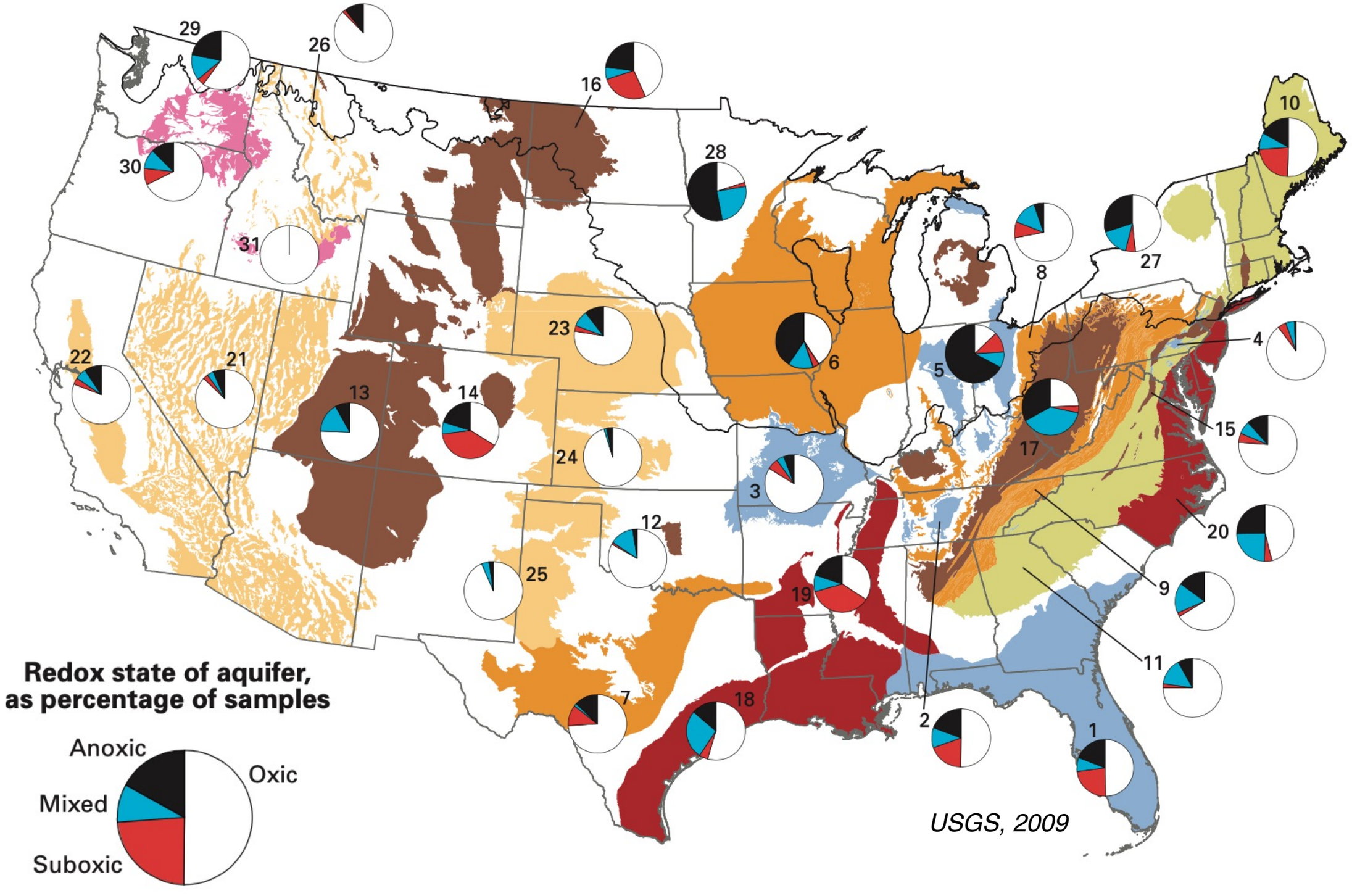
Arsenic in groundwater



Ayotte et al., 2017

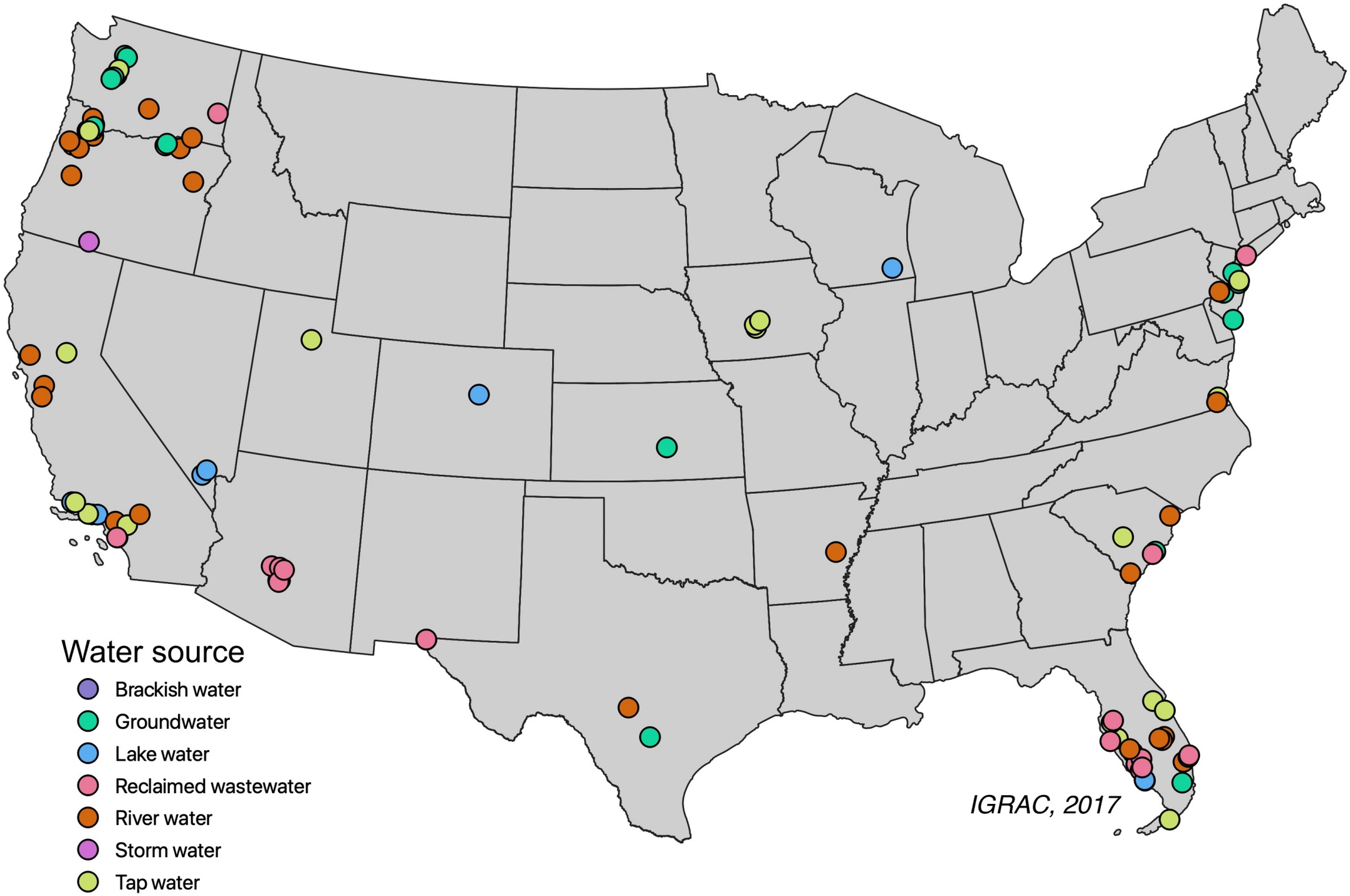
Biogeochemical conditions determine whether arsenic remains in aquifer solids or mobilizes to groundwater

Site-specific biogeochemical conditions

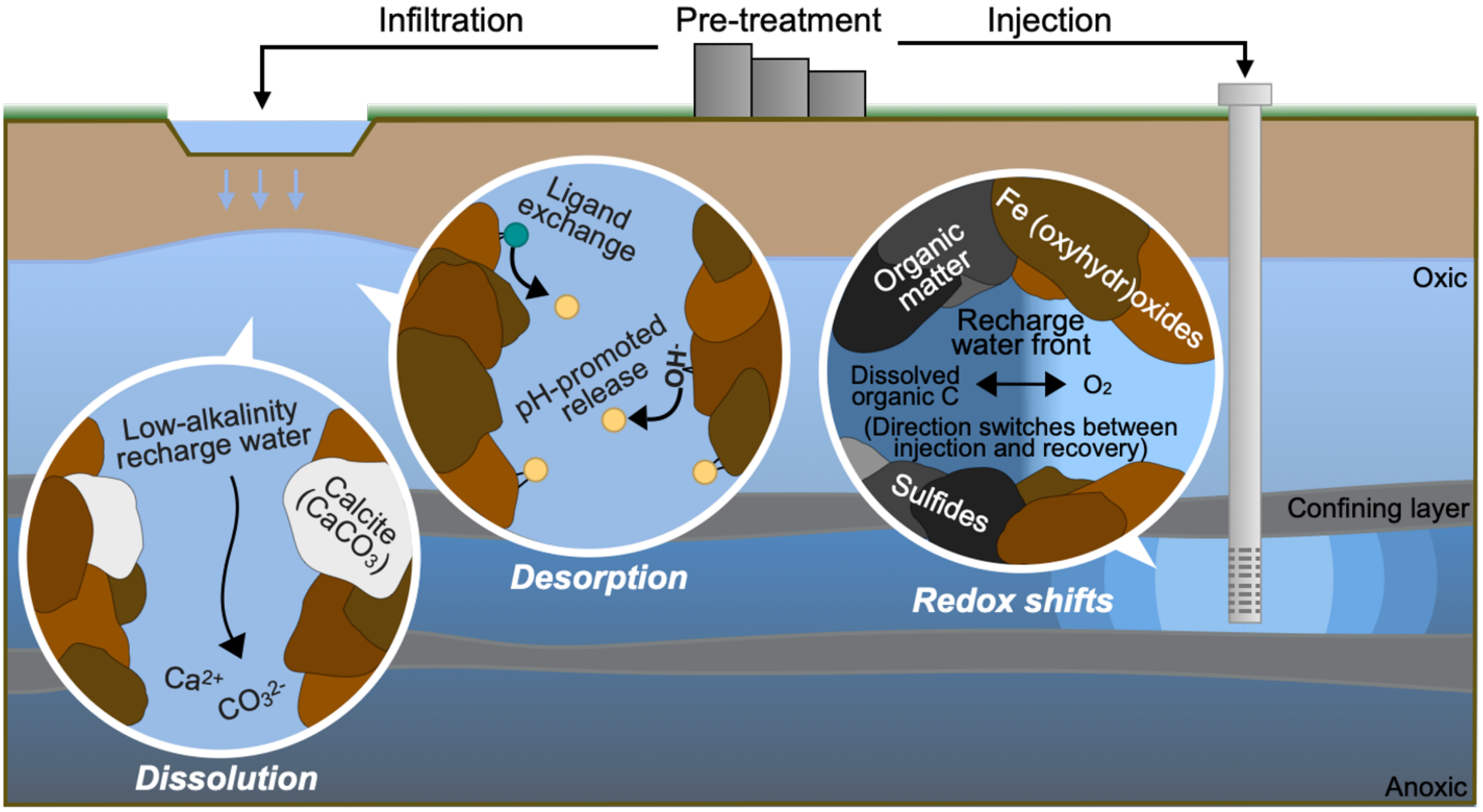


Various redox conditions in selected principal aquifers

Site-specific operational conditions



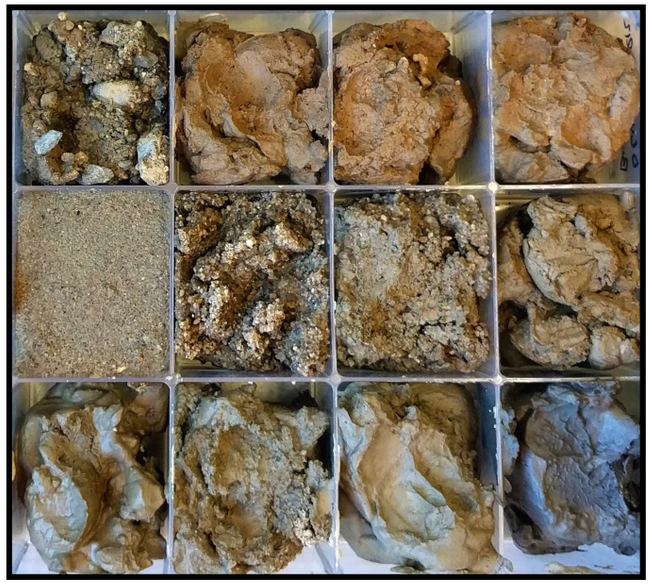
Site-specific biogeochemical compatibility



Fakhreddine et al., 2021

Various biogeochemical processes can occur between injection water and aquifer solids that control the mobility of natural and anthropogenic contaminants

Challenges to addressing potential arsenic mobilization during ASR



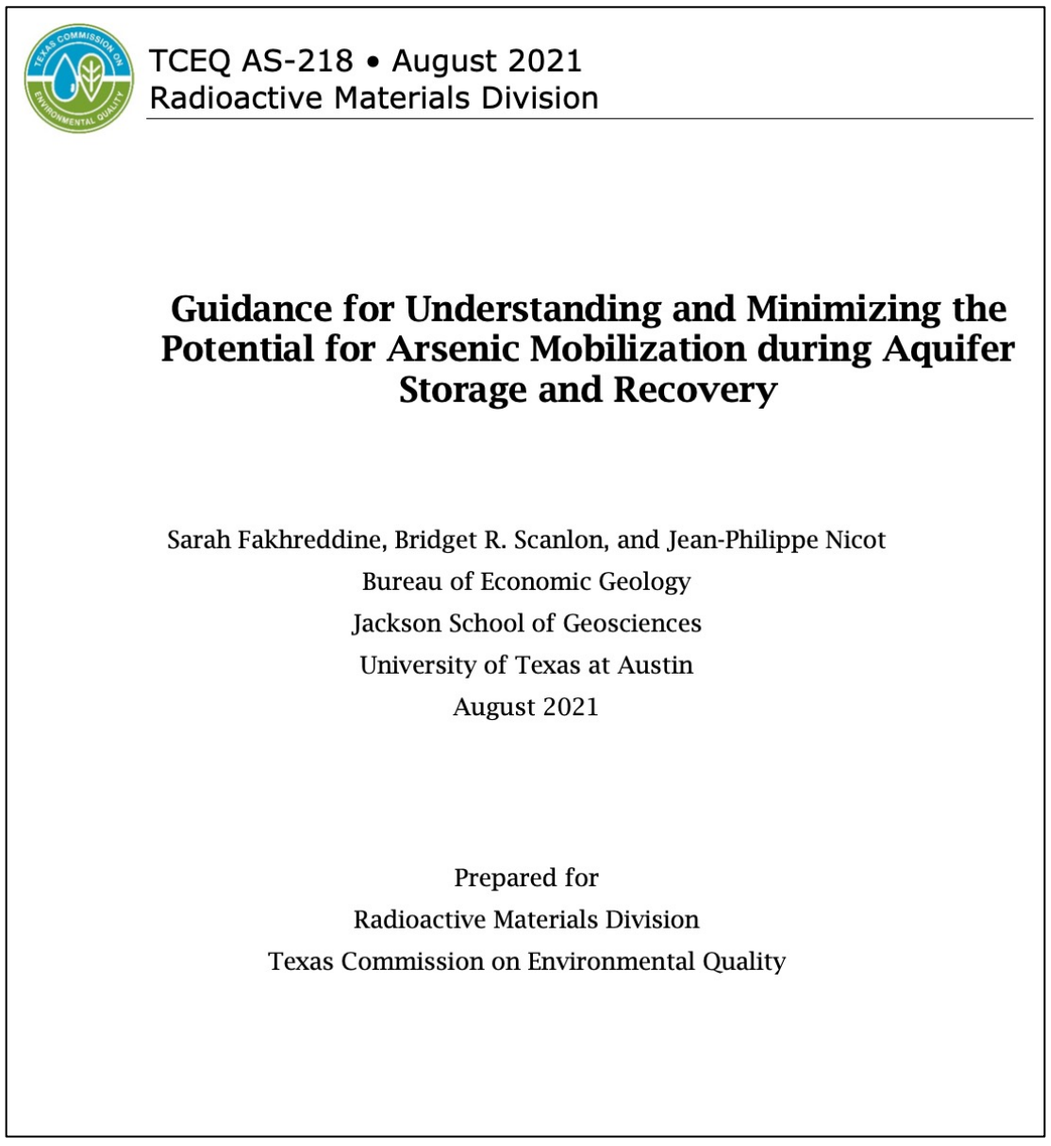
1. Arsenic is ubiquitous in soils and sediments and toxic at trace concentrations

2. Geochemical and hydrogeologic properties are highly heterogenous and site-specific

3. Subsurface data are often difficult and costly to obtain

4. Requires domain-specific geochemical knowledge

Guidance document objectives



TCEQ AS-218 • August 2021
Radioactive Materials Division

Guidance for Understanding and Minimizing the Potential for Arsenic Mobilization during Aquifer Storage and Recovery

Sarah Fakhreddine, Bridget R. Scanlon, and Jean-Philippe Nicot
Bureau of Economic Geology
Jackson School of Geosciences
University of Texas at Austin
August 2021

Prepared for
Radioactive Materials Division
Texas Commission on Environmental Quality

1. Provide understanding of geochemical processes controlling water quality during ASR

   How is arsenic mobilized at ASR sites? What to look out for?

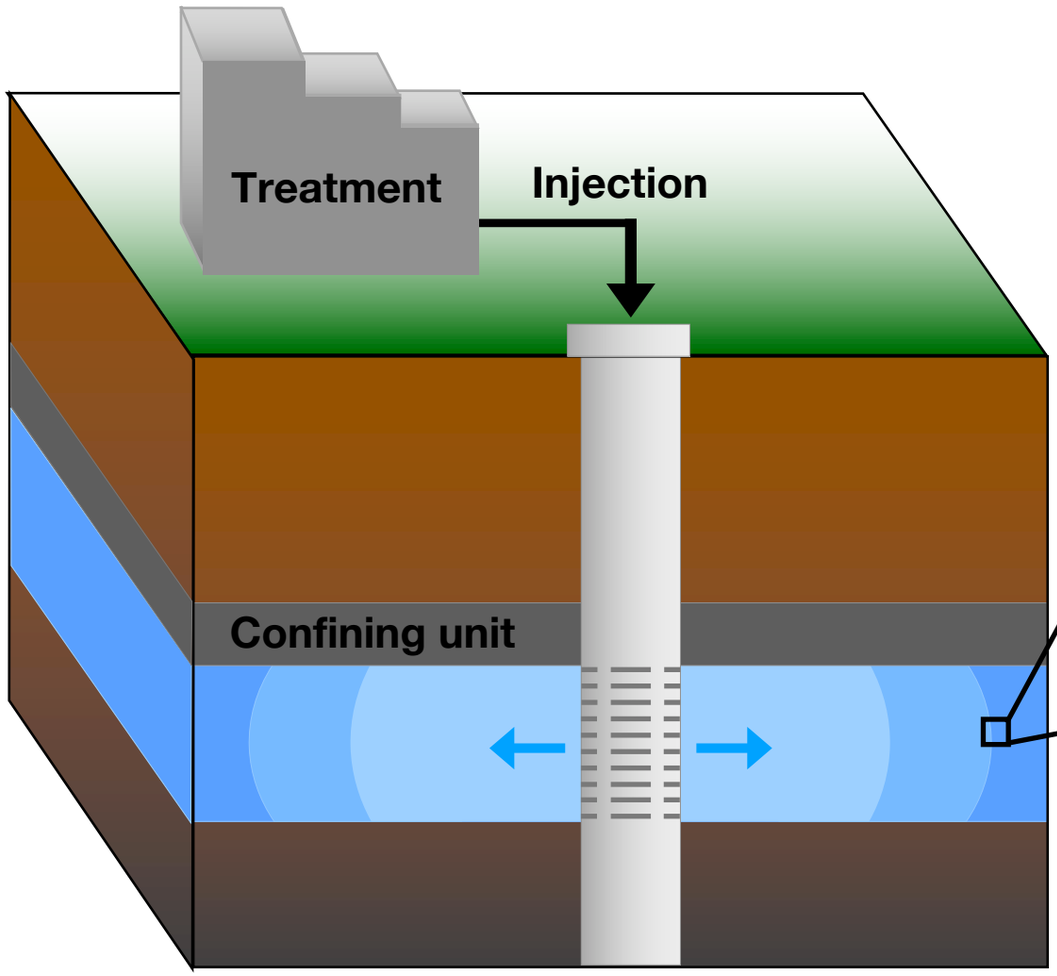
2. Develop framework for site-specific conceptualization of potential arsenic mobilization including geochemical assessments

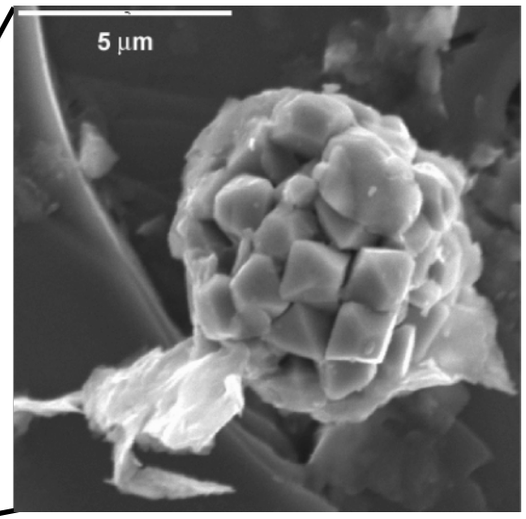
   How to collect the relevant data? How to make sense of it? Assessing risks?

3. Provide general guidance on monitoring and site assessment

   How to prevent problems? Collecting relevant data over time and updating conceptual model?

Most ASR sites attribute arsenic mobilization to the dissolution of arsenic-bearing sulfidic minerals



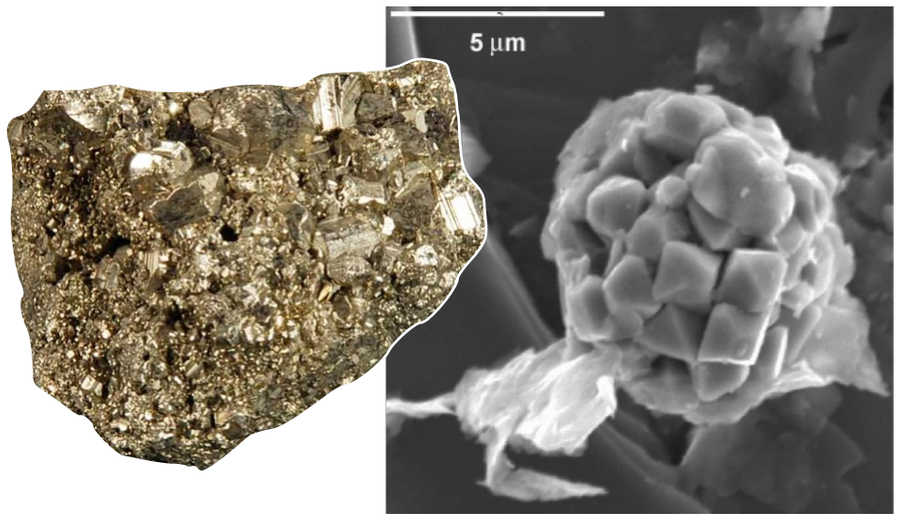


Arsenian pyrite
Fe[As,S]$_2$

The majority of ASR projects into native suboxic or anoxic, confined or semi-confined aquifers (ASR Systems & SFWMD, 2007)

Arsenic repartitioning during injection

Reduced



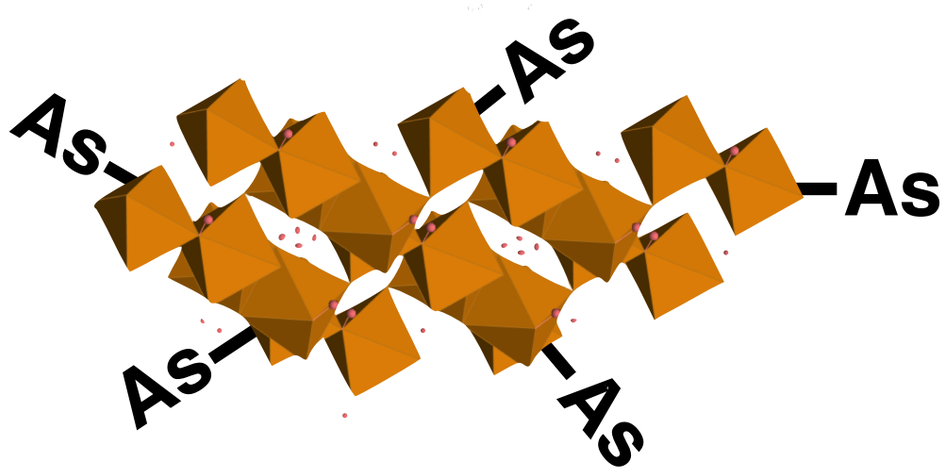
Arsenian pyrite

Fe[As,S]$_2$

O_2

NO_3^-

Oxidized



Strong sorption affinity of arsenic to Fe-(hydr)oxides

Except:
- shifts in redox
- increases in pH (> 8.5)
- competitive ion displacement

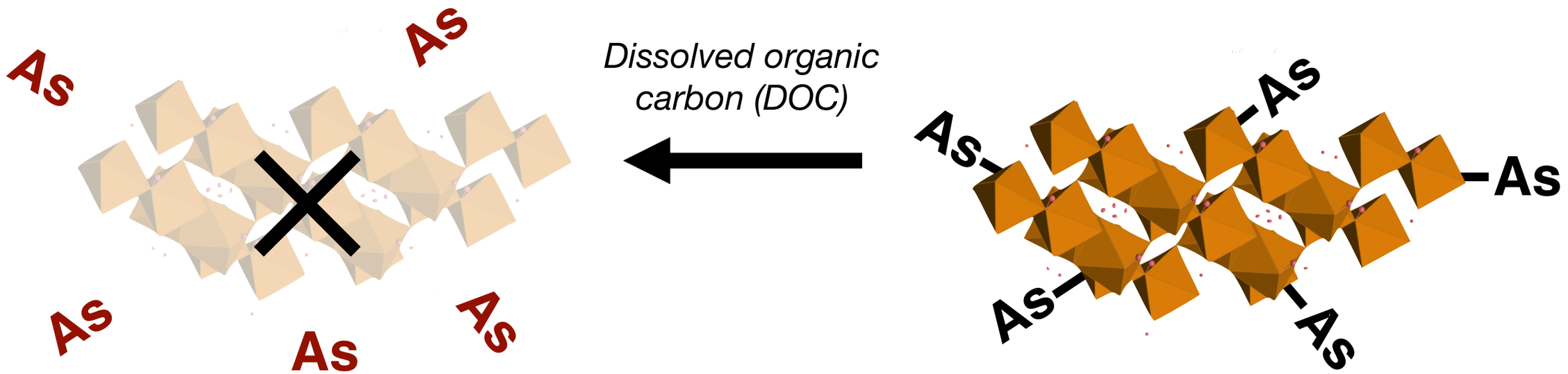
$$FeS_2 + 3.75O_2 + 3.5H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+$$

$$FeS_2 + 3NO_3^- + 2H_2O = Fe(OH)_3 + 2SO_4^{2-} + 1.5N_2 + H^+$$

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

Arsenic repartitioning during injection

Reductive Dissolution of Fe-(hydr)oxides



Strong sorption affinity of arsenic to Fe-(hydr)oxides

Except:
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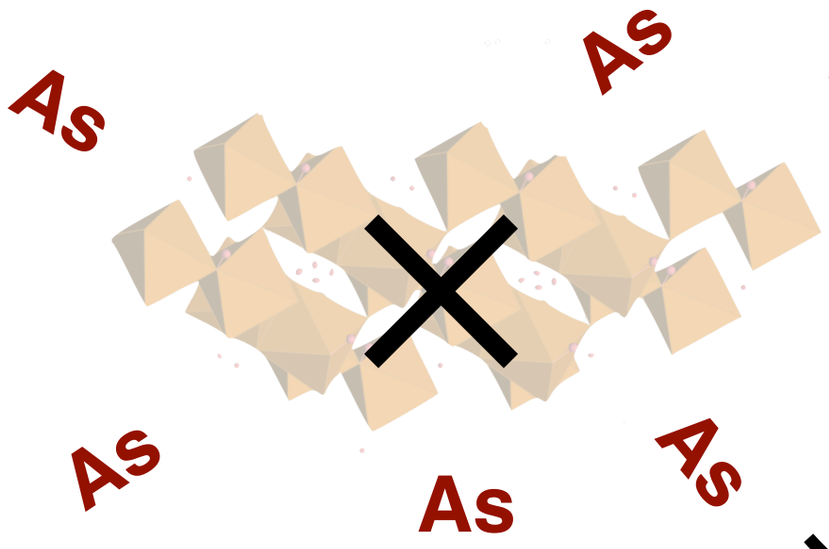
- increases in pH (> 8.5)
- competitive ion displacement

$$2Fe(OH)_3 \equiv H_2AsO_4^- + CH_2O \rightarrow 2Fe^{2+} + HCO_3^- + H_3AsO_3 + 2H_2O$$

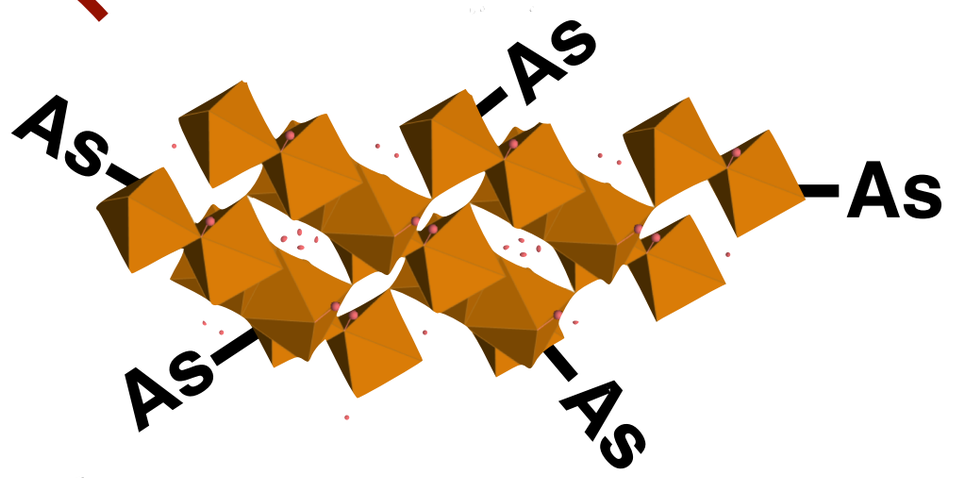
Arsenic mobilization during injection

Mobile
(Reduced during recovery and/or storage)



Reductive dissolution of Fe-(hydr)oxides and/or reduction of As(V) to As(III)

Immobile
(Oxidized during injection)

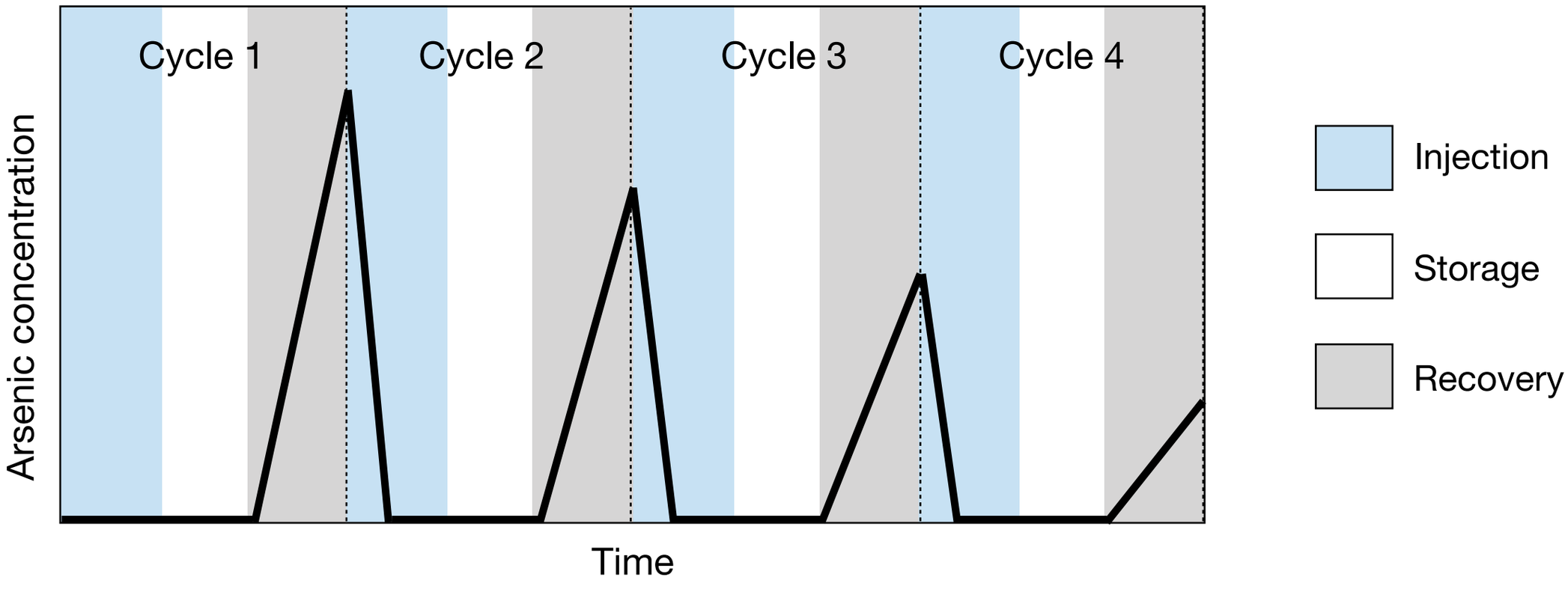


Strong sorption affinity of arsenic to Fe-(hydr)oxides

Can oscillate between immobile (oxic) conditions during injection and mobile (reducing) conditions during storage and recovery

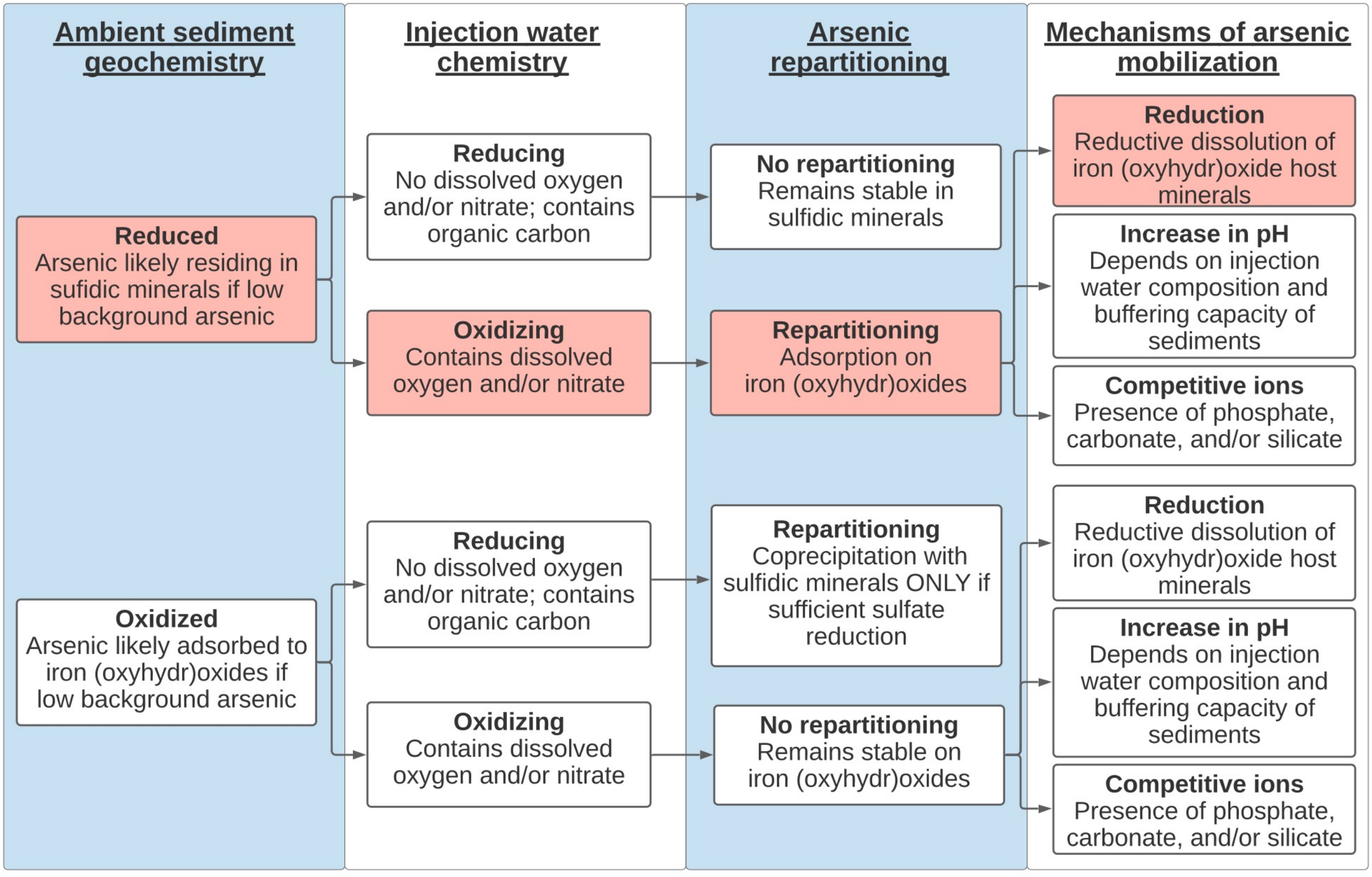
Temporal trends in arsenic mobilization

Simplified schematic of temporal trends in arsenic mobilization during ASR

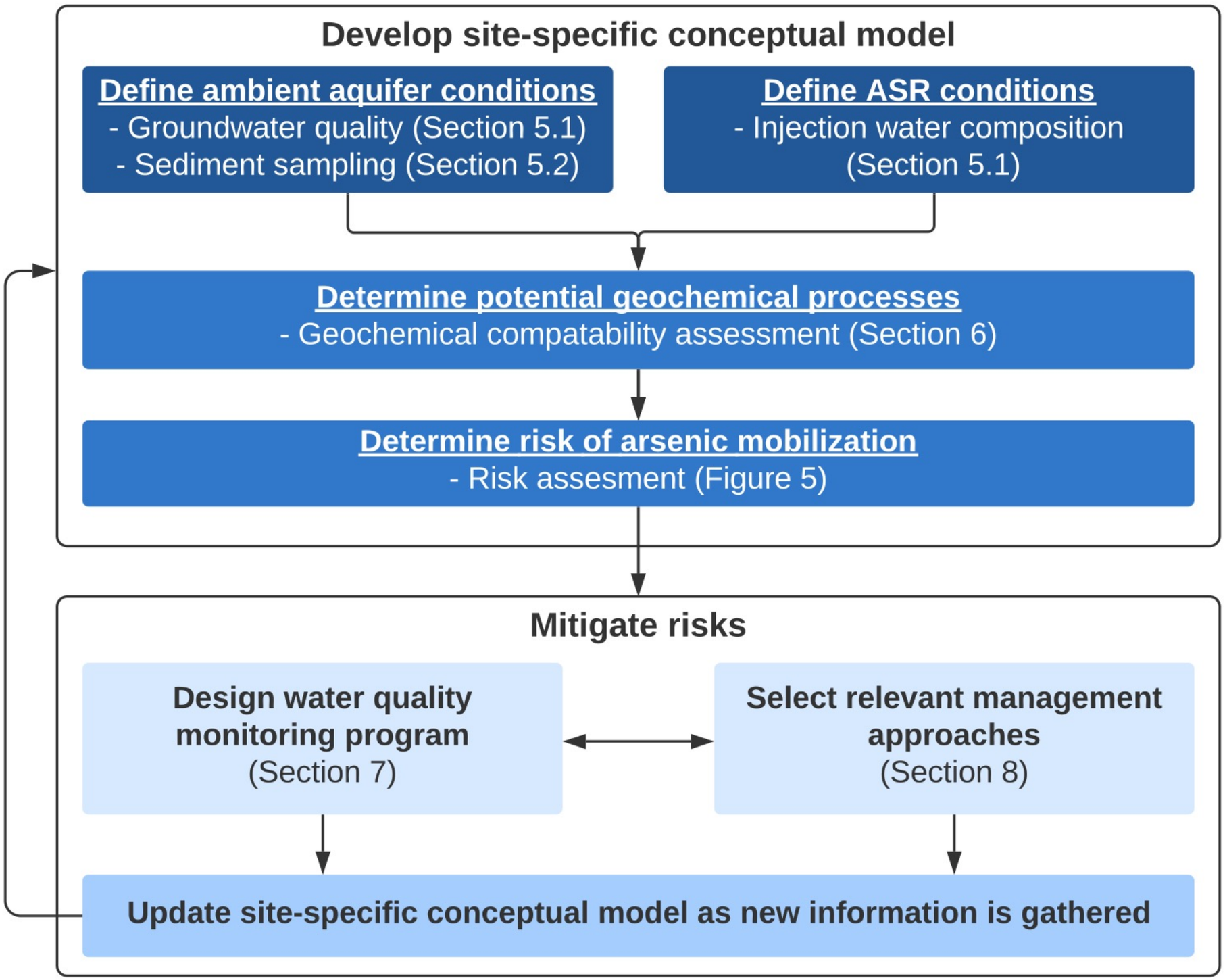


For ASR projects operated consistently (storage volumes, injection water quality, timing of cycles) arsenic concentrations can attenuate over time due to depletion of reactive fraction of arsenic-bearing pyrite and/or surface passivation of pyritic minerals

Summary of pathways of arsenic mobilization during ASR



Developing site-specific conceptual model



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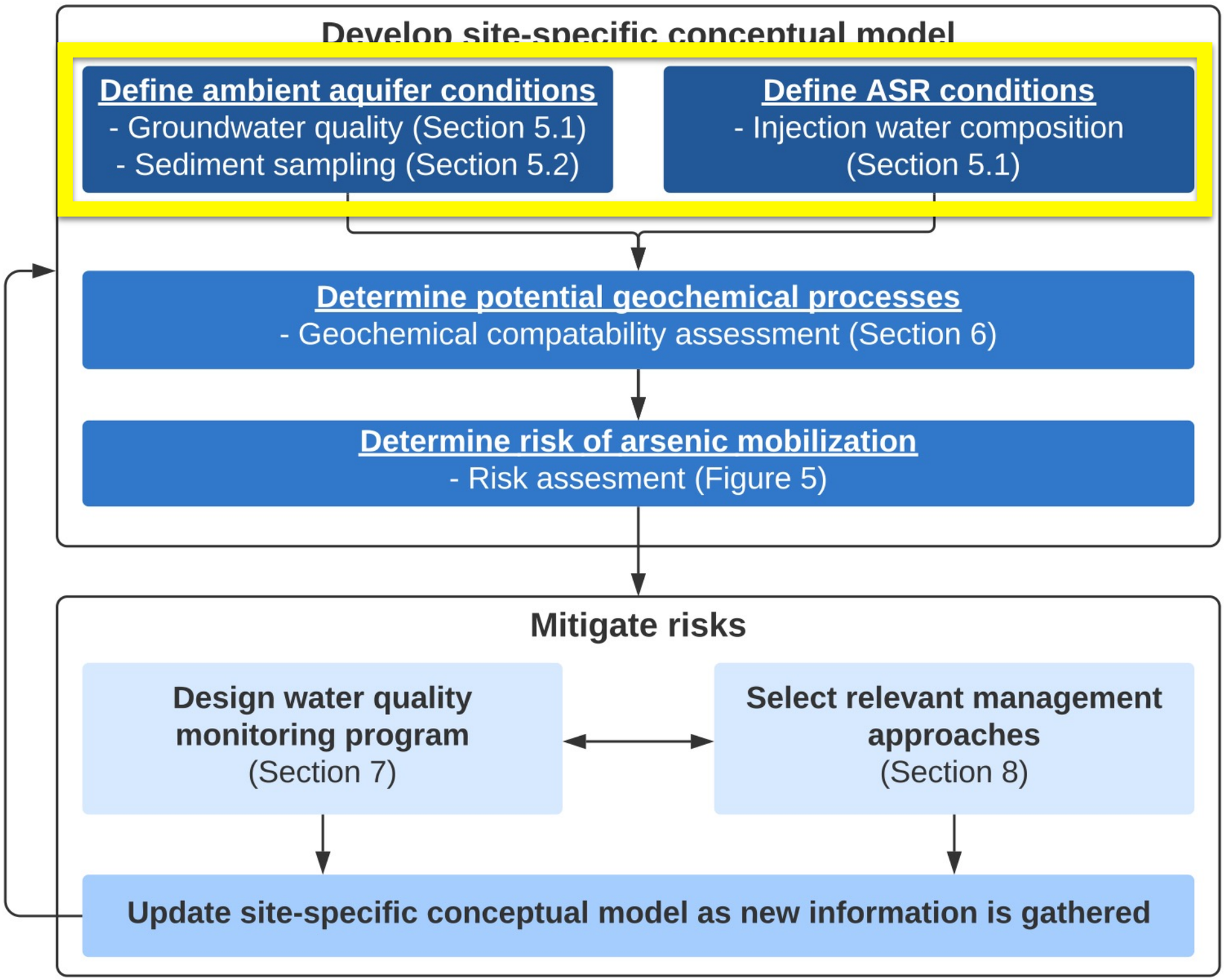
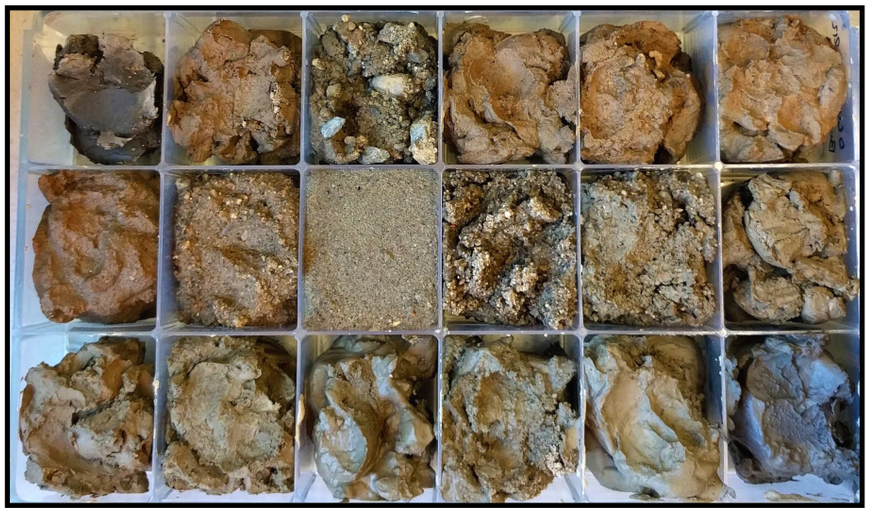


Defining ambient geochemistry and injection water composition



Sediment collection and sampling

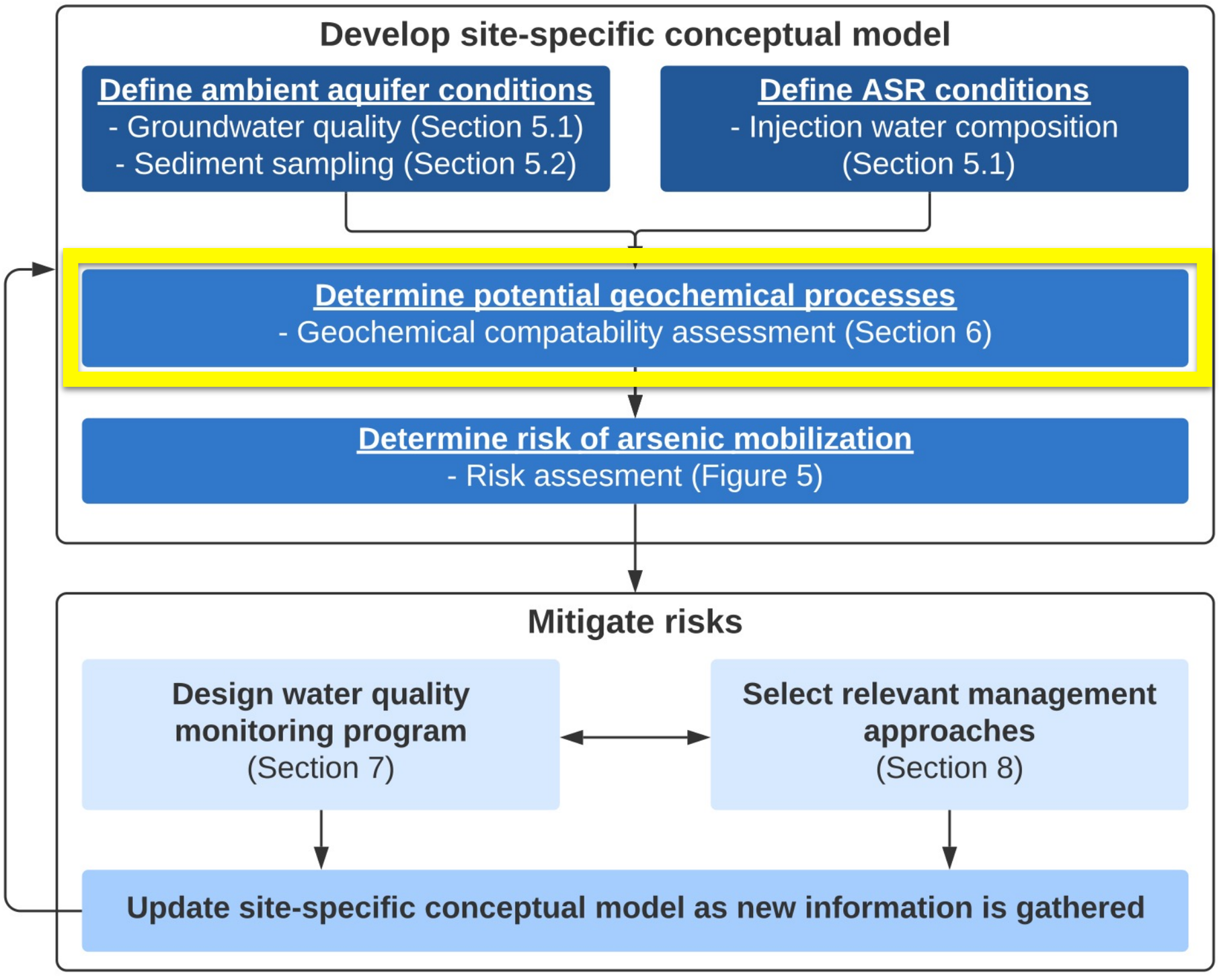
- Cores and drill cuttings
- Total arsenic concentration, speciation, and mineralogy of samples
- Methods including XRD, XRF, sequential extractions (various detection limits)

Aqueous sampling

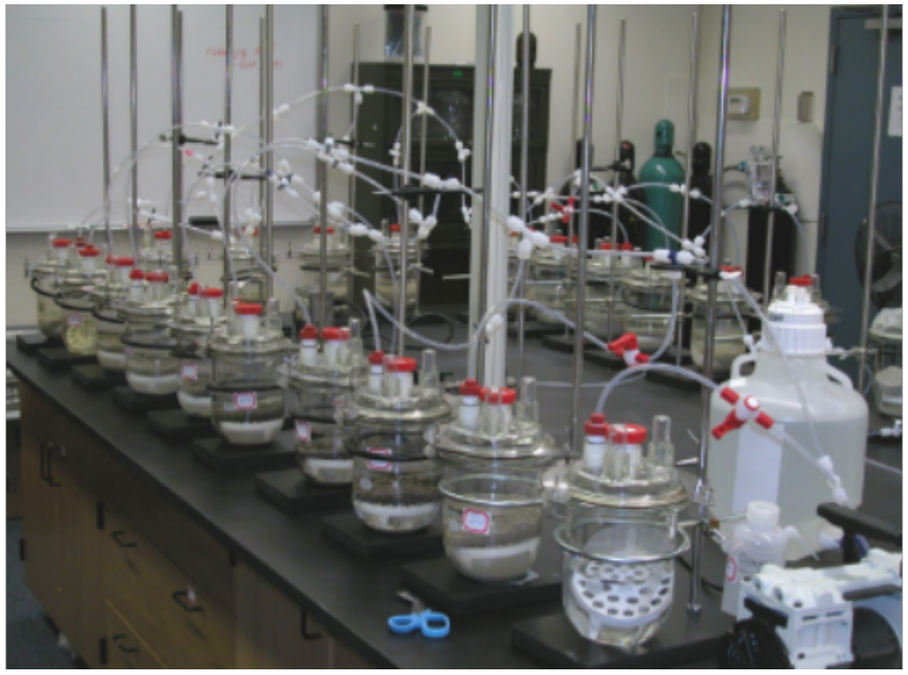
- Key analytes
- Redox: oxidation reduction potential, dissolved oxygen, nitrate, organic carbon
- pH and ionic composition

Interpreting solid and aqueous data together provides greatest insights to understanding biogeochemical conditions

Developing site-specific conceptual model



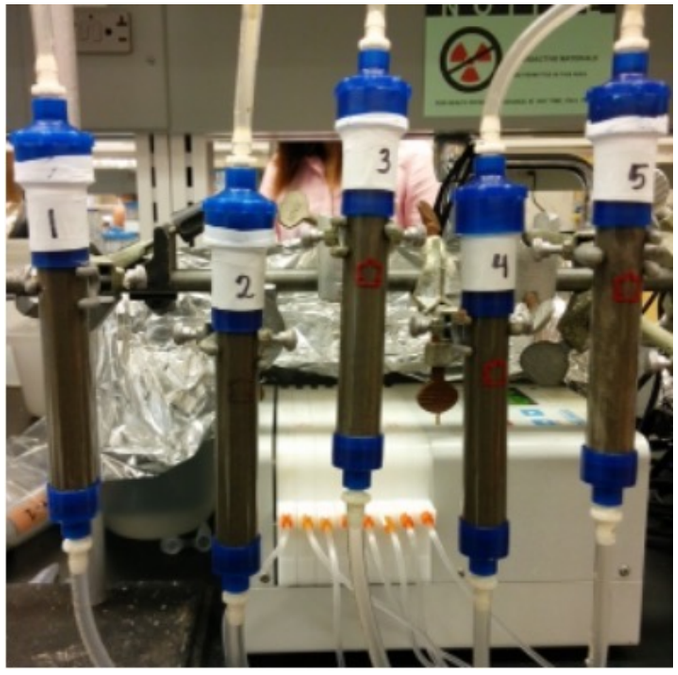
Assessing geochemical compatibility: Laboratory experiments



Florida Geological Survey

Batch experiments

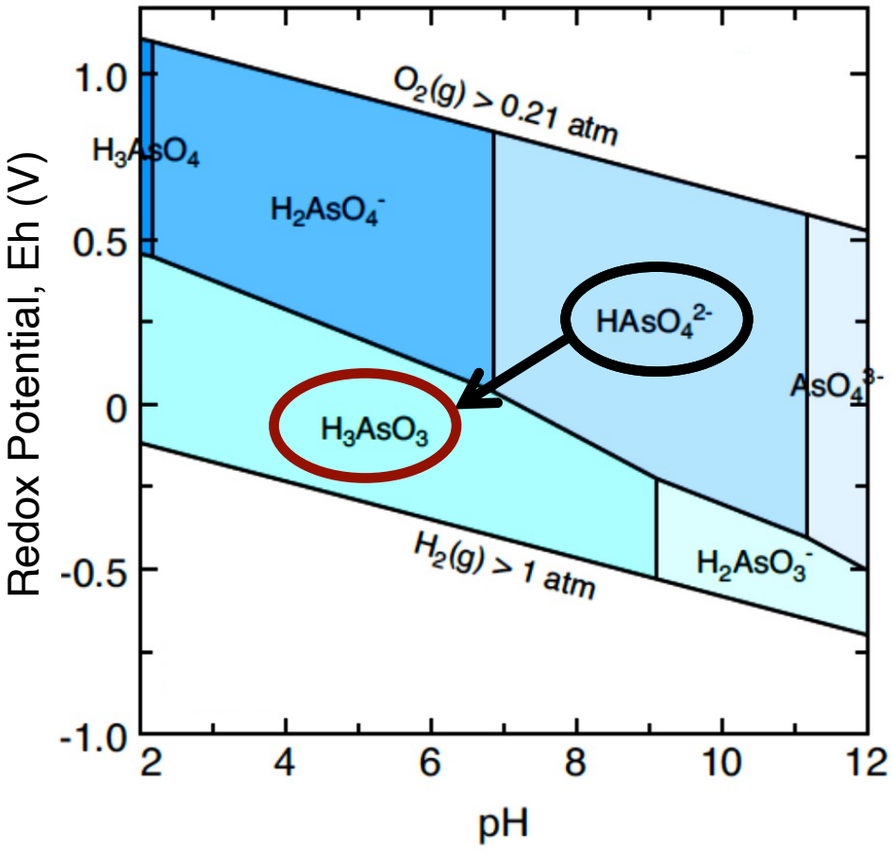
- Simple mixing/leaching experiments
- Equilibrium conditions
- Not fully representative of *in situ* conditions (e.g., transport, ASR cycling, solid to solution ratio)

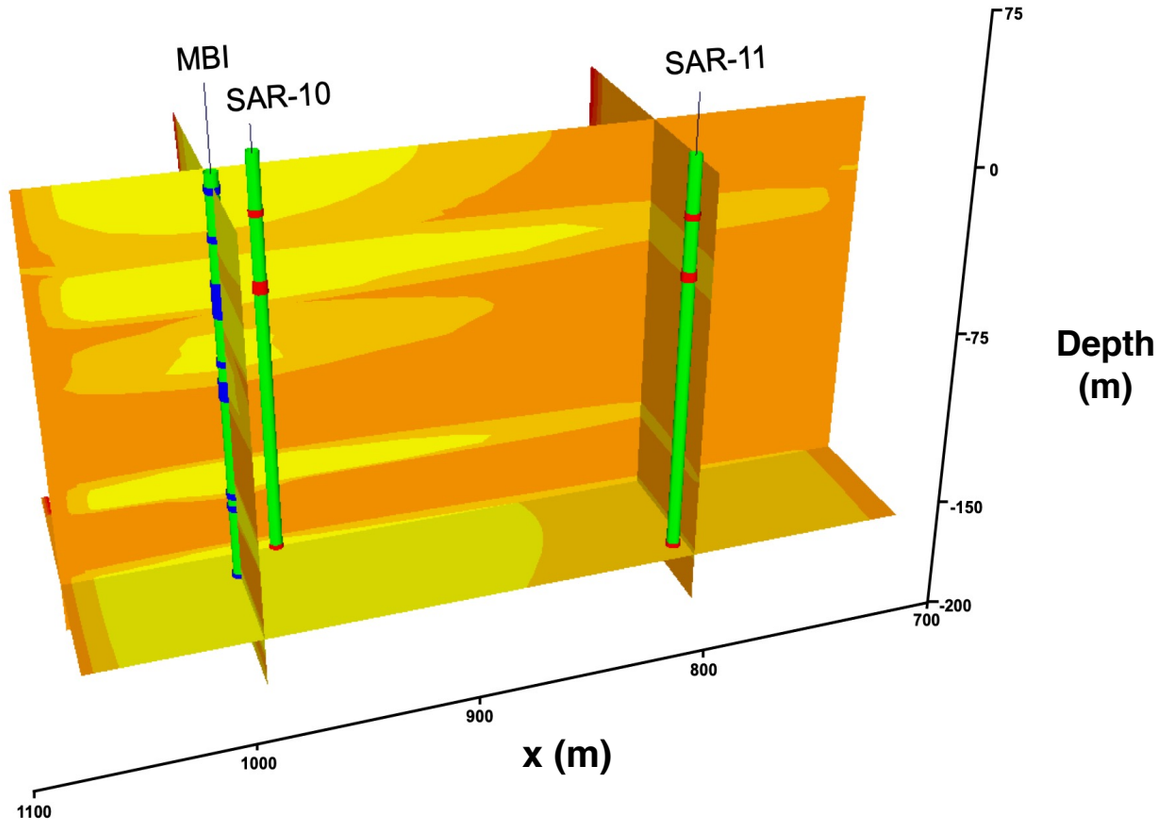


Column experiments

- Incorporates transport/kinetics
- Can experimentally simulate ASR cycling under various conditions (e.g., water composition, porewater velocities)

Assessing geochemical compatibility: Geochemical modeling





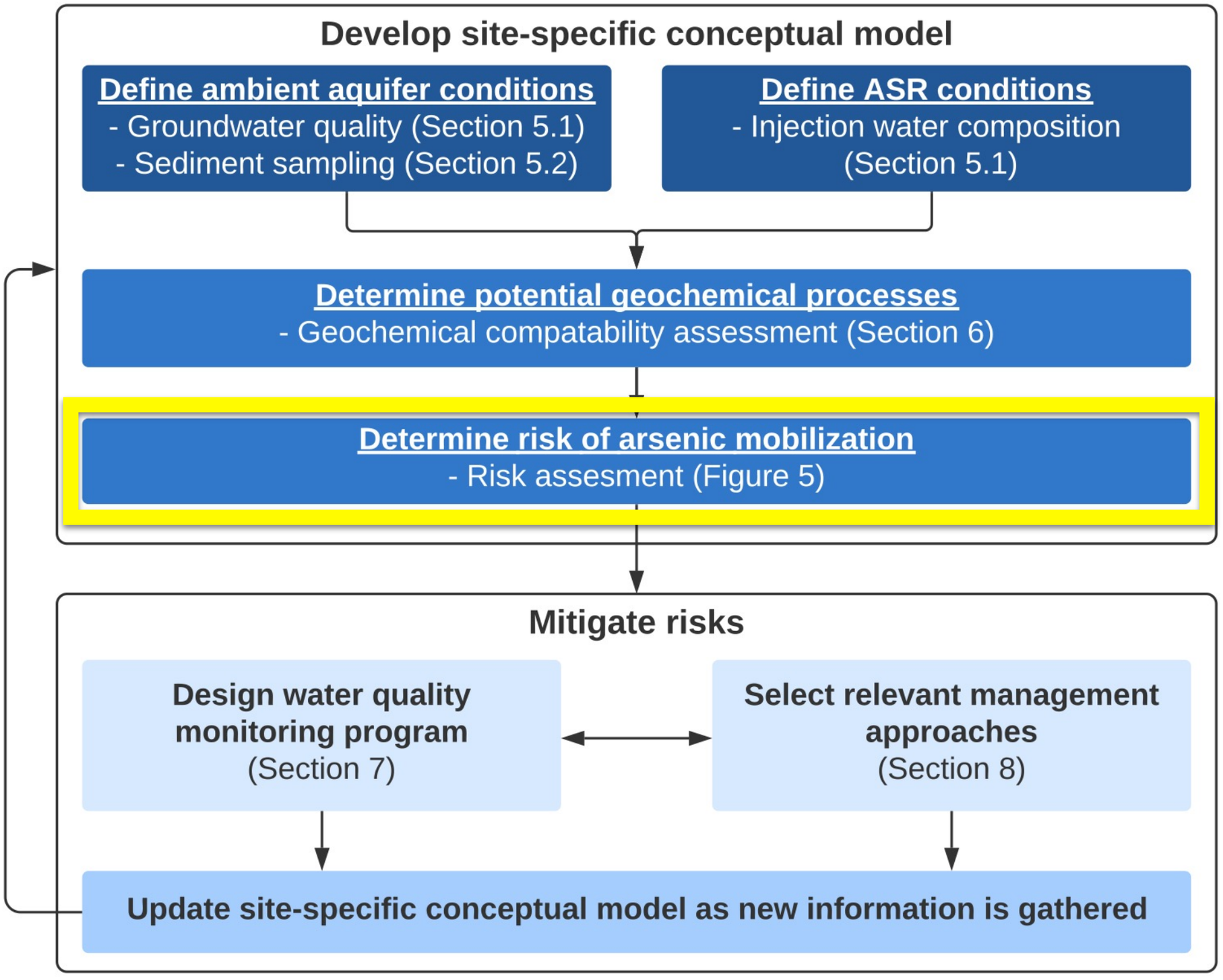
Batch modeling

- Mixing models
- Typically equilibrium conditions

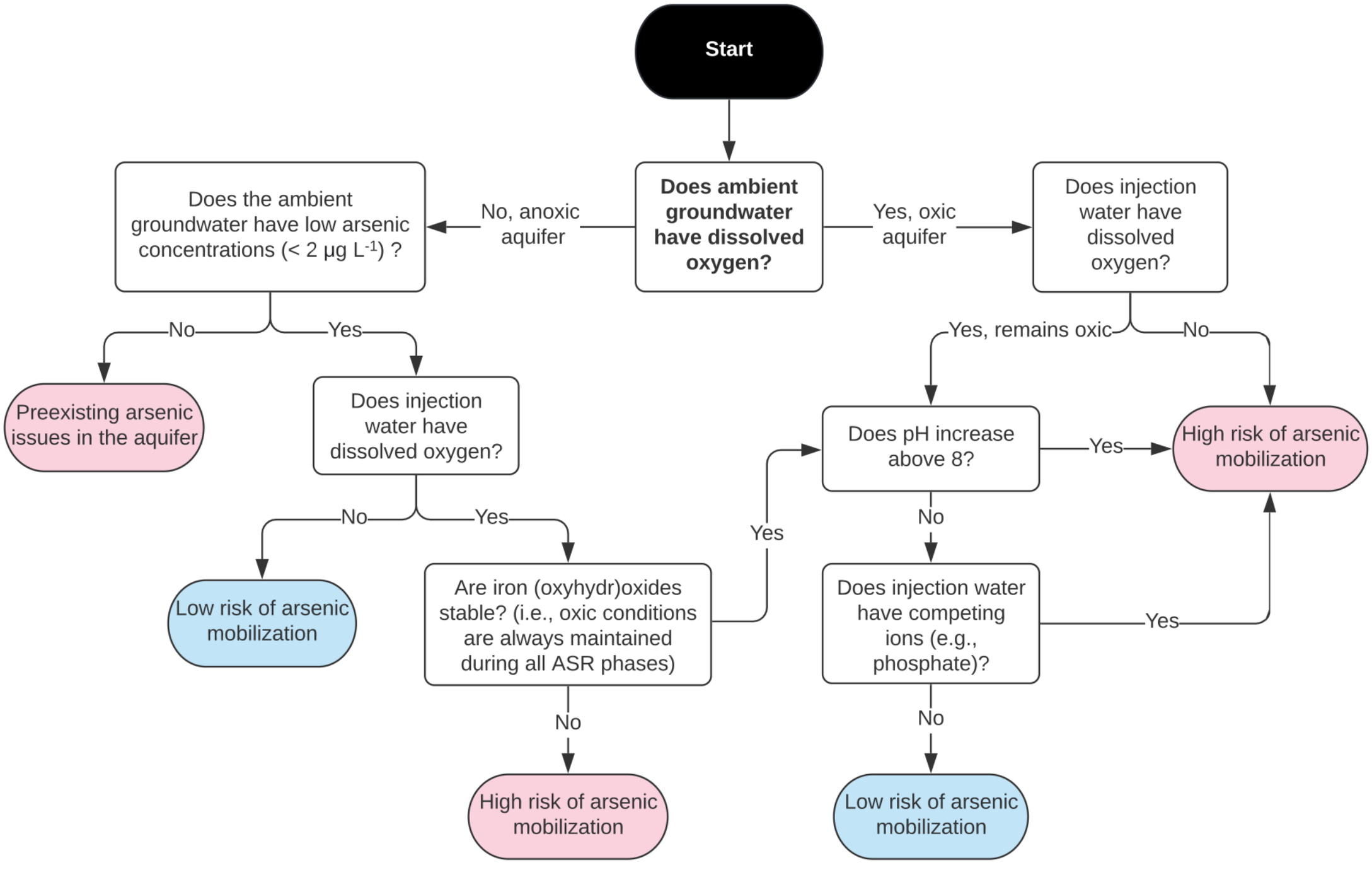
Reactive transport modeling

- More data and computationally intensive
- Better represents kinetic limitations
- Simulates transport and can test scenarios

Developing site-specific conceptual model



Assessing risk of arsenic mobilization during ASR



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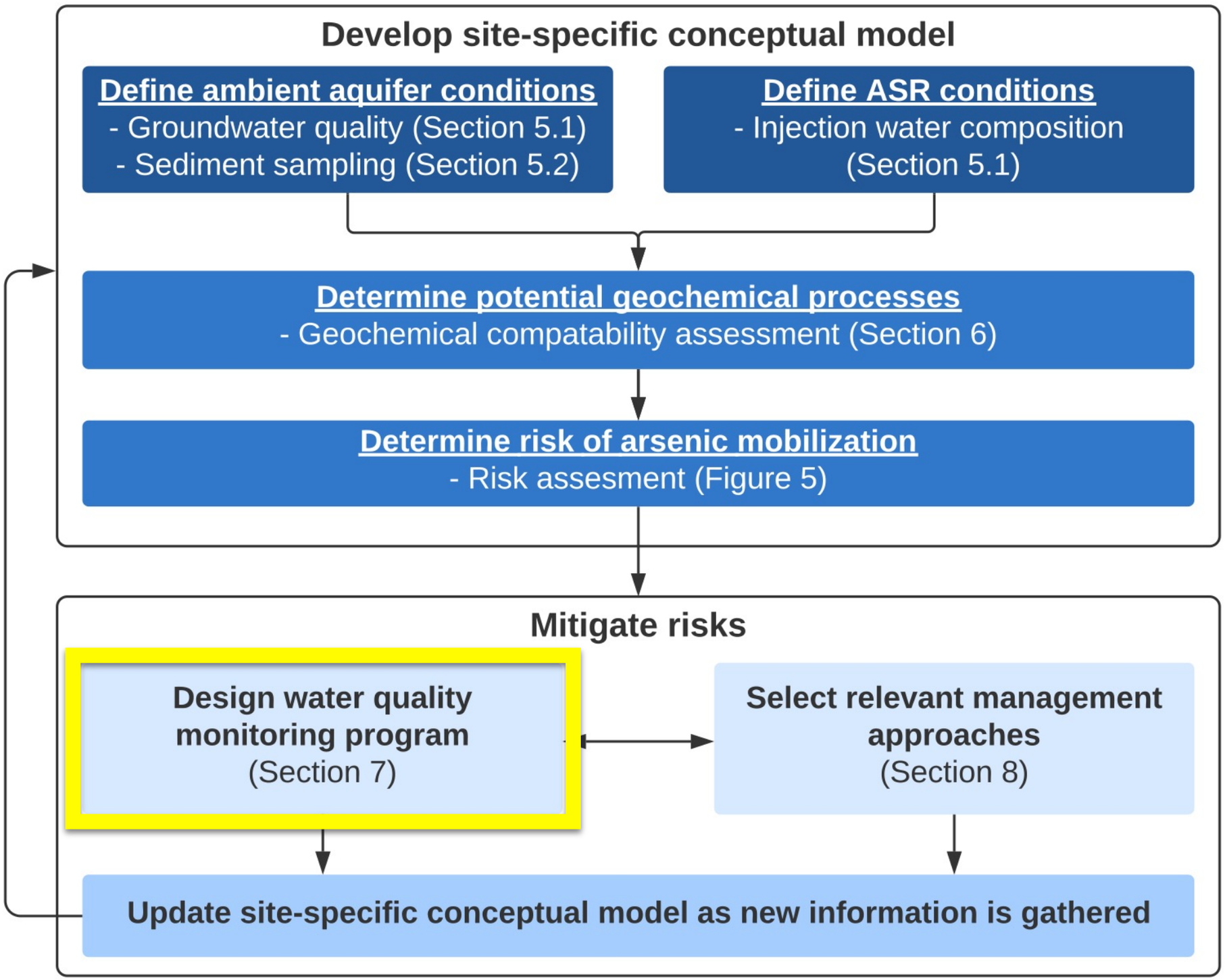
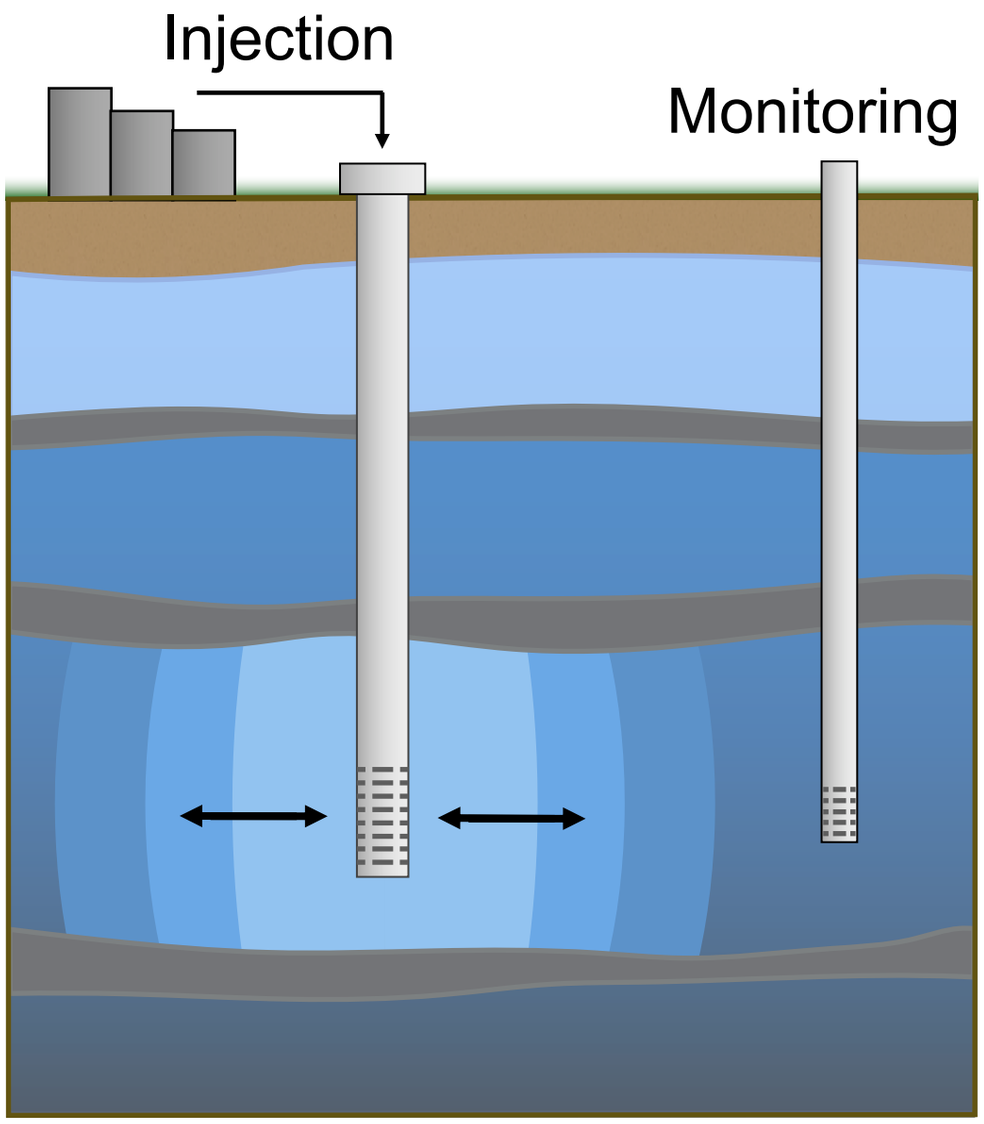


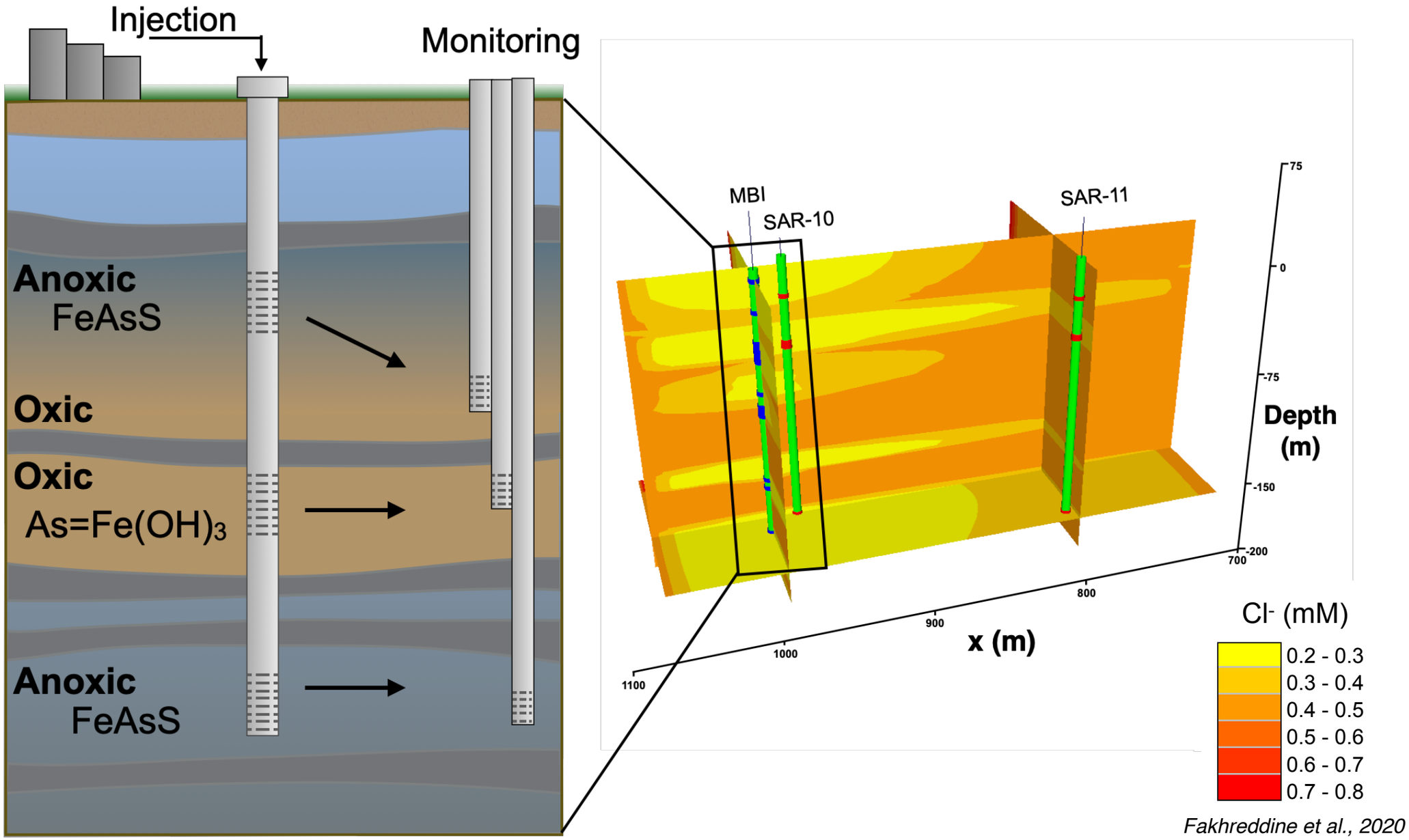
Water quality monitoring guidance



Water quality parameters to monitor in the context of geochemical controls on arsenic mobility

Parameter	Information provided
Oxidation reduction potential (ORP)	Serves as metric of redox conditions. ORP is a challenging measurement and should be interpreted as relative changes in ORP (e.g., if increases in ORP are observed, it can be inferred that redox conditions are becoming increasingly oxidizing and less reducing)
pH	Controls several processes related to arsenic mobilization, particularly surface complexation to aquifer solids and precipitation/dissolution of several minerals
Alkalinity	Related to pH-buffering capacity and saturation of carbonate minerals
Dissolved oxygen (DO)	Determines if groundwater conditions are oxic, suboxic, or anoxic. Indicates potential for oxidation of sulfidic minerals and other reduced species
Iron	Indicator of redox condition and solubility of iron (oxyhydr)oxides. Dissolved iron is typically predominantly Fe^{2+} and the presence of dissolved iron is often indicative of anoxic, reducing conditions
Manganese	Similar to iron, can serve as indicator of redox conditions. Dissolved concentrations of Mn are typically observed under anoxic, reducing conditions
Arsenic	Direct information on mobility and sources of arsenic
Phosphate	Competitive ion and can indicate likelihood of arsenic desorption processes
Nitrate	Strong oxidant with potential to oxidize sulfidic minerals and other reduced species
Sulfate	Can provide additional information on redox conditions. Released during oxidation of sulfidic minerals and can serve as indicator for amount of pyrite oxidation occurring during ASR
Calcium	Useful for determining saturation of carbonate minerals including calcite
Magnesium	Useful for determining saturation of carbonate minerals including dolomite
Total or dissolved organic carbon (TOC or DOC)	Indicates presence of energy source for microbially mediated reactions
Temperature	Can serve as tracer for injection water and several key geochemical reactions can be temperature-dependent (e.g., microbial oxidation of dissolved organic carbon)
Chloride	Can serve as tracer for injection water
Total dissolved solids (TDS)	Can serve as tracer for injection water

Water quality monitoring guidance

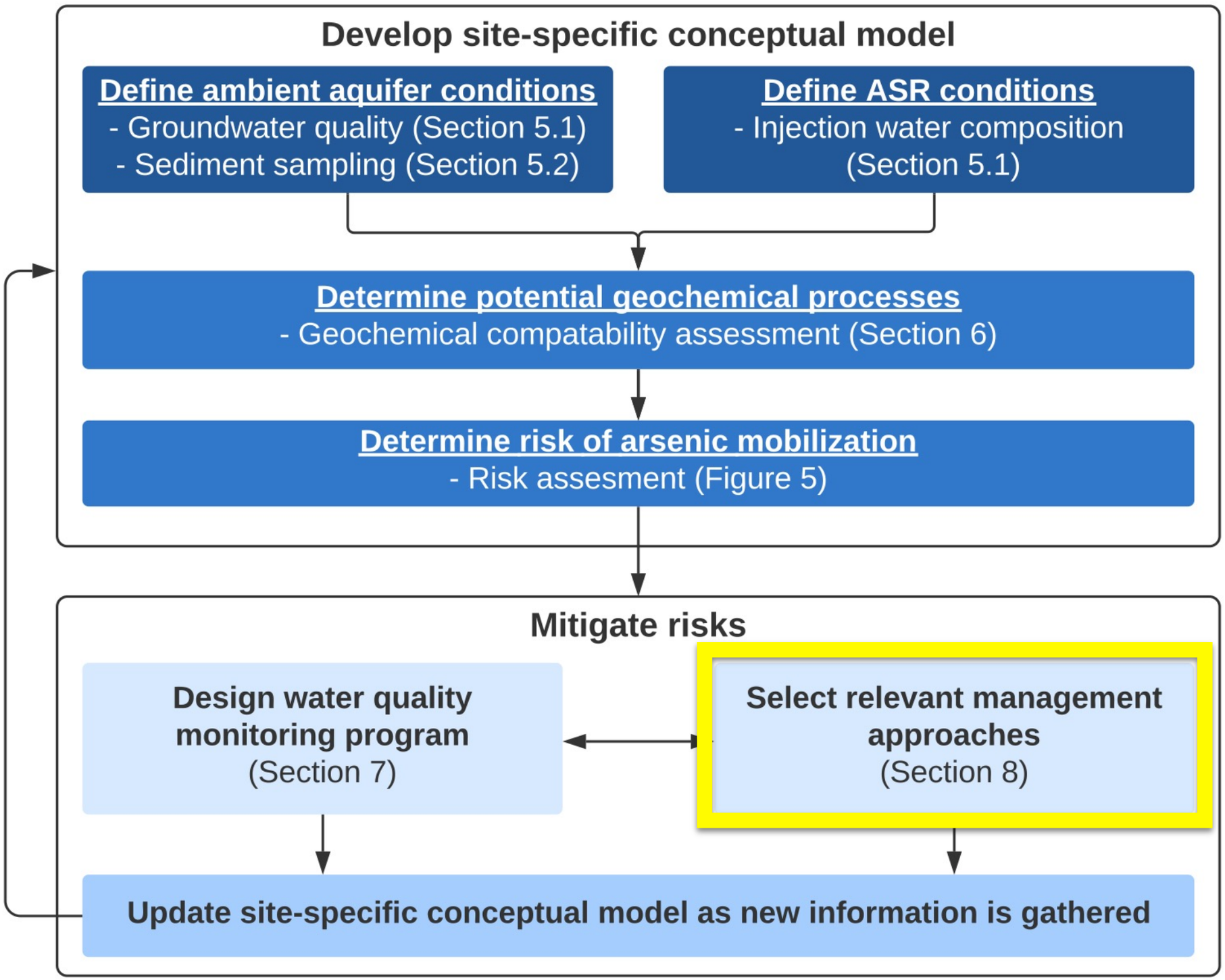


Fakhreddine et al., 2020

Spatial and temporal frequency of monitoring are key to capturing **heterogenous** trends in water quality (e.g., seasonal shifts in temperature of recharge water and shifts across ASR phases)

Common water quality parameters (e.g., DO, ORP, pH) can be used as more **cost-effective and frequent method** to monitor geochemical controls on arsenic mobility

Developing site-specific conceptual model



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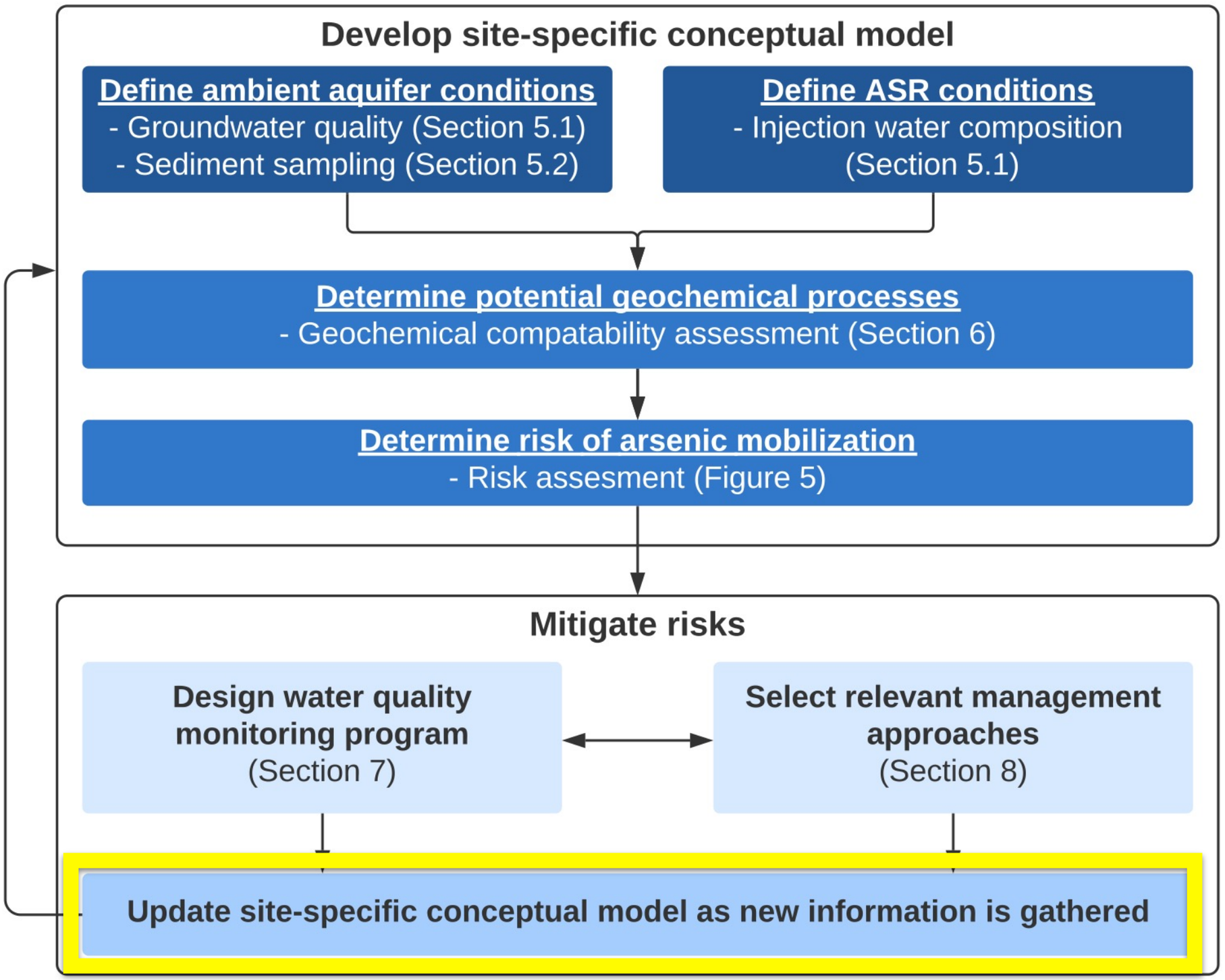
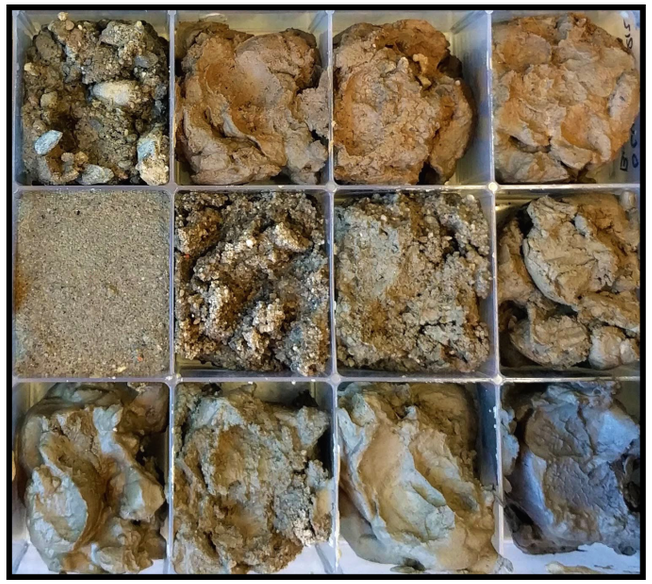


Summary and general management considerations



1. Consistent operations and **long-term planning**
   - future water availability for ASR and sources

2. **Technical advisory panels** for ASR planning
   - site-specific geochemical guidance

3. Contingency plans and **mitigation programs**
   - preparing alternative options if needed

4. Gathering **more geochemical data**
   - updating geochemical understanding

Thank you! Questions?

Guidance Document

“Guidance for Understanding and Minimizing the Potential for Arsenic Mobilization during Managed Aquifer Recharge”

Fakhreddine, S., Scanlon, B.R., and Nicot, J.P.

Texas Commission on Environmental Quality

TCEQ AS-218

Geochemical Review

“Mobilization of Arsenic and Other Naturally Occurring Contaminants during Managed Aquifer Recharge: A Critical Review”

Fakhreddine, S., Prommer, H., Scanlon, B.R., Ying, S.C., and Nicot, J.P.

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