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

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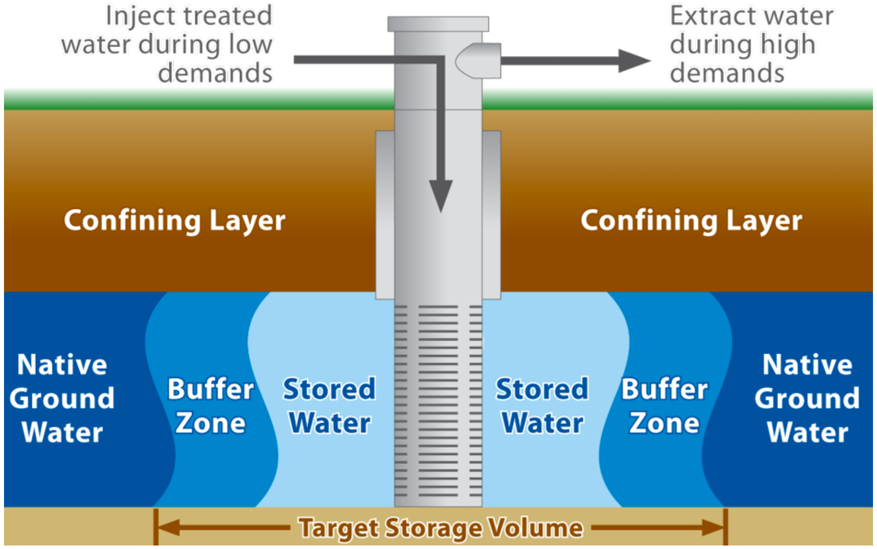
Aquifer storage and recovery:
an increasingly applied water enhancement strategy

Schematic of an ASR well



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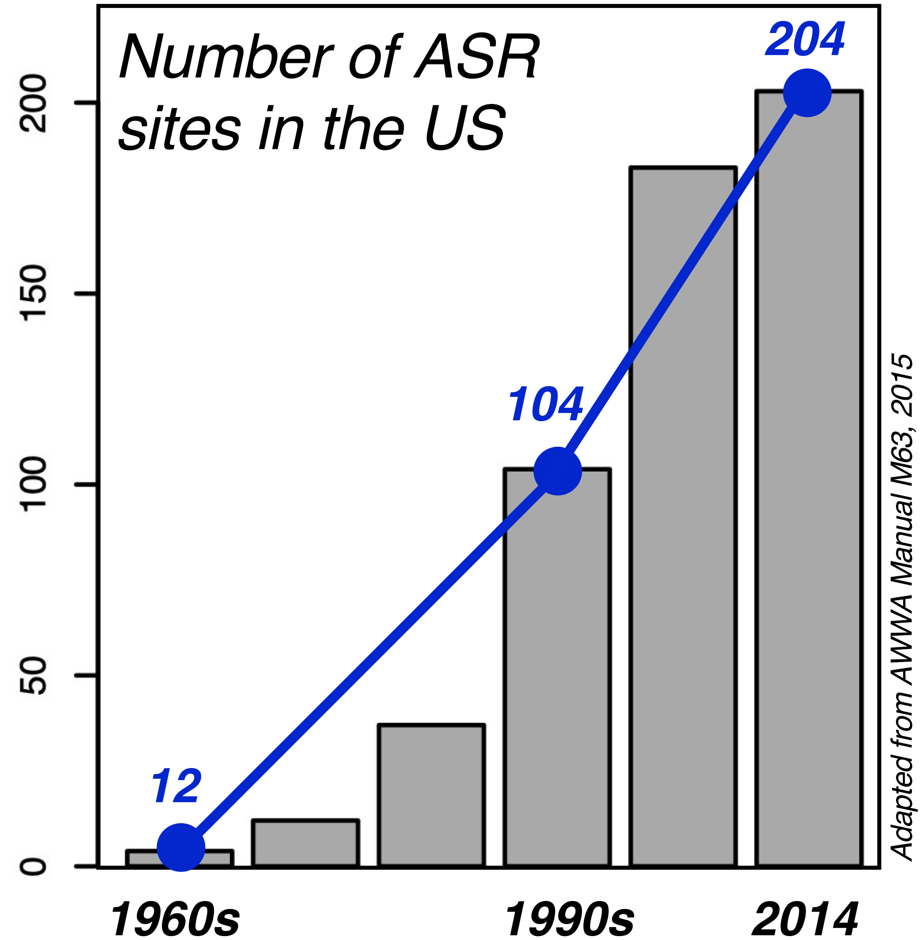

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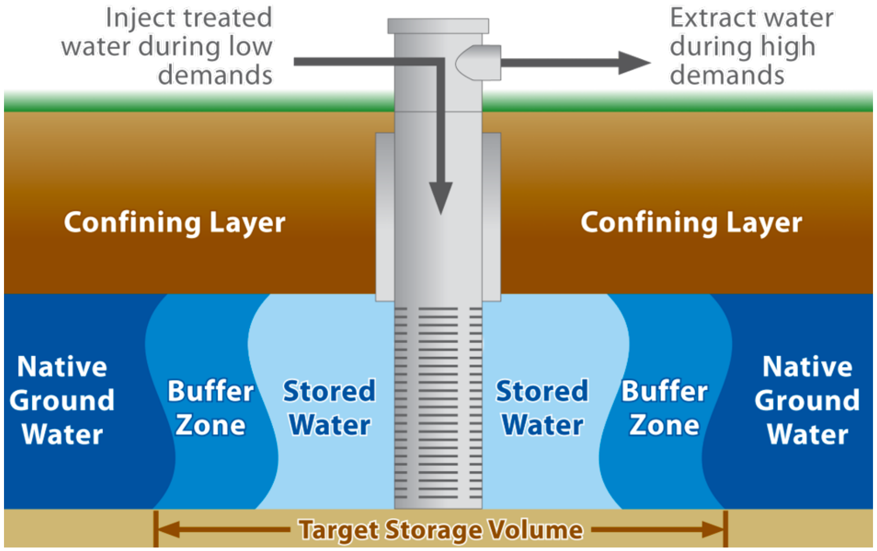

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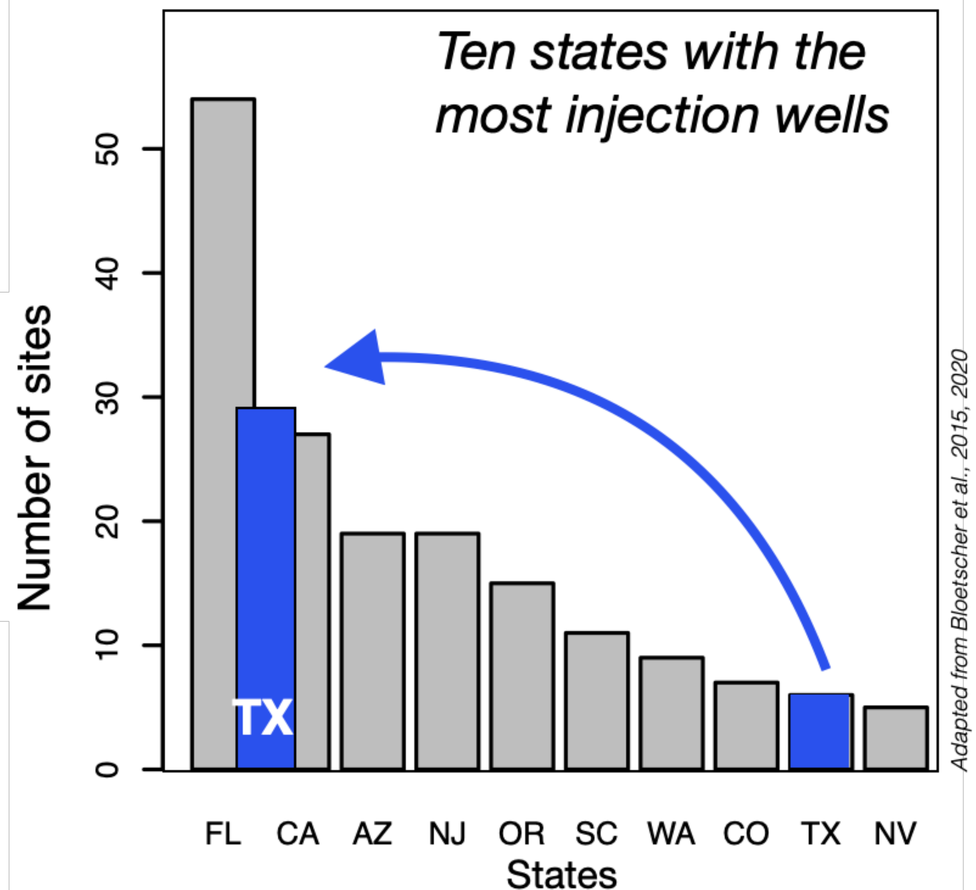
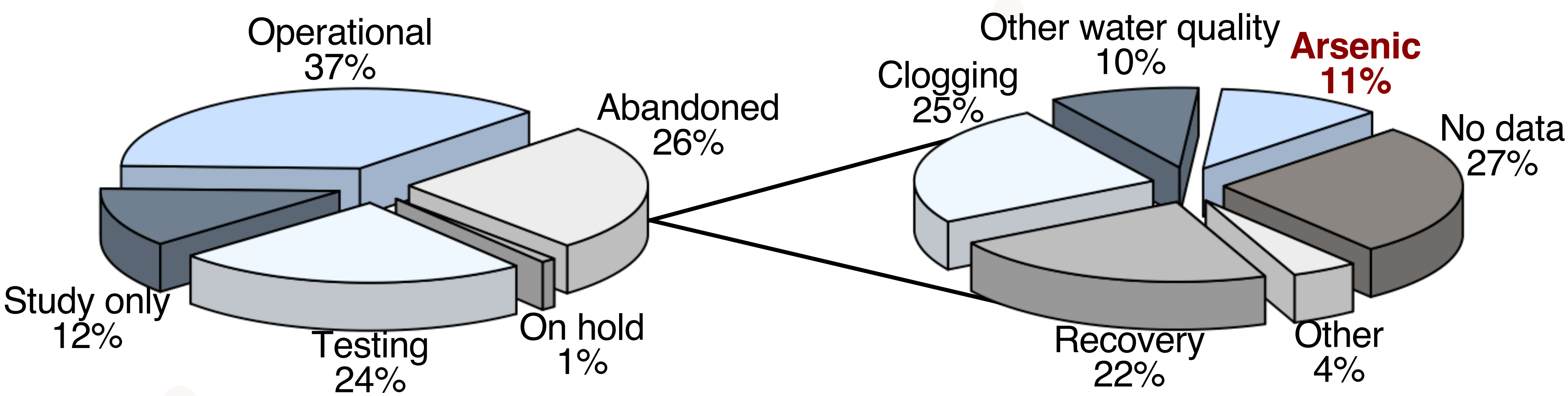


Threats to groundwater quality during ASR

Status of ASR wells in the US **Reasons for abandoning wells**



Adapted from AWWA, 2015

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

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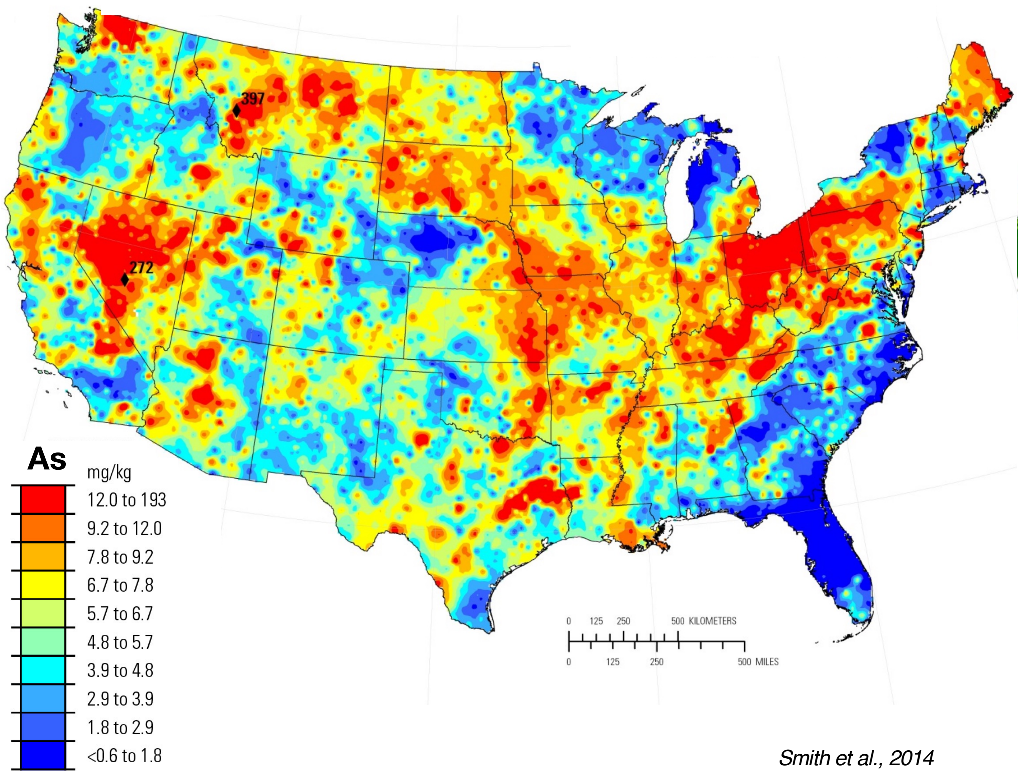
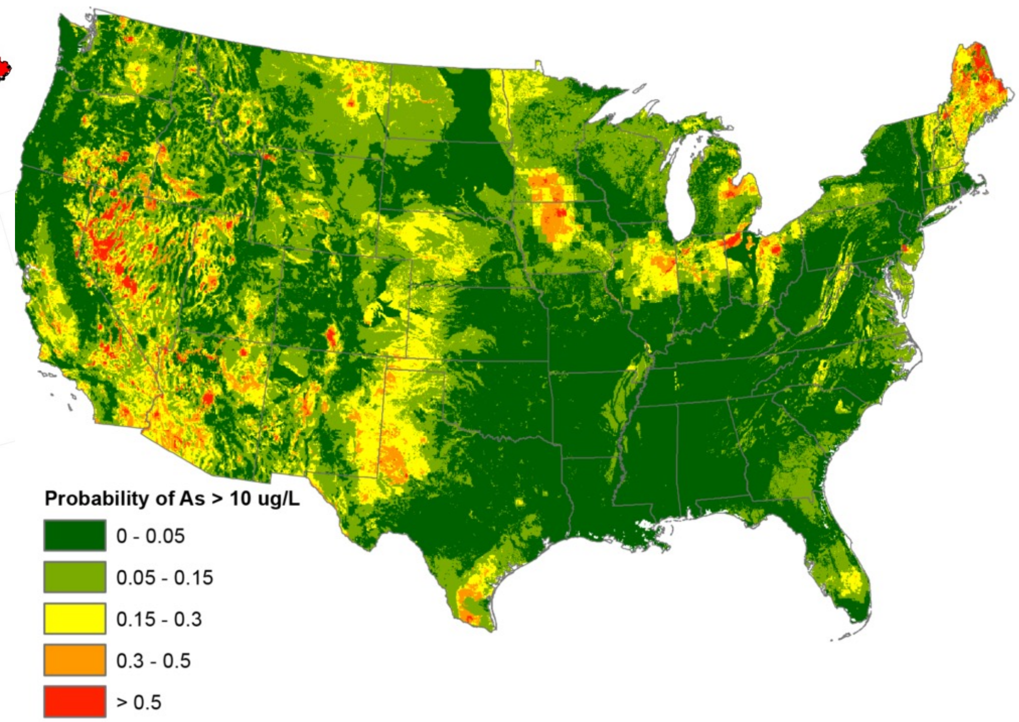
Arsenic in soils



Smith et al., 2014

Arsenic in groundwater



Ayotte et al., 2017

Biogeochemical conditions dictate whether arsenic will mobilize to groundwater – not the concentration of arsenic in soils and sediments

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 difficult and costly to obtain

4. Requires domain-specific geochemical knowledge

Guidance document objectives

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

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

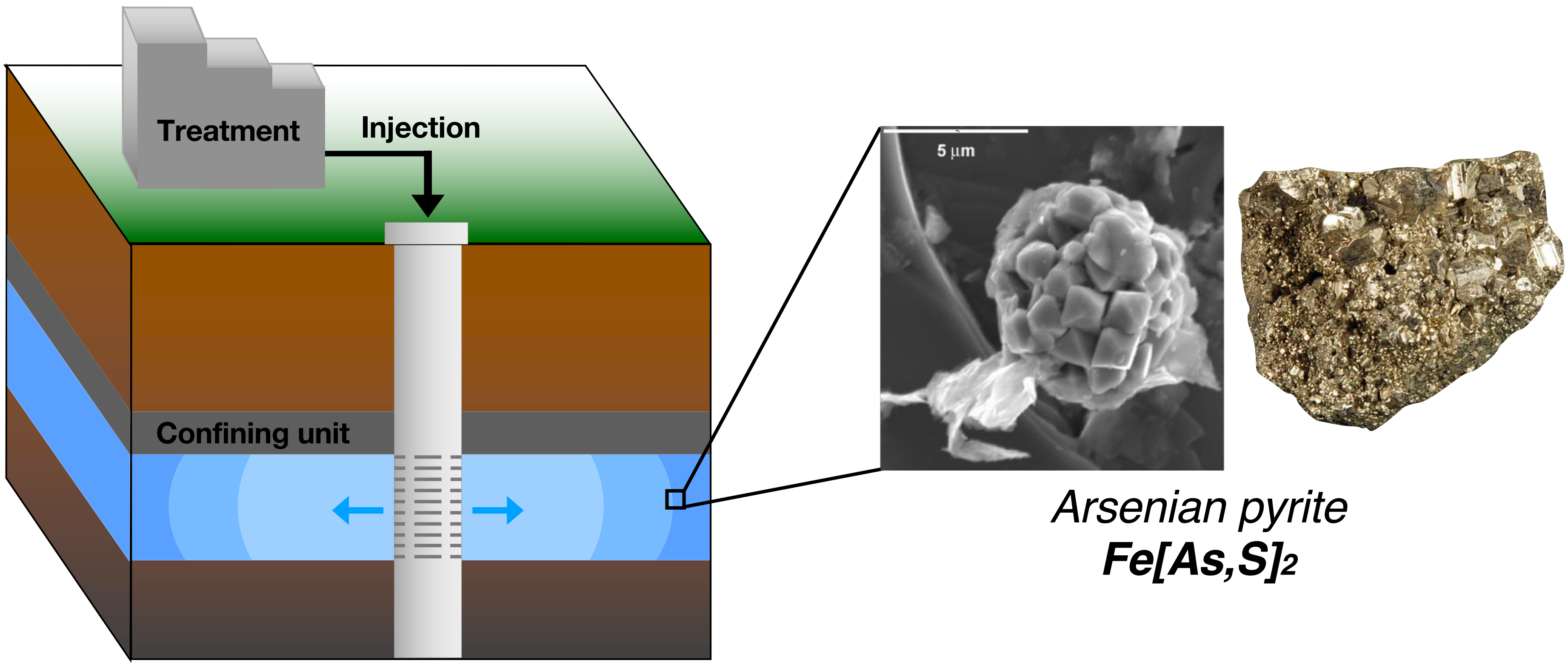
2. Develop framework for site-specific conceptualization of potential arsenic mobilization including geochemical assessments

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

3. Provide guidance on monitoring and management

   How to prevent problems? Potential ways to manage arsenic if mobilized?

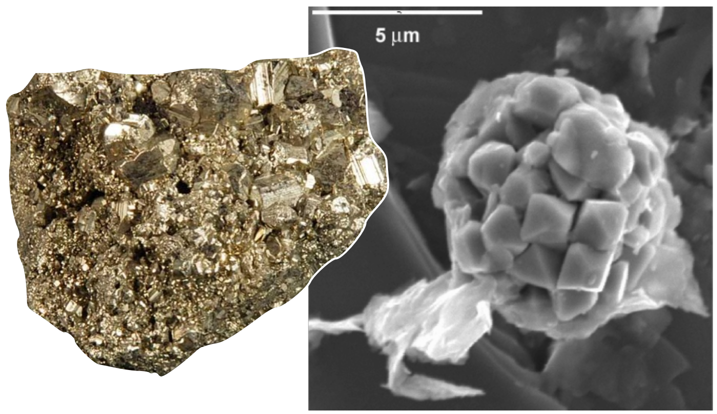
Most ASR sites attribute arsenic mobilization to the dissolution of arsenic-bearing sulfidic minerals



The majority of ASR projects in the United States inject oxic water into native suboxic or anoxic, confined or semi-confined aquifers (ASR Systems, 2007)

Arsenic repartitioning during injection

Reduced



Arsenian pyrite

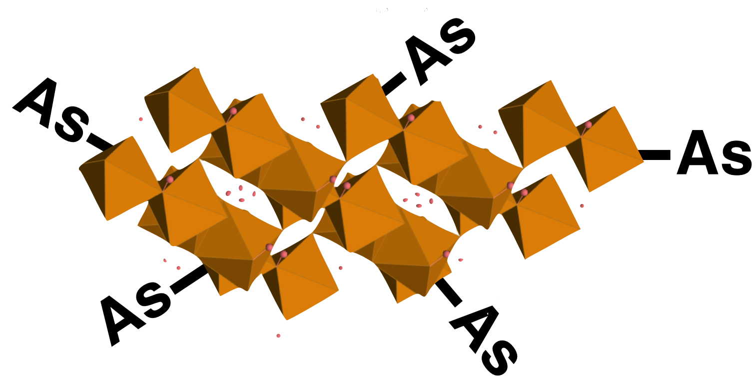
Fe[As,S]$_2$

O_2

NO_3^-

→

Oxidized



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

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

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

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

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

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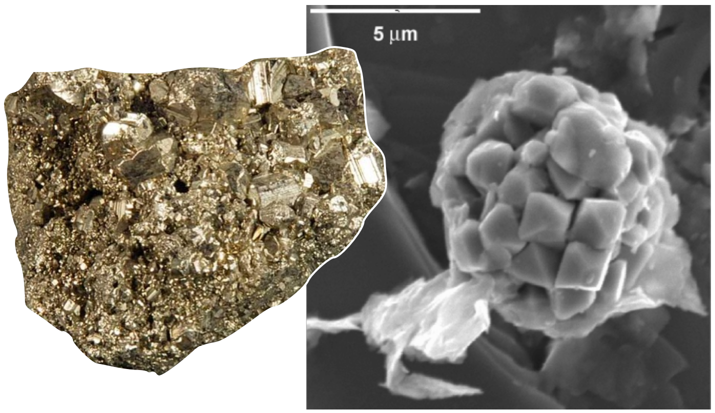

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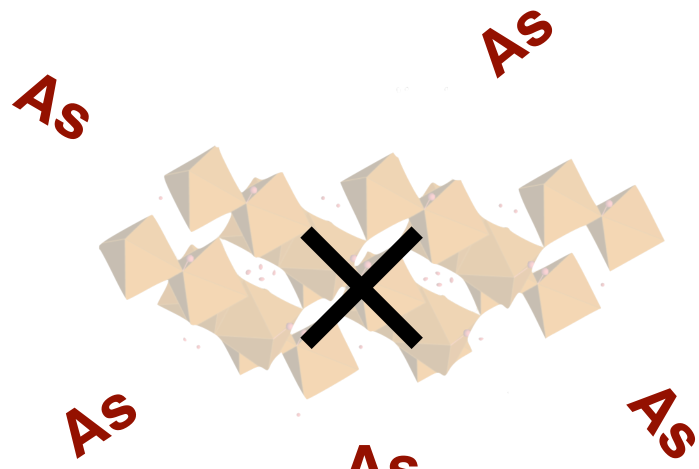

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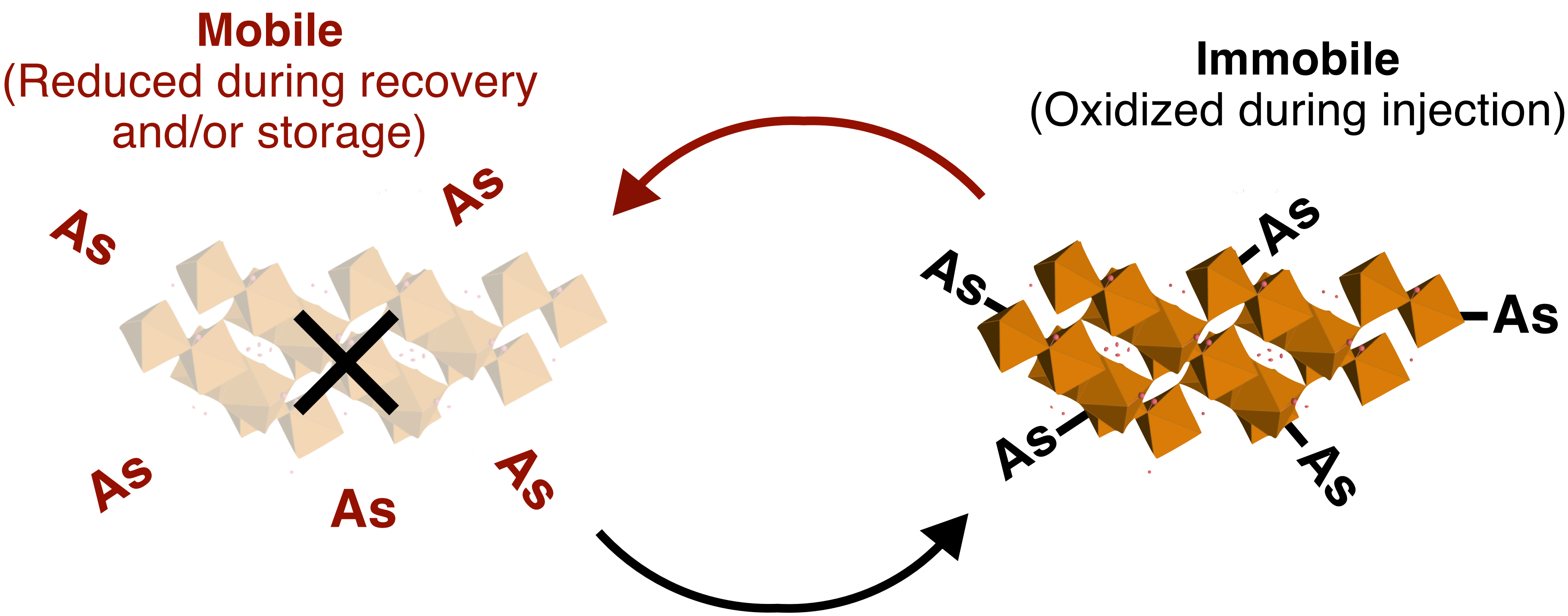
Arsenic mobilization during injection



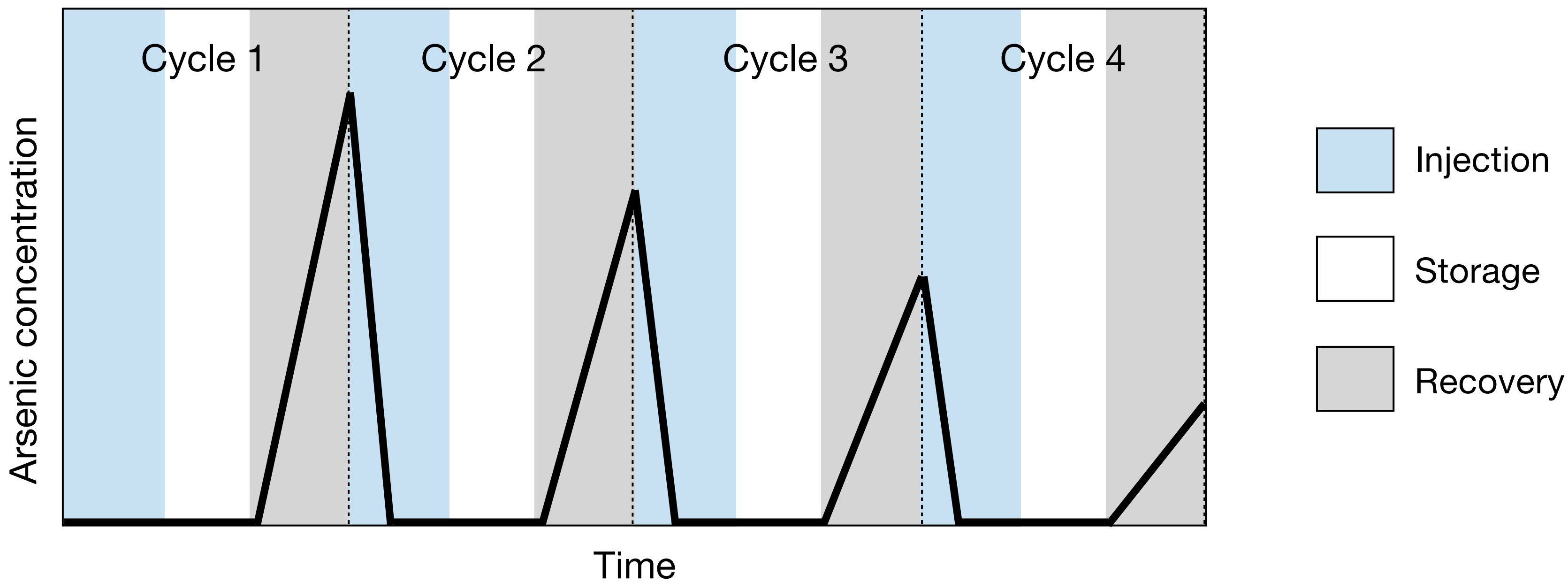
Reductive dissolution of Fe-(hydr)oxides and/or reduction of As(V) to As(III)

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

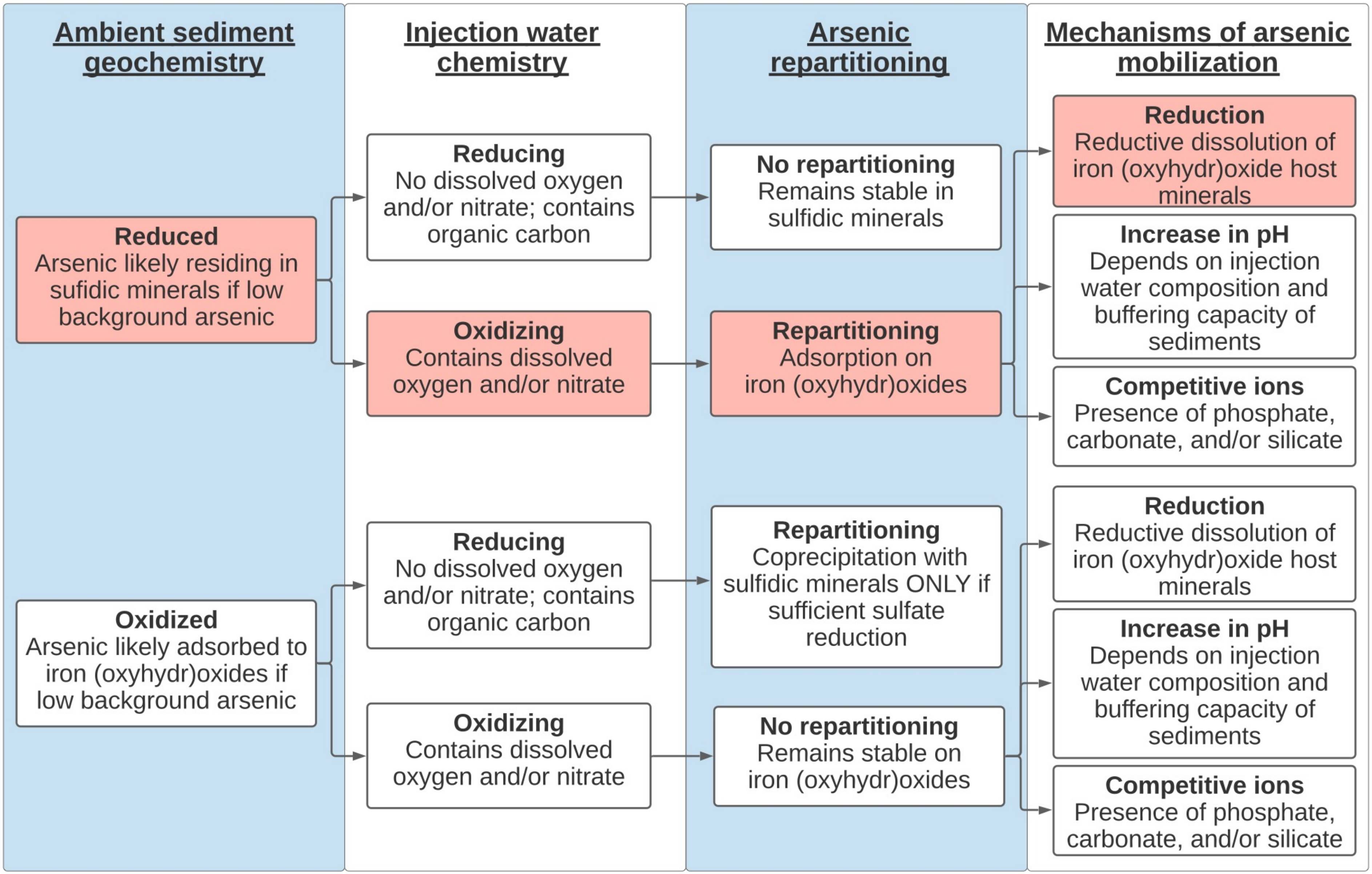
Temporal trends in arsenic mobilization

Simplified schematic of trends in arsenic mobilization during ASR



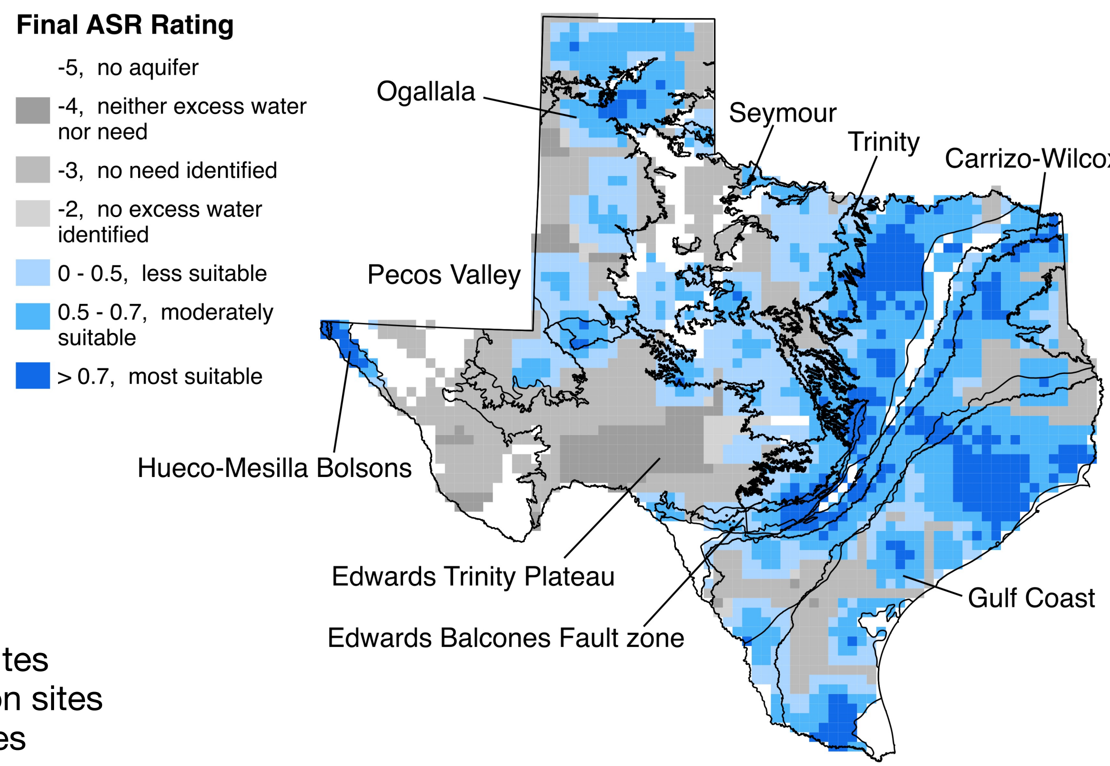
For ASR projects with consistent operation (storage volumes, timing of recharge/recovery) arsenic concentrations attenuate over time due to depletion of reactive fraction of arsenic-bearing pyrite and/or surface passivation of pyritic minerals

Summary of pathways of arsenic mobilization during ASR



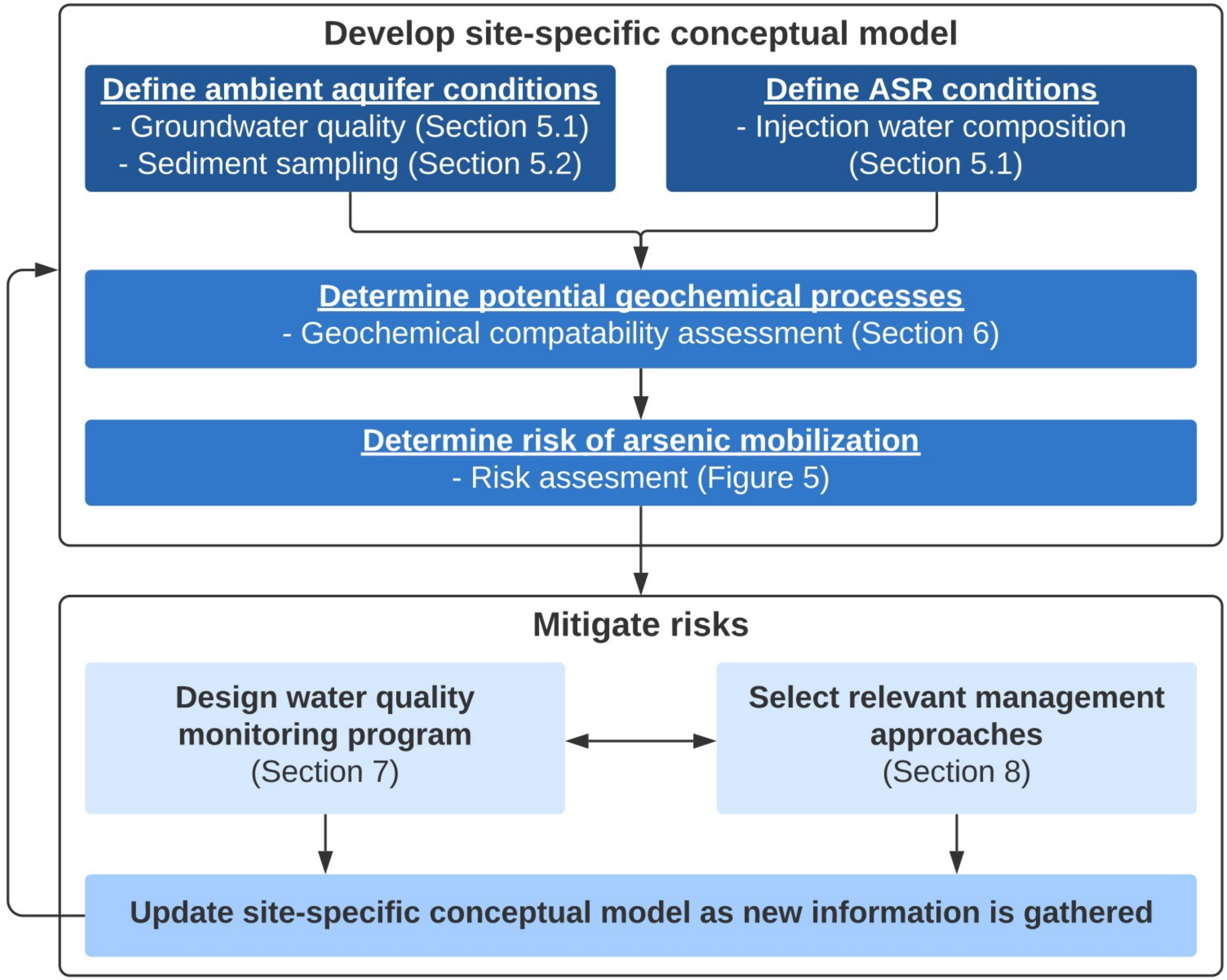
Applying a geochemical understanding to designing potential ASR sites

ASR sites in Texas



TWDB State-wide Site Suitability Study (HDR, 2020)

Developing site-specific conceptual model



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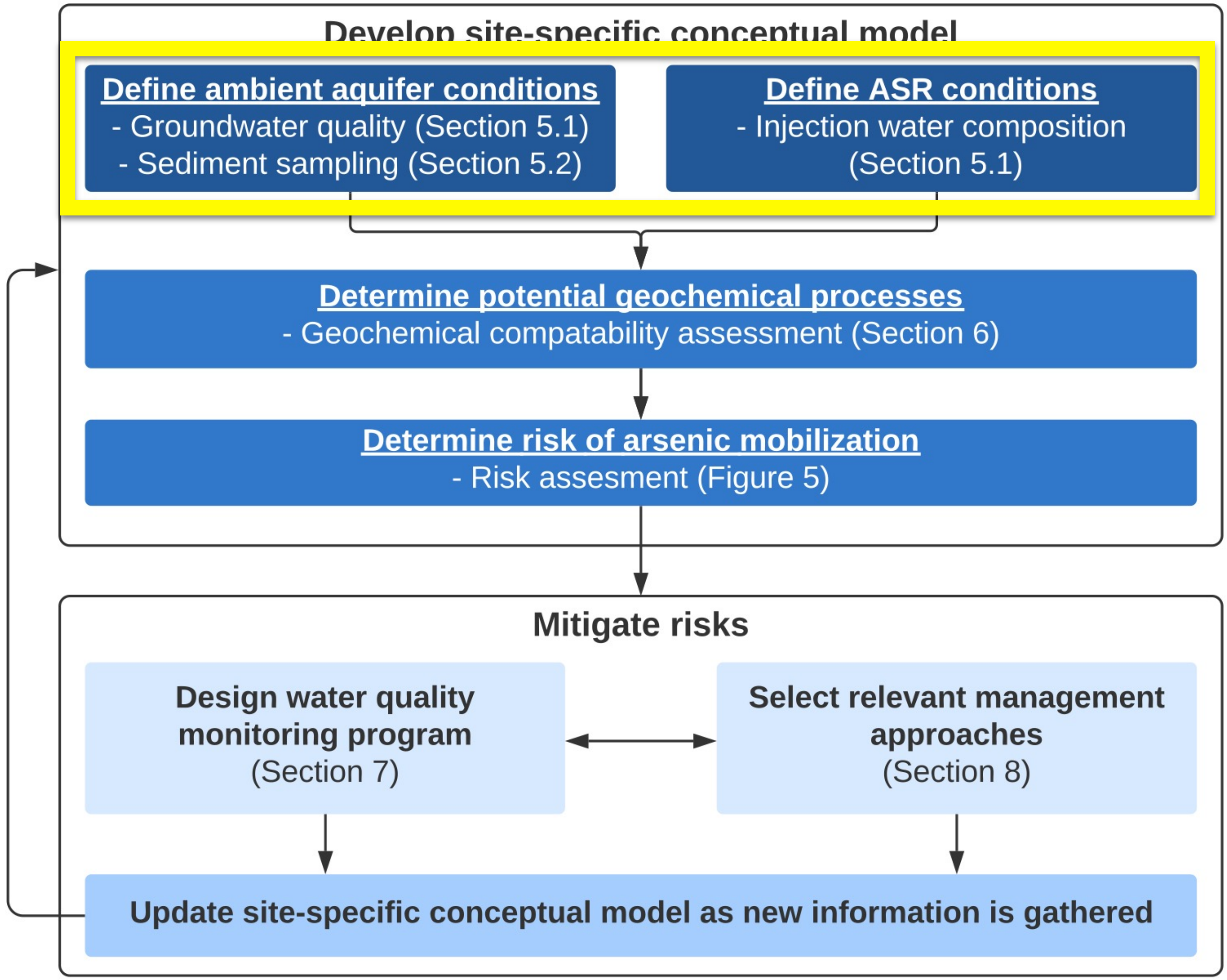
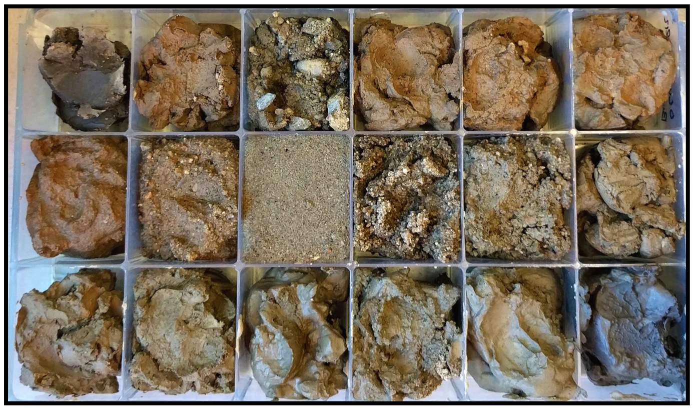


Defining ambient geochemistry and injection water composition



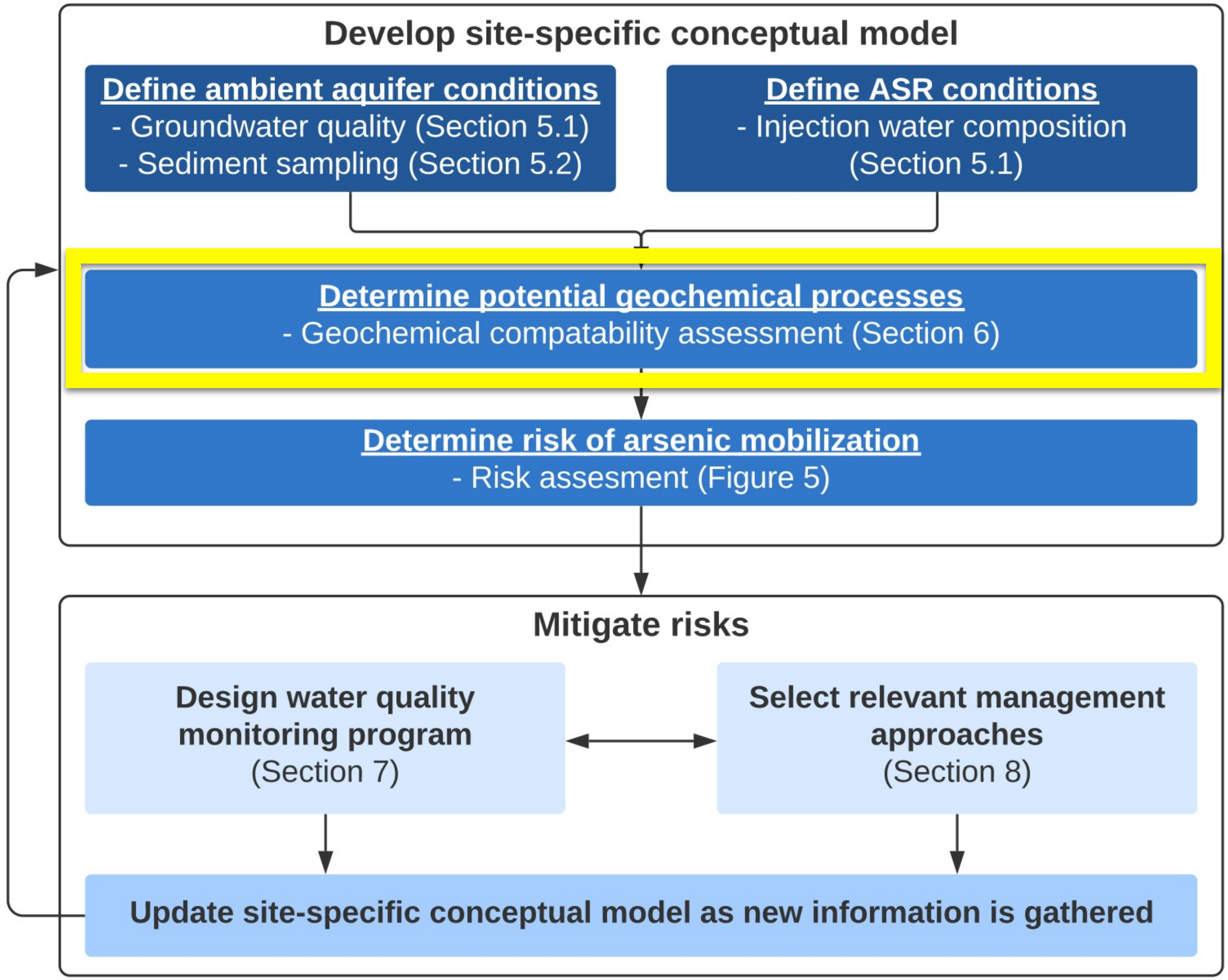
Sediment collection and sampling

- Cores and drill cuttings
- Total arsenic concentration, speciation, and mineralogy of samples
- Methods including XRD, XRF

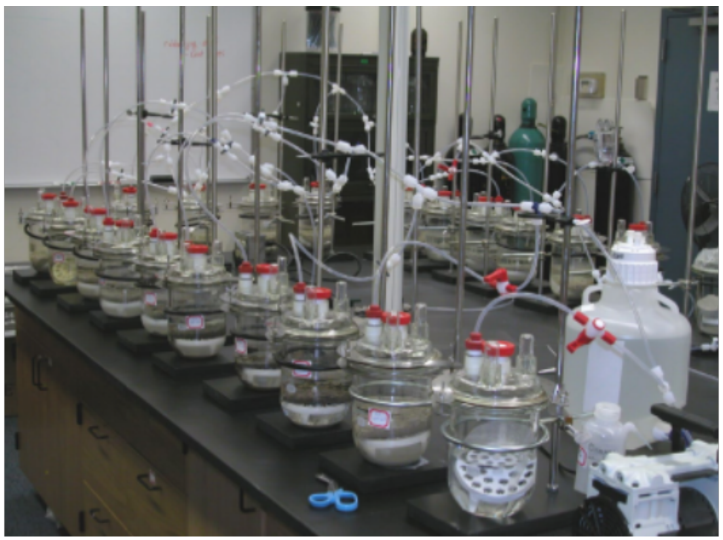
Aqueous sampling

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

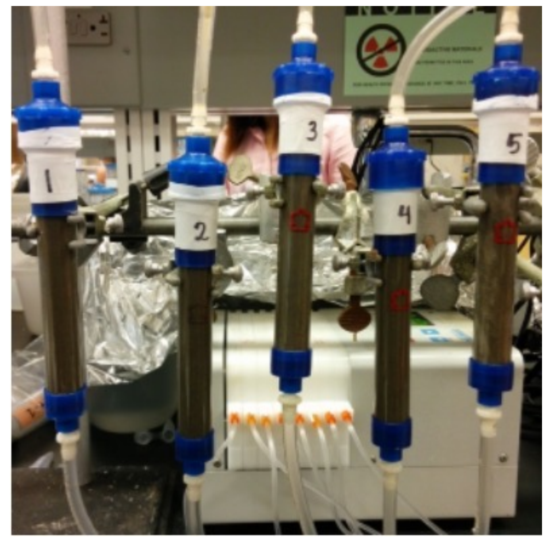
Developing site-specific conceptual model



Assessing geochemical compatibility: Laboratory experiments

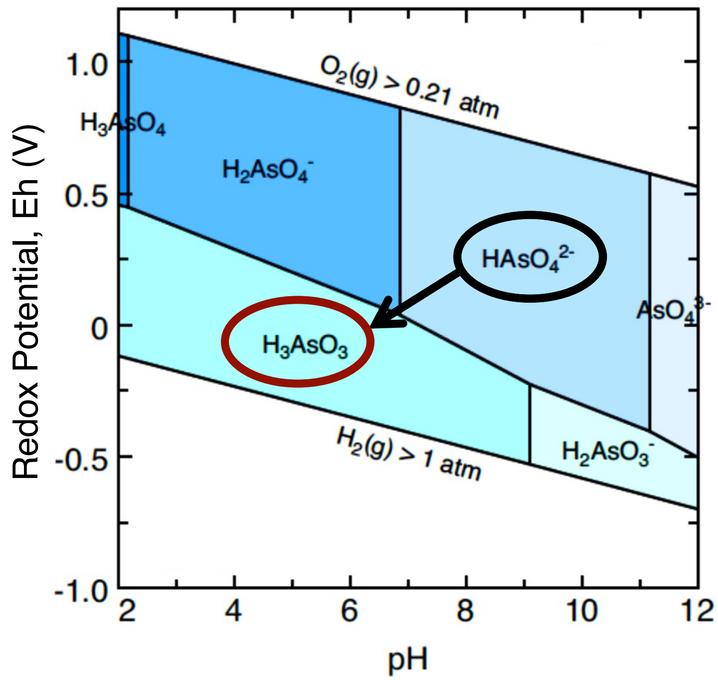


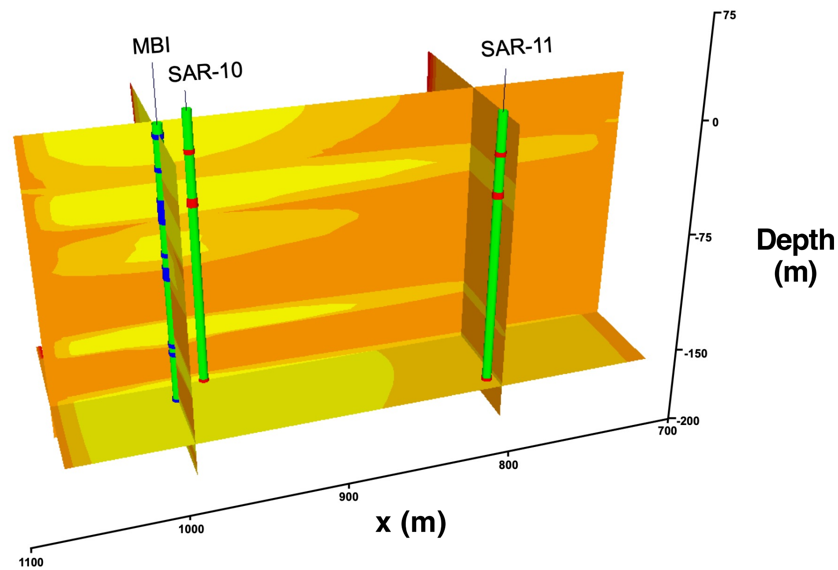
Batch experiments
- Simple mixing/leaching experiments
- Equilibrium conditions



Column experiments
- Incorporates transport
- Can experimentally simulate ASR cycling

Assessing geochemical compatibility: Geochemical modeling





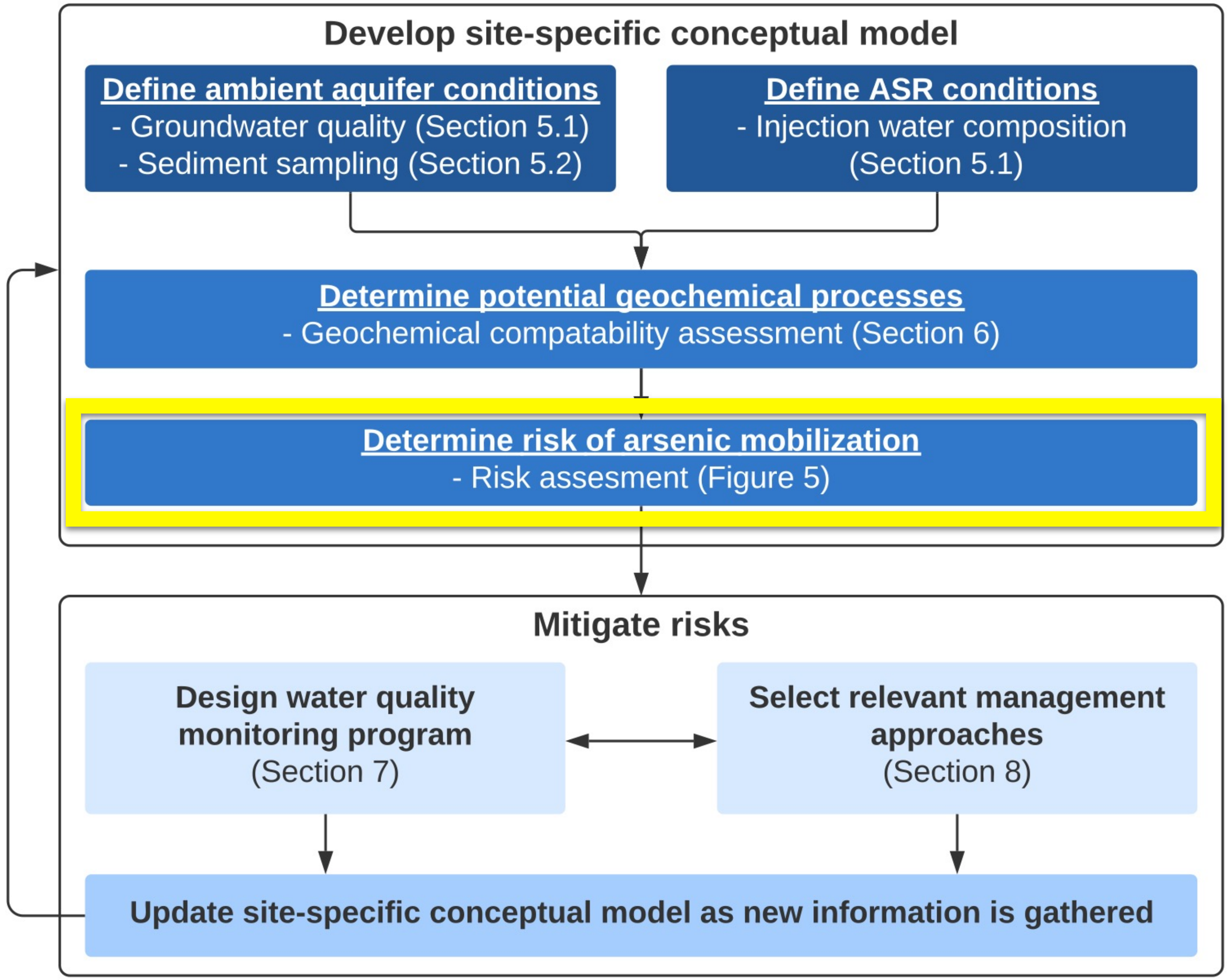
Batch modeling

- Mixing models
- Typically equilibrium conditions

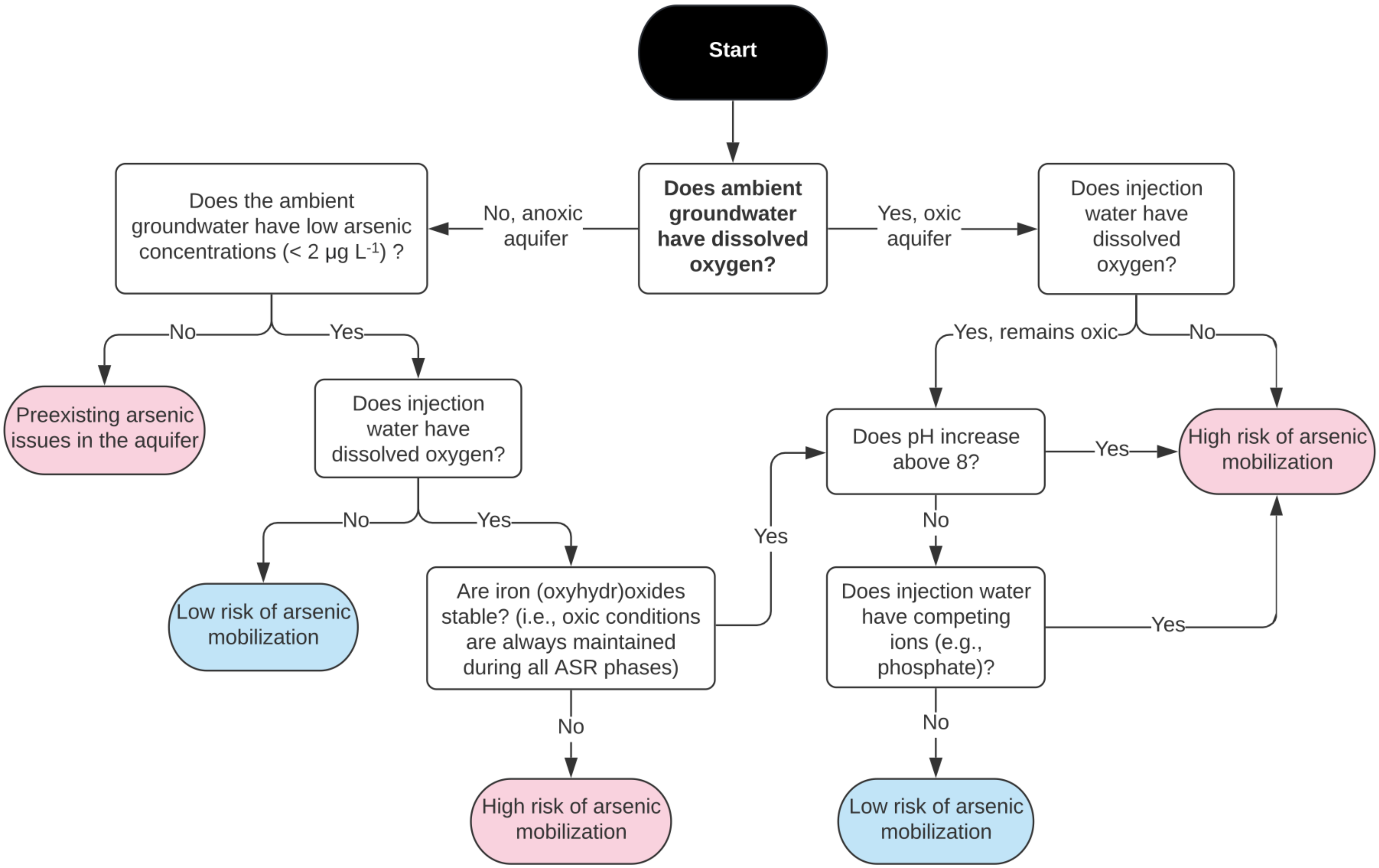
Reactive transport modeling

- More data and computationally intensive
- Simulates transport and can test scenarios

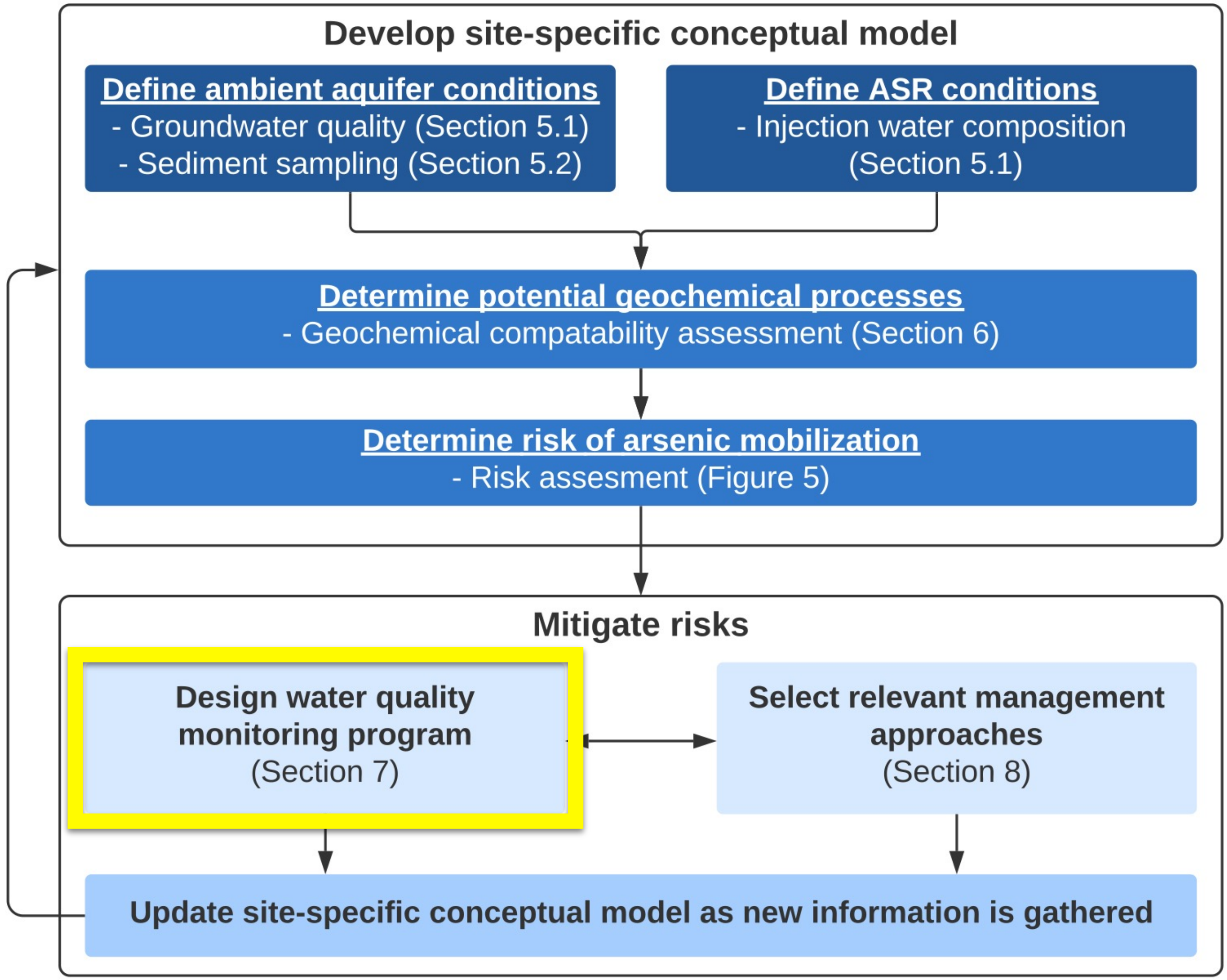
Developing site-specific conceptual model



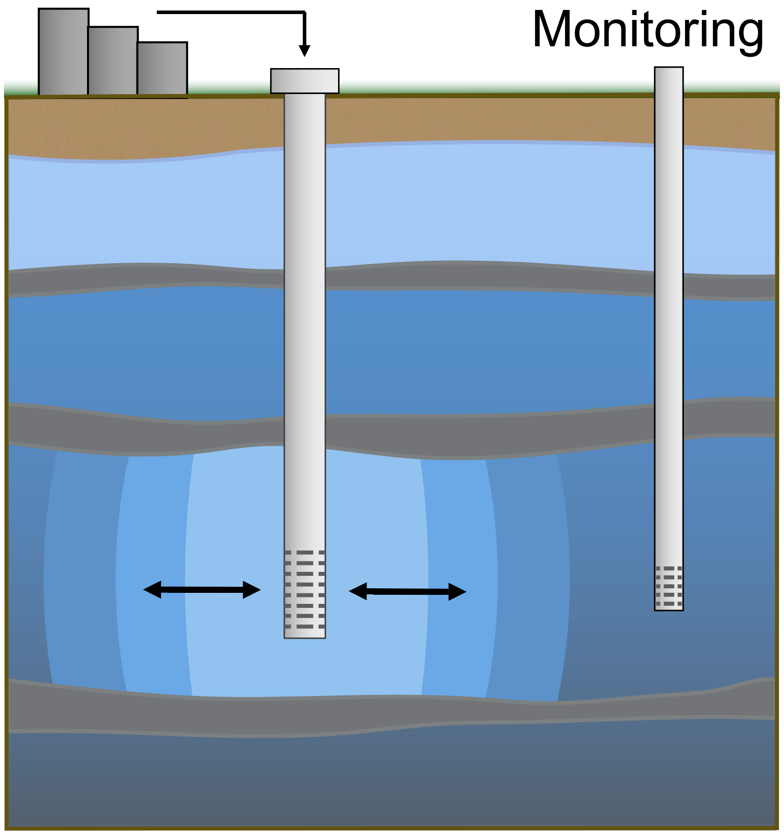
Assessing risk of arsenic mobilization during ASR



Developing site-specific conceptual model



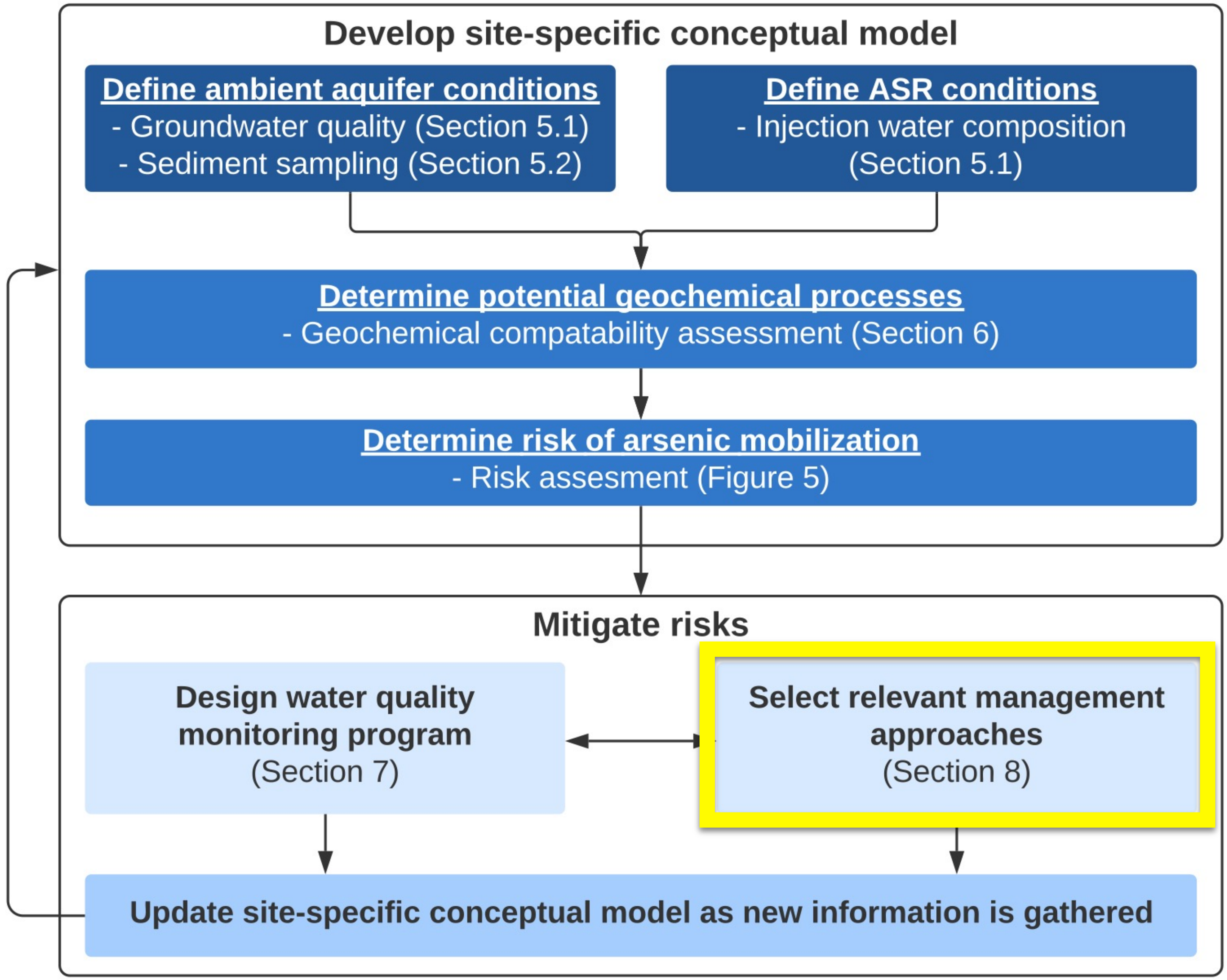
Water quality monitoring guidance



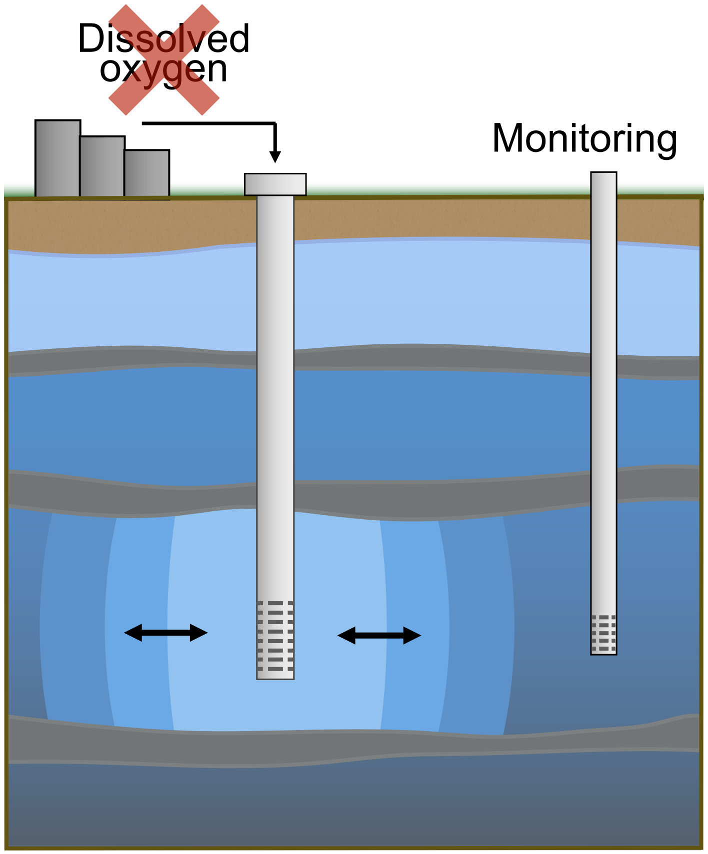
Water quality parameters to monitor in the context of geochemical controls on arsenic mobility

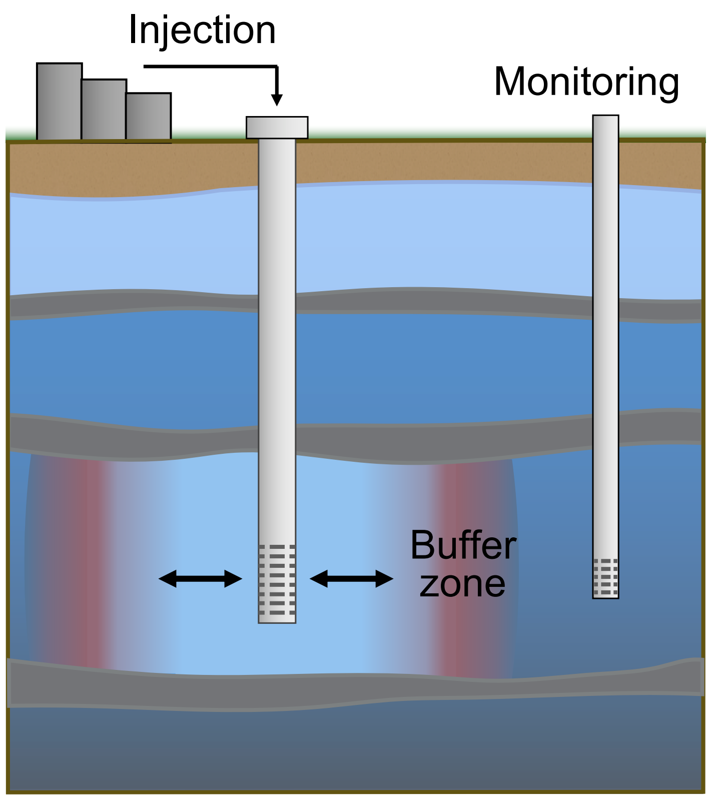
Parameter	Information provided
Oxidation reduction potential (ORP)	Serves as metric of redox conditions. ORP is a challenging measurement and should be interpreted as relative changes in ORP (e.g., if increases in ORP are observed, it can be inferred that redox conditions are becoming increasingly oxidizing 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

Developing site-specific conceptual model



Most common management strategies for arsenic mobilization





Deoxygenation of injection water

- Expensive
- Based on understanding of geochemical processes
- Requires continuous treatment
- *Prevents* arsenic mobilization

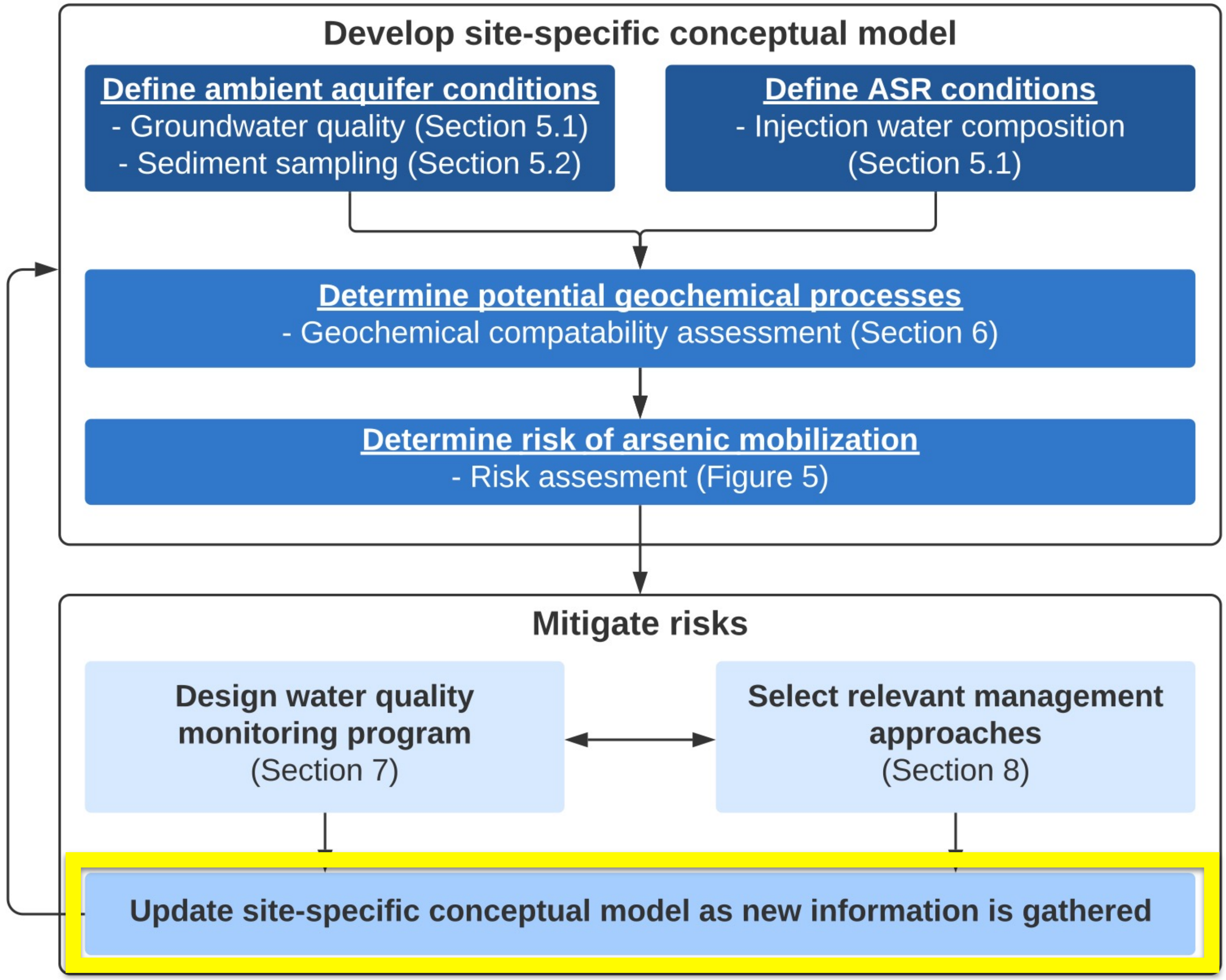
Maintenance of buffer zone

- More cost effective
- Based on operational rule-of-thumb
- *Limits spatial extent* of potential arsenic mobilization

Additional management strategies for arsenic mobilization during ASR

1. Pre-treatment approaches
    1. Organic carbon removal
    2. Modifying pH and/or ionic composition
    3. Pre-oxidizing target storage zone
2. Physical approaches
    1. ASR variants or multi-well systems
    2. Modifying operational controls

Developing site-specific conceptual model



Additional 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
   - future water availability and sources
4. Opportunities for gathering more geochemical data
   - sediment sampling

Summary

1. Arsenic mobility is controlled by a suite of site-specific conditions
2. Developing a site-specific conceptual model that can be updated over time is key to protecting water quality
3. Understanding geochemical processes (and designing management approaches) requires adequate data collection particularly since many proposed management approached are based on operational, site-specific observations
4. Recent drilling operations provide potential to improve geochemical understanding of future ASR sites in Texas

Thank you - Questions?