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

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Contents

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Acronyms

AR	aquifer recharge
ASR	aquifer storage and recovery
ASTR	aquifer storage transfer and recovery
Cl	chloride
DO	dissolved oxygen
DOC	dissolved organic carbon
Fe	iron
HB	house bill
MCL	maximum contaminant level
Mn	manganese
Mo	molybdenum
ORP	oxidation reduction potential
PVC	polyvinyl chloride
S	sulfur
SAWS	San Antonio Water System
SDWA	Safe Drinking Water Act
SI	saturation index
TAC	Texas Administrative Code
TCEQ	Texas Commission on Environmental Quality
TDS	total dissolved solids
TOC	total organic carbon
TSV	target storage volume
TWC	Texas Water Code
TWDB	Texas Water Development Board
UIC	Underground Injection Control
US EPA	United States Environmental Protection Agency
USDW	underground sources of drinking water
USGS	United States Geological Survey
XRD	X-ray diffraction
XRF	X-ray fluorescence

1. Introduction

Subsurface storage of excess water supplies in aquifers is increasingly used globally to alleviate temporal disparities in water supply and demand. Aquifer storage and recovery (ASR) involves the direct injection of excess water into deep aquifers during wet periods for later recovery during dry seasons or times of drought. While ASR has the potential to enhance water security, injection of water can alter the native hydrological and geochemical conditions of the receiving aquifer, potentially resulting in the mobilization of toxic, naturally-occurring (geogenic) contaminants from sediments and into groundwater where they pose a much larger threat to human and ecosystem health. Arsenic is a particular challenge at ASR sites due to its ubiquity in sediments and toxicity at trace concentrations with a federal maximum contaminant level (MCL) of 10 µg L^{-1} (US EPA, 2006). Additionally, once mobilized, arsenic and other naturally-occurring contaminants are challenging and costly to remediate, which can result in project abandonment. Water quality degradation accounts for approximately 21% of abandoned ASR wells nationally. Arsenic mobilization was reported for at least 11% of inactive wells in the United States, rendering it the most reported water quality contaminant during ASR (Bloetscher et al., 2014).

In Texas, interest in ASR has rapidly grown with recent regulatory changes aimed at promoting the adoption of ASR as a water enhancement strategy. A recent inventory of ASR projects across the United States showed Texas to be the second leading state in number of ASR projects, following Florida (Bloetscher et al., 2020). The inventory included planned and proposed ASR sites that have not yet begun drilling wells. In contrast, in 2015, a similar survey reported Texas as the ninth leading state for number of ASR wells, indicating rapid expansion of ASR over the last few years in Texas relative to other states (Bloetscher, 2015). To support the adoption of ASR and ensure safe and reliable water supplies, the purpose of this document is to (1) provide an overview of processes controlling arsenic mobility during ASR, (2) develop a framework for evaluating the risk of arsenic mobilization at a given site, and (3) provide general guidance on initial site assessments, geochemical compatibility studies, water quality monitoring, and available management strategies for limiting arsenic mobilization. The processes controlling arsenic mobilization, and subsequently the appropriate management strategies for protecting water quality, depend on site-specific hydrological, geochemical, and operational conditions. Therefore, this document focuses on broad guidance for developing a site-specific conceptual model to assess the risk of arsenic mobilization and potential strategies to mitigate risks.

Section 2 provides an overview of hydrological and geochemical processes controlling arsenic mobility and ASR site conditions that can indicate a high risk of arsenic mobilization. Section 3 contains background information related to ASR in Texas including relevant regulations for underground injection and the status of ASR projects across the state. Section 5 presents a framework for developing a site-specific conceptual model of geochemical conditions at a given ASR site to determine appropriate management strategies. As part of conceptual model development, Sections 6 and 7 summarize methods for initial site assessments including water and sediment sampling and geochemical compatibility studies, respectively. Section 8 provides an overview of management strategies for limiting arsenic mobilization which have been previously used or proposed at ASR sites. Section 9 highlights other key considerations for project development including the need for long-term planning, technical advisory panels, and contingency plans for water quality issues. Finally, additional tools, guidance documents, and resources related to ASR development and water quality protection are listed in Appendix A.

2. Overview of general processes controlling water quality during ASR

Several hydrological and geochemical shifts occur during ASR impacting the mobility of naturally-occurring contaminants in the receiving aquifer. First, during injection, injection water physically displaces the ambient groundwater, typically moving radially away from the injection well. Idealized conceptual models describe the stored water as a homogenous "bubble" (Figure

1). In reality, preferential flow paths in higher permeability zones will result in heterogenous porewater velocities surrounding the injection zone. The term "bottle brush" has been proposed as a more descriptive representation of injected water within the storage zone (Vacher et al., 2006). Near the injection well, flow is dictated by ASR-induced fluxes while regional-scale flow patterns dominate at distances farther away. Geochemical reactions will occur at the plume front, referred to as the buffer or mixing zone (i.e., the interface between ambient groundwater and injected water, Figure 1). However, reactions occurring in the mixing zone have limited spatial extent, and subsequently, limited impact on overall water quality. Rather, primary reactions occurring between the injected water and aquifer solids exert a dominant control on water quality. Common geochemical processes controlling water quality include (1) precipitation/dissolution reactions due to changes in redox and/or mineral saturation conditions and (2) adsorption/desorption from mineral surfaces by competitive ion displacement or pH shifts. pH shifts can impact both the speciation of dissolved species and/or surface charge of minerals which can control adsorption/desorption reactions. Other processes occurring during ASR that can influence overall water quality include oxidation of dissolved organic carbon and cation exchange reactions.
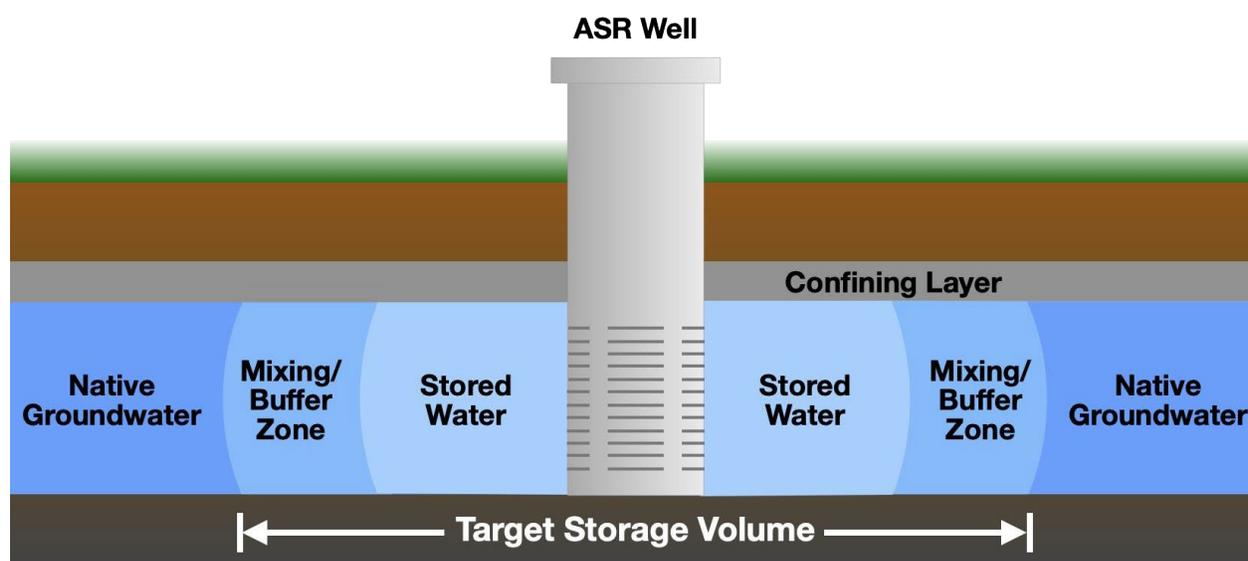
Figure 1. Idealized schematic of injected water in the storage zone at an ASR site

ASR most commonly involves the injection of oxic water into a previously anoxic or suboxic aquifer causing an abrupt shift in redox conditions. Deep suboxic sediments are often characterized by the presence of sulfidic minerals (e.g., pyrite, FeS_2) which can contain trace concentrations of toxic metal(loid)s including arsenic, nickel, molybdenum, and cadmium. Oxic injection water (containing dissolved oxygen and/or nitrate) can trigger the oxidative dissolution of sulfidic minerals and oxidation of organic matter resulting in a complex network of redox reactions. The spatial and temporal extent of these reactions depends on several site-specific conditions including ambient geochemical conditions. Notably, ASR can cause strong local oscillations in redox conditions as oxic water is injected, stored, and recovered from aquifers characterized by ambient anoxic or suboxic environments. During storage, the supply of oxidants via the injection water ceases. If sufficient reducing capacity exists (e.g., sulfidic minerals, sediment-bound organic matter, dissolved organic carbon in the injection water) within the storage zone, oxidants can be consumed during storage and reducing conditions may reemerge. During recovery, pumping causes ambient groundwater to migrate back towards the injection well and ambient geochemical conditions reemerge. Over successive ASR cycles, aquifer conditions oscillate back and forth between geochemical conditions induced by

injection water and ambient groundwater. Over multiple cycles and depending on the hydrological and geochemical setting, aquifer reactivity may decline and shifts in redox conditions may become less pronounced with each successive cycle. The observed patterns of redox and other geochemical shifts differ across nontraditional variants of ASR. For example, during aquifer storage transfer and recovery (ASTR), particularly if operated continuously, repeated oscillations of redox conditions are less likely to occur owing to separate injection and recovery wells.

Mineral precipitation/dissolution reactions are also triggered by non-redox mechanisms during ASR. When water is over- or undersaturated with respect to a given mineral, precipitation or dissolution reactions become favorable, respectively. For example, in aquifers containing calcite ($CaCO_3$), calcite dissolution is commonly observed when low-alkalinity recharge water is injected resulting in undersaturated conditions with respect to calcite.

While groundwater pH can be controlled by the internal buffering capacity and pH of the injection water, it is most commonly dictated by the buffering capacity and reactivity of the aquifer sediments. In particular, carbonate mineral dissolution controls the pH evolution of groundwater during ASR (Wallis et al., 2010). Therefore, the presence of carbonates is a key indicator of pH buffering capacity at a given ASR site. Other pH buffering processes during ASR include aluminosilicate dissolution and proton buffering (Descourvières et al., 2010; Seibert et al., 2016). The combined evolution of these geochemical conditions, particularly redox and pH, in space and time control the mobility of naturally-occurring contaminants at ASR sites.

2.1. Background on arsenic speciation in aquifers

Arsenic is a particular challenge at ASR sites due to its ubiquity in soils and sediments and its toxicity at trace concentrations with a maximum contaminant level (MCL) of 10 µg L^{-1} in drinking water (US EPA, 2006). The global average concentration of arsenic in unconsolidated sediments is 3 – 10 mg kg^{-1} (Smedley and Kinniburgh, 2002). While arsenic is ubiquitous in soils and sediments, total solid-phase concentrations of arsenic are not considered a strong predictor of arsenic concentrations in groundwater. Rather, the geochemical environment (primarily redox, pH, and ionic composition) determines whether arsenic remains benignly in aquifer solids or mobilizes to groundwater where it poses a larger threat to human and ecosystem health. Accordingly, the geochemical shifts induced by ASR dictate the potential for arsenic mobilization rather than the solid-phase concentrations of arsenic.

As a redox-active element, the toxicity and mobility of arsenic in the environment depend on its redox state. In its more oxidized form, arsenic resides as As(V), arsenate, and is generally considered less mobile and less toxic. Arsenate is predominately found as oxyanions $H_2AsO_4^-$ and $HAsO_4^{2-}$ at circumneutral pH (~7) and binds extensively to aquifer solids. In its reduced form, arsenic exists as As(III), arsenite, and is generally considered more mobile and more toxic. Arsenite exists as the uncharged specie H_3AsO_3 at circumneutral pH (Figure 2). Several geochemical pathways affect both the retention and release of arsenic from aquifer solids to groundwater. When arsenic is immobilized in aquifer solids, it is commonly retained in either (1) surface complexes to aquifer solid surfaces and/or (2) precipitated as arsenic-bearing solid phases. Arsenic forms surface complexes with common aquifer minerals, including iron (oxyhydr)oxides and aluminum (hydr)oxides, aluminosilicate clay minerals, and organic matter (Smedley and Kinniburgh, 2002). Arsenate binds strongly to these aquifer solids under well-aerated conditions and pH values < 8.5 (Smedley and Kinniburgh, 2002; Smith et al., 1998) which is why arsenate is generally not considered mobile in well-aerated environments unless alkaline pH values (> 8.5) prevail. While arsenite also binds extensively to iron (oxyhydr)oxides, it forms a more labile surface complex than arsenate and is therefore considered the more mobile form of arsenic (Fendorf, 2010).

Reduced arsenic minerals include sulfidic minerals like arsenopyrite (FeAsS), realgar (As_4S_4), and orpiment (As_2S_3) which are typically formed in high-temperature environments rather than authigenically. Arsenian pyrite ($FeS_{(2-X)}As_X$), also referred to as arsenic-bearing pyrite, typically

contains less than 10% arsenic by weight (Kolker and Nordstrom, 2001; Neil et al., 2018; Paktunc, 2008). Arsenic-bearing pyrite is more common than arsenopyrite and is considered the most important source of arsenic in ore zones (Nordstrom, 2000).
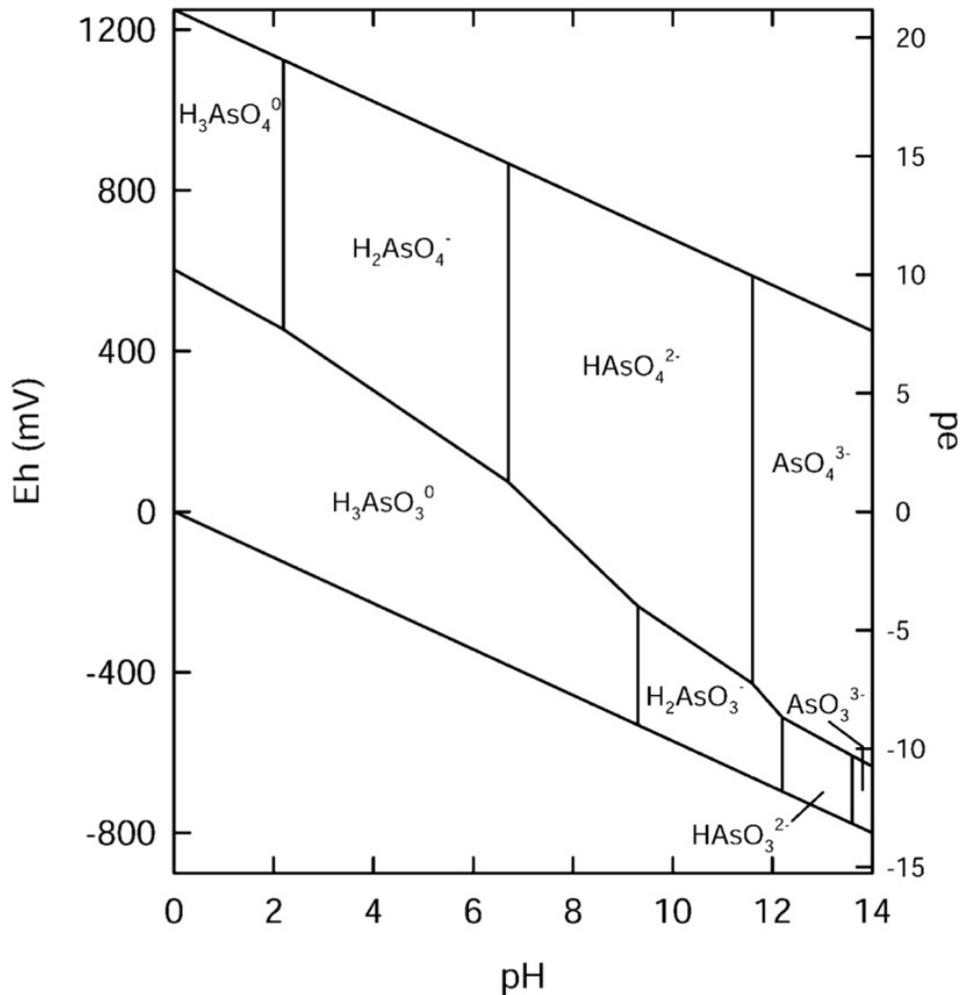
Figure 2. Eh-pH diagram for dissolved arsenic species at 25°C and 1 bar (from Smedley and Kinniburgh, 2002)

2.2. Mechanisms of arsenic mobilization during ASR

Arsenic mobilization from aquifer solids to groundwater is commonly attributed to (1) dissolution of arsenic-bearing solids, including oxidative dissolution of sulfidic minerals and reductive dissolution of iron (oxyhydr)oxides, (2) reduction of arsenate to the more labile arsenite, (3) desorption of arsenic from iron (oxyhydr)oxide surfaces at alkaline pH values (> 8.5), and (4) displacement of arsenic by competitively adsorbing ions, including phosphate and carbonate (Figure 3) (Fendorf, 2010). ASR can trigger these mechanisms through various combinations of physical and chemical processes. An in-depth literature review of geochemical mechanisms controlling arsenic mobility during ASR is provided in Fakhreddine et al. (2021).
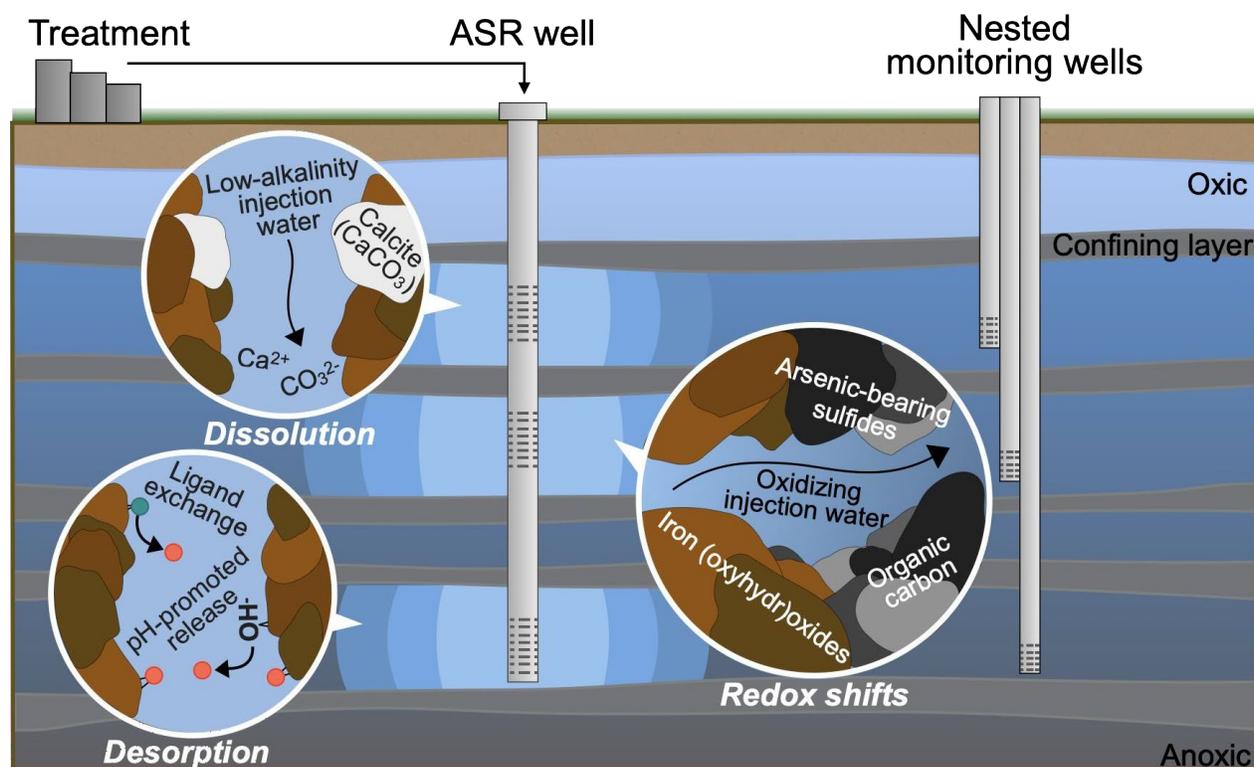
Figure 3. Simplified schematic of key geochemical processing occurring during ASR. Ligand exchange includes competitive ion displacement.

The specific mechanism of arsenic mobilization during ASR depends on the native aquifer geochemistry and the chemical composition of the injection water. While numerous combinations of ambient aquifer conditions and injection water composition are possible, the main pathways of arsenic mobilization are summarized in Figure 4. Arsenic mobilization during ASR has been most commonly reported during the injection of treated, oxic water into deep aquifers which are typically characterized by ambient anoxic or suboxic conditions. Anoxic and suboxic conditions are often associated with trace concentrations of arsenic-bearing pyrite in aquifer sediments. The injection of oxidizing water (containing dissolved oxygen and/or nitrate) results in the oxidative dissolution of sulfidic minerals, including arsenic-bearing pyrite. The oxidative dissolution of pyrite and arsenopyrite by dissolved oxygen follow the reactions in Equations 1 and 2.

$$FeS_2 + 3.75O_2 + 3.5H_2O \Rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \tag{1}$$

$$FeAsS + 3O_2 + 4H_2O \Rightarrow Fe(OH)_3 + SO_4^{2-} + 2H^+ + H_3AsO_3 \tag{2}$$
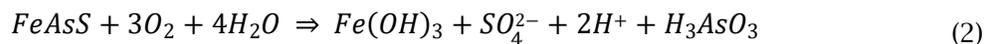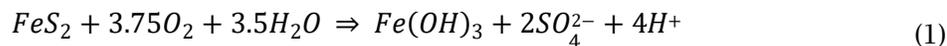
The dissolution of pyrite and arsenopyrite results in the release of iron(II) which is rapidly oxidized and precipitates as ferrihydrite, an amorphous iron (hydr)oxide with a strong adsorption affinity for arsenic. The subsequent adsorption of both arsenite and arsenate on iron (oxyhydr)oxides (denoted as Fe(OH)₃) can be expressed in Equations 3 and 4:

$$Fe(OH)_3 + H_3AsO_3 \Rightarrow Fe(OH)_3 \equiv H_3AsO_3 \tag{3}$$

$$Fe(OH)_3 + H_3AsO_4 \Rightarrow Fe(OH)_3 \equiv H_3AsO_4 \tag{4}$$
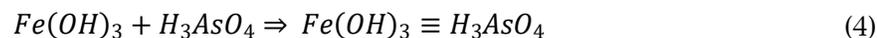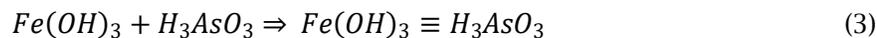
where $\equiv$ denotes a surface complex. Thus, arsenic repartitions from one solid phase (pyrite) to another solid phase (iron (oxyhydr)oxides) and will typically remain immobile on aquifer solids unless any of the previously mentioned processes occur: (1) reductive dissolution of iron (oxyhydr)oxides, (2) reduction of arsenate to the more labile arsenite, (3) an increase in pH (> 8.5) causes desorption of arsenic from iron (oxyhydr)oxide surfaces, or (4) competitive ions cause the desorption of arsenic (Figure 3). The most commonly reported mechanism is the reductive dissolution of freshly formed iron (oxyhydr)oxides during the storage and recovery phases of ASR. During storage and recovery periods, ambient reducing aquifer conditions can reemerge. This is particularly relevant during recovery when pumping induces the transport of native groundwater towards the ASR well or if the injection water contains appreciable concentrations of dissolved organic carbon. The reductive dissolution of iron (oxyhydr)oxide by dissolved organic carbon (denoted at CH_2O) and subsequent release of arsenic follows Equation 5 (Benner and Fendorf, 2010).

$$2Fe(OH)_3 \equiv H_2AsO_4^- + CH_2O \Rightarrow 2Fe^{2+} + HCO_3^- + H_3AsO_3 + 2H_2O \qquad (5)$$
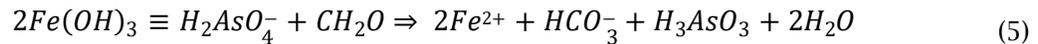
With repeated ASR cycles, redox conditions cycle between oxidizing and reducing causing the subsequent cycling between immobile and mobile conditions for arsenic, respectively. The timing and magnitude of peak arsenic concentrations is coupled to the onset of iron-reducing conditions which depends on the availability of reductants in the aquifer or in the injection water if the source water contains an appreciable supply of reductants (e.g., dissolved organic carbon) (Wallis et al., 2011).
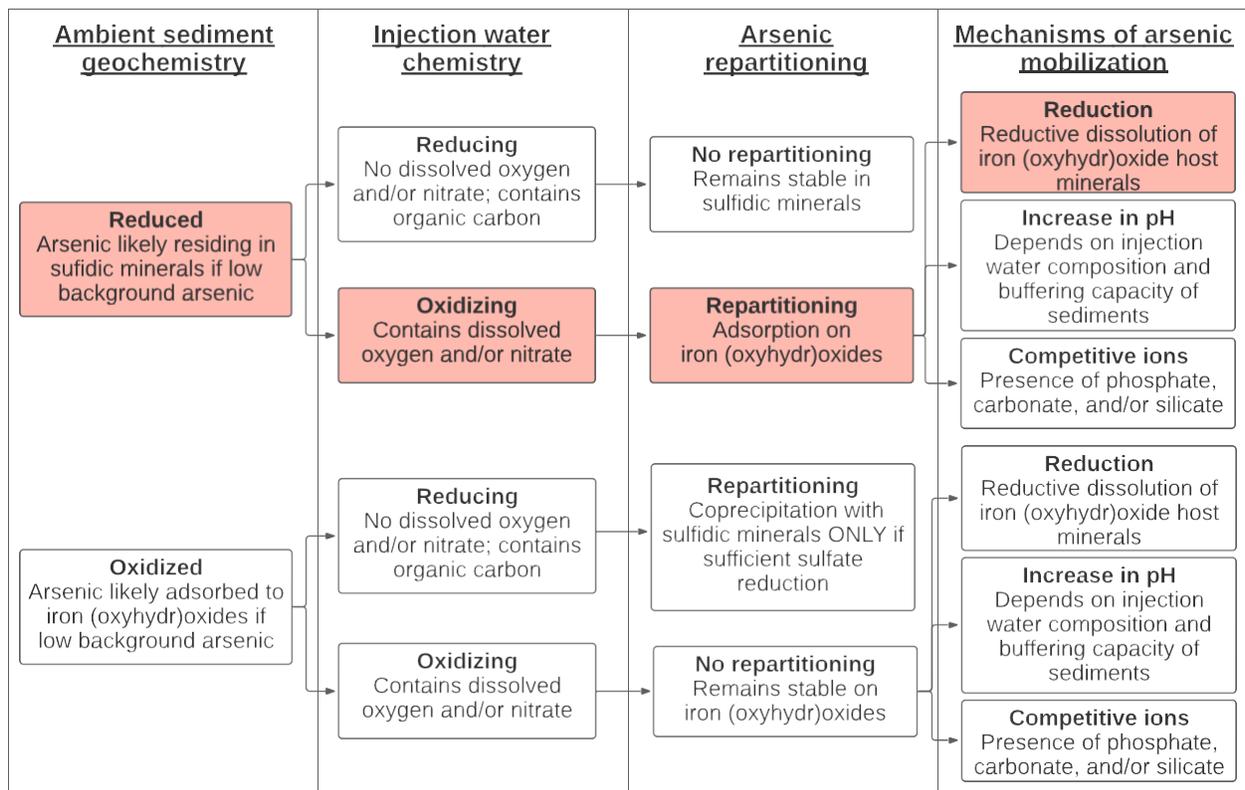
Figure 4. Main pathways of arsenic mobilization during ASR. Oxidative dissolution of arsenic-bearing sulfidic minerals is the most commonly reported pathway (highlighted in red).

Many sites report that the amount of arsenic mobilized declines with each successive ASR cycle. If ASR cycles are operated consistently with similar storage and recovery volumes, peak arsenic concentrations typically decrease over successive cycles as the adsorption capacity of the aquifer continues to increase while pyrite oxidation rates decrease (Arthur et al., 2005; ASR Systems, 2007; Mirecki et al., 2013; Verrastro and Kraft, 2018; Wallis et al., 2011). Decreasing pyrite reactivity over repeated ASR cycles or continuous injection has been attributed to depletion of a significant fraction of reactive pyrite (Arthur et al., 2005; Fakhreddine et al., 2020) and/or surface passivation limiting the rate of oxidation (Battistel et al., 2020; Descourvières et al., 2010). However, when an ASR cycle injects a greater storage volume than previous injection cycles, arsenic concentrations in the recovered water can increase (Arthur et al., 2005) highlighting the importance of consistent ASR operations.

Examples of non-redox related mechanisms of arsenic mobilization during ASR include arsenic desorption from iron (oxyhydr)oxides when ASR causes an increase in pH to values > 8.5. In Orange County, California, arsenic desorption from iron (oxyhydr)oxides was attributed to increased pH during ASTR (Fakhreddine et al., 2020). The presence of carbonate minerals, particularly calcite, can control the evolution of groundwater pH during ASR with potential secondary impacts on the adsorption affinity of arsenic to iron (oxyhydr)oxides. In addition, if recharge water introduces competitive ions, arsenic desorption from iron (oxyhydr)oxide and other mineral surfaces can occur. Competitive desorption was observed during an ASR trial in Bolivar, Australia where injection water containing phosphate caused the competitive desorption (and limited resorption) of arsenic from iron (oxyhydr)oxide surfaces (Vanderzalm et al., 2011). Potential sources of phosphate in injection water may include the addition of orthophosphates during water treatment for corrosion control. The adsorption of arsenic to clay minerals and organic matter can also control dissolved concentrations of arsenic. However, these mechanisms are thought to play a minor role in arsenic mobilization at ASR sites due to the relatively larger impacts of other processes including redox, pH, and competitive ions.
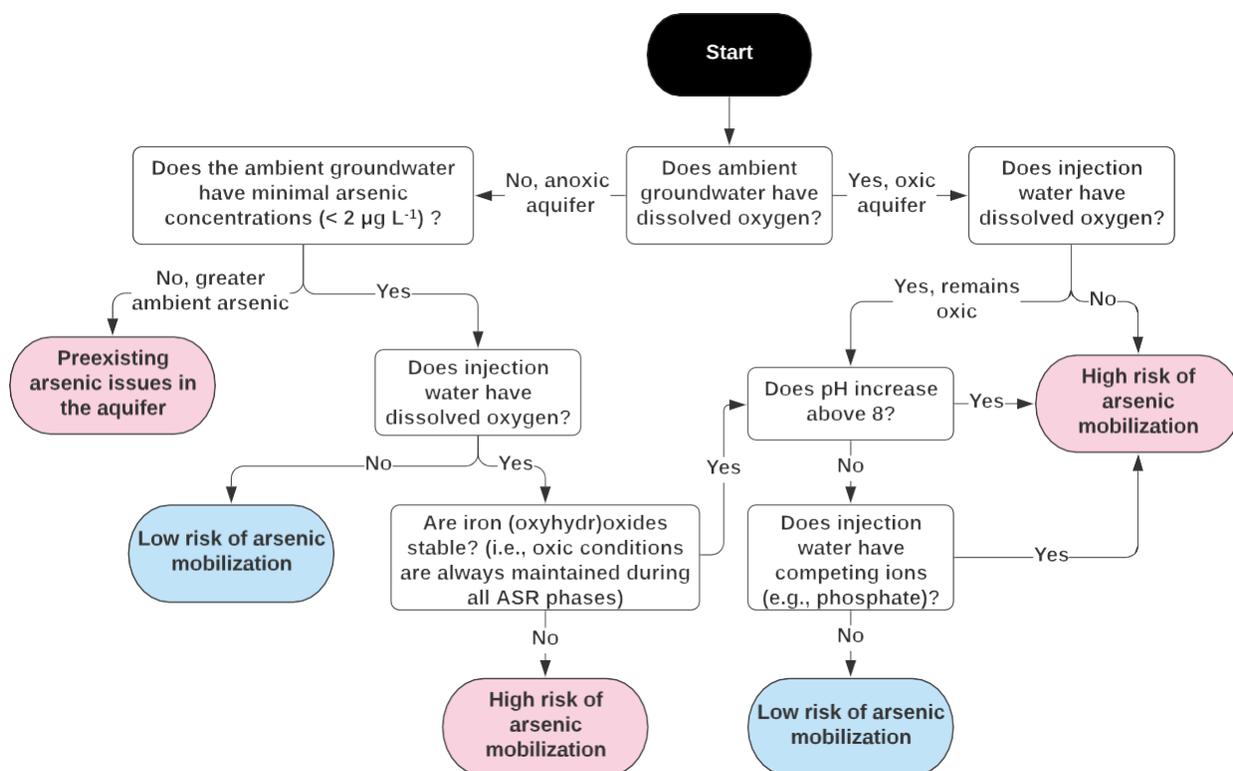
Figure 5. Decision tree for determining risk of arsenic mobilization during ASR based on site-specific conditions

Additionally, hydrological conditions in the aquifer are fundamentally linked to the geochemical processes controlling arsenic mobilization. At higher porewater velocities (e.g., higher velocities induced by injection wells), aquifer solids may not have sufficient time to equilibrate with the surrounding porewater. Kinetically limited processes play a role in arsenic release/retention during ASR. For example, oxidative dissolution of pyrite during deep injection was found to be a temperature-dependent, kinetically limited process at a test site in the Netherlands (Prommer and Stuyfzand, 2005). Similarly, kinetically limited oxidation of arsenite to arsenate was suspected to limit arsenic adsorption to iron (oxyhydr)oxides at an injection site in the Netherlands (Wallis et al., 2011).

Thus, arsenic mobility will ultimately depend on (1) the native groundwater conditions, particularly the native aquifer mineralogy and redox conditions, (2) the composition of the recharge source water, and (3) the site-specific operational setting (e.g., consistent operations and storage volumes). Figure 5 provides a framework for determining the risk of arsenic mobilization depending on these conditions which can be used in initial ASR feasibility assessments.

2.3. Other naturally occurring contaminants of concern during ASR

While arsenic is the most prevalent naturally occurring contaminant at ASR sites, increased concentrations of fluoride, molybdenum, manganese, and iron have also been reported during ASR. A limited number of mechanistic ASR studies exist for these contaminants compared to arsenic, potentially attributed to the health threats associated with these contaminants occurring at higher concentrations than arsenic. Other contaminants including uranium, chromium, nickel, vanadium, strontium, and barium have been noted during ASR. However, limited information is available on the behavior of the latter contaminants during ASR, therefore they are not discussed further in this document. Water quality monitoring for these contaminants can help improve understanding of the mobility of these contaminants during ASR.

Fluoride mobilization has occurred during injection of low-alkalinity recharge water due to dissolution of carbonate-rich fluorapatite minerals in the Leederville Aquifer, Australia (Schafer et al., 2020b). While limited information is available on the likelihood of fluoride mobilization during ASR in Texas, concentrations of naturally occurring fluoride are elevated in some portions of the Ogallala and Edwards-Trinity Aquifers (Reedy et al., 2012) suggesting the presence of fluorapatite minerals. Additional investigation and monitoring of fluoride are warranted given the naturally elevated fluoride concentrations in regions of the state. Monitoring of fluoride concentrations during recharge cycle tests can help determine potential mobility of fluoride where it is suspected to occur in the aquifer matrix. The current MCL for fluoride is 4 mg L^{-1} (US EPA, 2015a).

Molybdenum release has been observed at ASR sites in Florida and Australia (Fischler and Arthur, 2014; Pichler and Koopmann, 2019; Prommer et al., 2018). Like arsenic, molybdenum is known to occur in pyrite and may be mobilized via oxidative dissolution of sulfidic minerals. In Australia, the release of molybdenum was commensurate with arsenic (Prommer et al., 2018). In the Floridan Limestone Aquifer, molybdenum may be initially adsorbed to organic matter within the aquifer matrix and mobilized via oxidation of organic matter rather than pyrite (Pichler et al., 2017; Pichler and Koopmann, 2019; Pichler and Mozaffari, 2015). Despite these reported occurrences, the mobilization of molybdenum has not been mechanistically evaluated during ASR. In general, limited attention has been given to molybdenum, likely due to the fact that it currently has no formal drinking water limit based on low observed concentrations (< 10 µg L^{-1}) in most freshwaters (Smedley et al., 2014; Smedley and Kinniburgh, 2017). Recently, studies have suggested that molybdenum might be a potentially overlooked issue at ASR sites that warrants further evaluation (Pichler et al., 2017; Pichler and Koopmann, 2019). Given the growing attention on molybdenum, it may deserve further investigation and monitoring at sites in Texas.

Iron and manganese are primarily problematic at ASR sites due to operational (e.g., biofouling, clogging) and aesthetic issues (e.g., taste and odor). Iron and manganese have secondary MCLs of 0.3 and 0.05 mg L^{-1}, respectively. In addition to operational and aesthetic issues, iron and manganese cycling is tightly coupled to the release of arsenic and other toxic contaminants due to the strong adsorption capacity and reactivity of iron and manganese (oxyhydr)oxides. Generally, under oxic conditions, dissolved concentrations of iron and manganese are not likely to occur due to the formation of iron and manganese (oxyhydr)oxides. Dissolved concentrations of iron and manganese are typically indicative of reducing conditions and often correlate to mobile conditions of arsenic. Release of dissolved iron occurs mainly when organic carbon causes the reductive dissolution of iron (oxyhydr)oxides. It can also occur with dissolution of pyrite if formation of iron (oxyhydr)oxides after pyrite oxidation is limited. Strong decreases in pH to acidic conditions can also cause dissolution of iron (oxyhydr)oxides and release of dissolved iron, though sharp decreases in pH have not been previously reported during ASR. A decision tree for determining likelihood of dissolved iron issues during ASR is provided in the *Australian Guidelines for Water Recycling* (NRMMC et al., 2008). Similarly, manganese (oxyhydr)oxide dissolution is likely to be linked to reactions with organic carbon and/or shifts in pH.

3. Regulatory background on ASR in Texas

Regulatory oversight of ASR wells is administered by the United States Environmental Protection Agency's (US EPA) Underground Injection Control (UIC) program. ASR wells are regulated as Class V injection wells. The UIC program protects underground sources of drinking water (USDWs) from potential endangerment by underground injection as part of the Safe Drinking Water Act (SDWA). USDWs are defined as aquifers containing groundwater with total dissolved solids (TDS) concentrations less than 10,000 mg L^{-1}. Regulations often focus on the injection portion of ASR wells rather than regulating recovery operations. States can apply to have primary enforcement authority (i.e., primacy) of UIC programs. Currently, 33 states have primacy over their UIC programs for Class V injection wells, 7 states have partial primacy, and the US EPA has oversight over the remaining 10 state programs. State primacy may adopt additional regulations for ASR wells, but state-specific regulations do not supersede federal regulations on USDW endangerment. In states with primacy, the UIC program is typically integrated into groundwater protection programs (Bloetscher, 2015; US EPA, 2015b; Yang et al., 2017).

Texas is among the 33 states with primacy over their UIC programs. In Texas, ASR wells are regulated by the Texas Commission on Environmental Quality's (TCEQ's) Class V Injection Well Program with statutory requirements defined in the Texas Water Code (TWC) in Chapters 27 and 36, respectively titled *Injection Wells* and *Groundwater Conversation Districts*. TCEQ regulations applicable to ASR are in Title 30, Chapter 331, Subchapters A, H, and K of the Texas Administrative Code (TAC) (TCEQ, n.d.). In recent years, the state legislature has passed several bills to promote the adoption of ASR. These bills included HB 655, passed in 2015 by the 84th legislature, which revised water quality requirements in Chapter 27 of the Texas Water Code. Herein, we highlight revisions most applicable to the discussion of arsenic mobilization.

State UIC regulations on groundwater quality protection standards of the injected water for ASR can no longer be more stringent than federal standards (§27.154 TWC). Previously, injection water used for ASR was required to meet primary drinking water standards. Currently, ASR cannot cause the degradation of groundwater quality in any aquifer containing freshwater (30 TAC §331.184). Degradation of groundwater quality includes metals mobilization during ASR.

HB 655 also specifies reporting requirements for injection and recovery volumes and water quality. Operators are required to monitor all ASR injection and production wells and provide TCEQ reports of monthly volumes of water injected for storage and recovered for beneficial use (§27.155 TWC). While monthly reporting is required for injected and recovered volumes, water

quality testing is only required on an annual basis for injected and recovered water (§27.156 TWC). Specific project permits may have additional requirements for water quality testing and reporting if deemed applicable by TCEQ. From a geochemical perspective, annual reporting of water quality may not be sufficient to capture metals mobilization or transient shifts in water quality.

Additional reporting requirements related to water quality include the submission of results of several analyses within 30 days of completion of an ASR well. Operators are required to submit (1) well drilling and completion data, (2) well logging and testing data, (3) formation fluid analyses, (4) injection fluid analyses, (5) injectivity and pumping tests determining well capacity and reservoir characteristics, (6) hydrogeologic modeling, with supporting data, predicting mixing zone characteristics and injection fluid movement and quality, and (7) other information determined necessary for protection of USDWs (30 TAC §331.186).
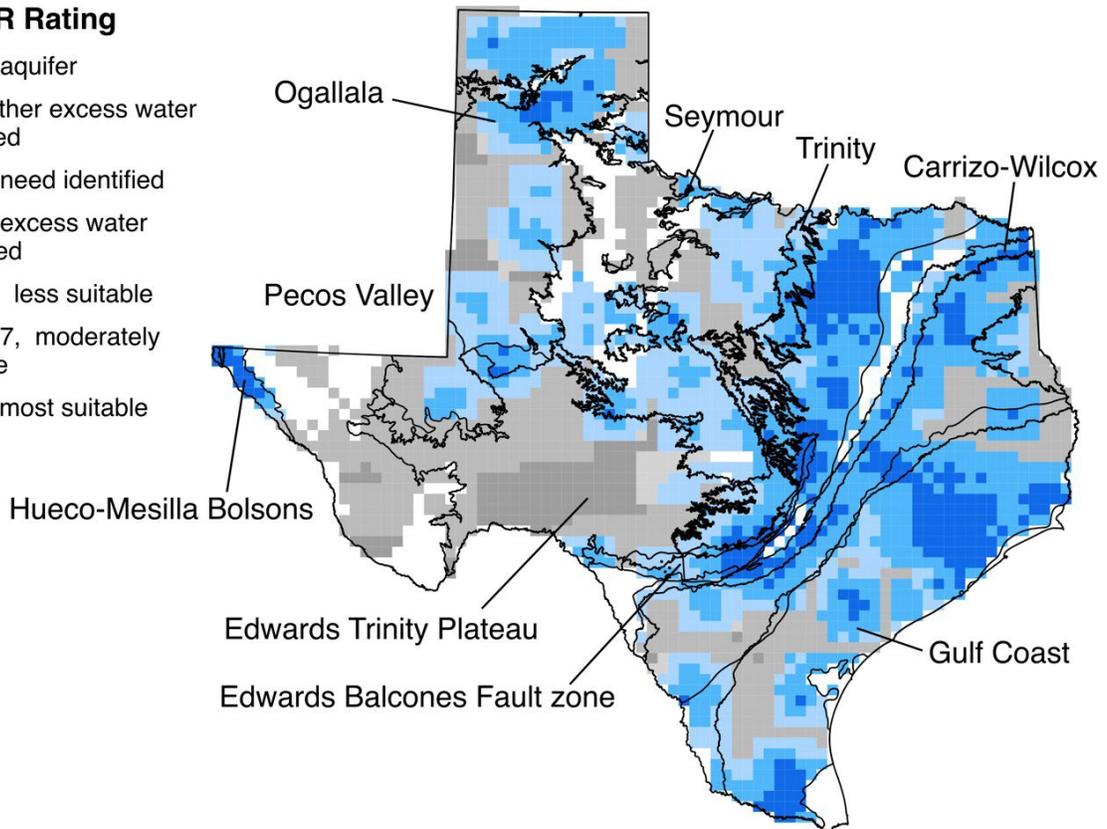
Figure 6. ASR site-suitability rating with outlines of the major aquifers (adapted from HDR, 2020)

In 2019, the 86th legislature passed HB 720 and 721. HB 720 allows the use of unappropriated water to be appropriated for AR or ASR projects, including stormwater and flood water. This expands the potential use of ASR to capture excess water supplies for dry periods and raises questions on the water quality of stormwater and flood water and potential impacts on metals mobilization. HB 721 required a statewide site suitability study to determine the feasibility of AR and ASR which was published in 2020 (HDR, 2020). The study found the Carrizo-Wilcox, Trinity, Gulf Coast, and Sparta Aquifers to have the highest ASR suitability rankings (Figure 6). The major aquifers are generally composed of sand and gravel, which is conducive to ASR including the Carrizo-Wilcox, Gulf Coast, Hueco-Mesilla Bolsons, Ogallala, Pecos Valley, Seymour, and Trinity Aquifers. The Edwards Balcones Fault Zone and Edwards-Trinity Aquifers

consist of limestone and dolomitic beds. Additionally, given the large spatial extent of the Trinity Aquifer, some production occurs in limestone beds of the Glen Rose and Cow Creek Formations of the Trinity Aquifer (HDR, 2020).

4. Developing a site-specific conceptual model

A site-specific conceptual model should be developed to determine the risk of arsenic mobilization and appropriate strategies to mitigate potential risks (Figure 7). The conceptual model provides a framework for defining the potential geochemical pathways controlling arsenic mobility at a given site. As described previously, the risk of arsenic mobilization and associated geochemical pathways depends on (1) ambient aquifer conditions, (2) injection water composition, and (3) ASR operating conditions. Therefore, each of these parameters needs to be defined and potential variations (e.g., seasonal shift in injection water composition) need to be estimated in order to rigorously assess potential shifts in water quality during ASR. The accuracy of the conceptual model will depend on the availability of information which varies at different stages of ASR planning. As more information becomes available (e.g., additional monitoring, well drilling, cycle testing) or major changes occur in ASR operations (e.g., switching injection source water), the conceptual model should be reassessed and updated. Based on the identified geochemical processes in the conceptual model, operators can design robust water quality monitoring programs and select the management strategies that are most suitable. Specific aspects of this framework are discussed in more detail in Sections 5 – 9.
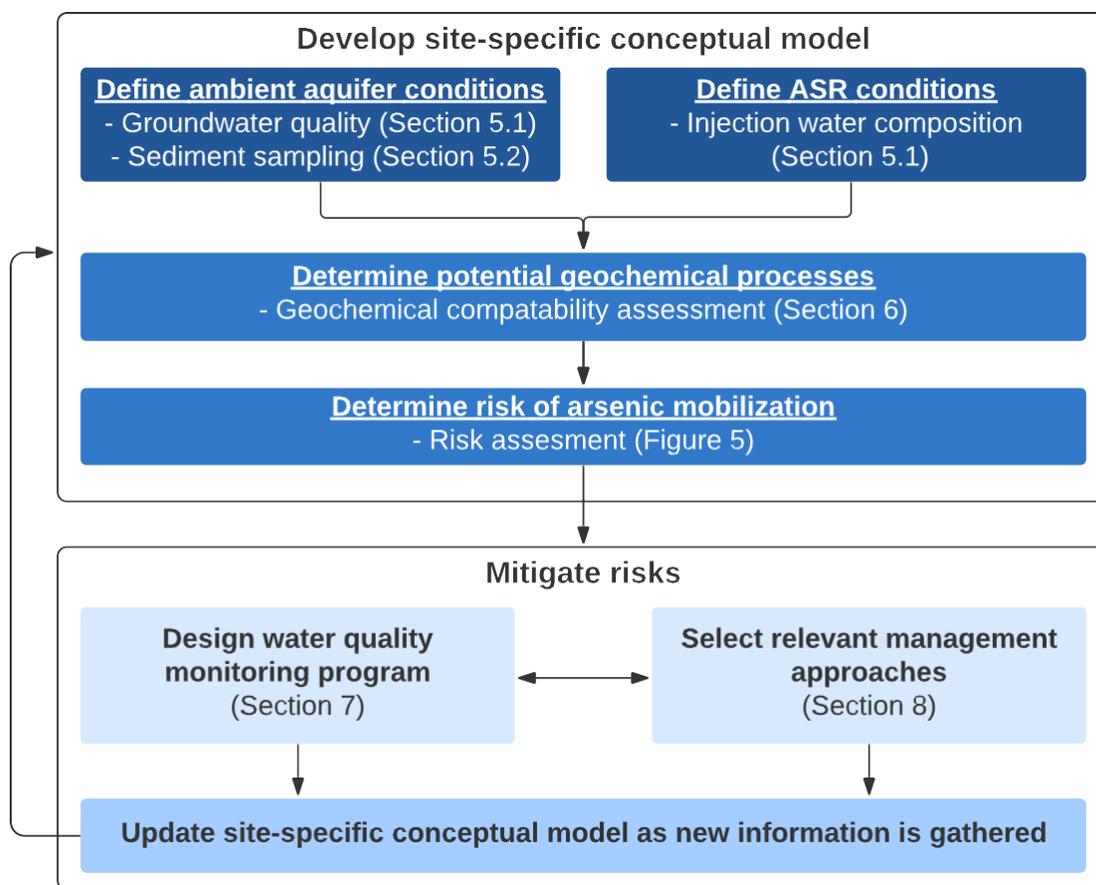
Figure 7. Framework for developing a site-specific conceptual model of arsenic mobilization during ASR to mitigate potential risks for degradation of water quality

5. Initial geochemical assessment

Initial site assessment is a key step for understanding geochemical compatibility issues and assessing the risk of arsenic mobilization for a given ASR project. Using multiple analyses and sampling of both groundwater quality and sediment characterization provides a stronger basis for understanding geochemical processes controlling arsenic mobility. Notably, geochemical conditions can vary greatly even at small spatial scales within aquifers. Therefore, if possible, sample collection at multiple depths and lateral spatial extents can help better characterize conditions within the storage zone.

5.1. Aqueous sampling of ambient groundwater and injection water

Aqueous sampling of both the ambient groundwater in the target storage zone and the injection water is critical for understanding potential geochemical interactions. Analysis of ambient groundwater quality provides information to infer potential reactivity and mineralogy of aquifer solids during ASR. Injection water quality should be analyzed at a frequency sufficient to capture potential temporal variations in chemical composition. For example, surface water sources can have seasonal variations in water quality parameters (e.g., dissolved oxygen, temperature, organic carbon) or variations associated with large storm events which can impact geochemical processes in the receiving aquifer. Any perturbations in injection water composition can impact arsenic mobilization in the storage zone. The more similar the composition of ambient groundwater and injection water, the less likely arsenic mobilization is to occur.

Table 1 lists key water quality analytes relevant for arsenic mobilization that should be analyzed during initial project assessments. Analyzing background concentrations of arsenic in the ambient groundwater and injection water is also critical for understanding sources of arsenic in the aquifer (i.e., mobilization from sediments vs migration of contaminated groundwater) should increases in arsenic concentrations be observed during ASR. While measuring the relative proportion of arsenite to arsenate can be useful for determining geochemical processes occurring during ASR, arsenic speciation is not a commonly measured and accessible analysis. Rather, knowledge of total arsenic concentrations along with pH and redox conditions can be used to estimate speciation of arsenic under equilibrium conditions using geochemical modeling (Section 6.2.1).

Measurement of dissolved oxygen (DO), oxidation-reduction potential (ORP), total or dissolved organic carbon (TOC or DOC), and pH is required for assessing the risk of arsenic mobilization. The presence of dissolved oxygen represents oxic conditions and potential for oxidation of sulfidic minerals and organic carbon. ORP is a challenging water quality measurement to interpret due to the sensitivity of ORP probes and the dependence of the measurement on the specific type of ORP probe (e.g., silver chloride probe readings differ from standard hydrogen electrode readings which represent Eh). Therefore, ORP data are most useful when interpreted for relative differences in ORP measurements between ambient groundwater and injection water and changes in ORP over time. Organic carbon (whether TOC or DOC) is important for understanding how injection water may stimulate microbially-mediated reactions in the aquifer and consume available oxidants.

Understanding pH shifts is critical for assessing potential adsorption/desorption reactions of arsenic and other trace contaminants from iron (oxyhydr)oxides and other aquifer solids. The pH of the injection water is not necessarily representative of groundwater pH that will emerge during ASR. Shifts in groundwater pH are often controlled by the buffering capacity of aquifer sediments which is largely related to carbonate content of the solids as described in Section 2. Accordingly, measurement of alkalinity and dissolved calcium and magnesium concentrations can be used to infer the buffering capacity of the storage zone and potential carbonate precipitation/dissolution reactions during ASR.

Table 1. Key water quality sampling parameters for geochemical assessment of ASR sites (adapted from Brown et al., 2011)

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

Parameter	Information provided
Total dissolved solids (TDS)	Can serve as tracer for injection water

Other key redox-active species to measure include nitrate, sulfate, dissolved iron, and dissolved manganese. Nitrate, manganese oxides, iron (oxyhydr)oxides, and sulfate can all serve as terminal electron acceptors in redox reactions though they are less thermodynamically preferred than DO. In addition to their importance as secondary contaminants, measurement of iron and manganese also provides information on redox conditions. Dissolved iron and manganese concentrations can signal the dissolution of iron (oxyhydr)oxides and manganese oxides and release of adsorbed arsenic and other trace contaminants if present. Sulfate is released during pyrite oxidation and can serve as an indicator of potential pyrite oxidation. For additional resources for estimating redox parameters, the USGS provides a workbook for inputting water quality data and assessing redox conditions in the aquifer (Appendix A).

Phosphate is an important analyte due to its competitive adsorption effects with arsenate. Injection of phosphate-rich water can cause arsenic mobilization from sediments. Increasing phosphate concentrations in groundwater can indicate corresponding arsenic mobilization.

Temperature and chloride can both serve as intrinsic tracers to signal the presence of injection water. Additionally, temperature increases can cause increases in microbial activity and reaction rates in the storage zone (Prommer and Stuyfzand, 2005). While typically groundwater temperatures are stable, injection water (e.g., surface water sources) temperature can vary seasonally with surface temperature and introduce seasonable temperature effects into the receiving aquifer. Therefore, potential shifts in temperature in source water should be monitored.

5.2. Sediment sampling

Sediment collection and sampling can provide valuable information on aquifer mineralogy, arsenic abundance, and potential geochemical reactions that will occur during ASR. Sediment sampling is less commonly performed compared to aqueous sampling and can be cost prohibitive, particularly for collection and preservation of samples from deep formations. Interpretation of results of sediment sampling should consider the sediment collection and preservation methods and limitations of specific types of analyses.

Ideally, sediments should be collected and stored in a manner that preserves the geochemical conditions of the aquifer. Collection of continuous core samples is less destructive than collection of drill cuttings, however it is much more costly. When core sampling is cost prohibitive, grabbing drill cuttings during ASR well drilling or other drilling operations (e.g., production or monitoring wells) in the vicinity of the project area can provide a source of sediment samples for analysis. To the extent possible, sediments should be stored at 4° C to slow geochemical reactions and in anoxic environment (e.g., laboratory glove box) to limit oxidation by atmospheric oxygen. When access to an anoxic environment for sediment storage is not available, samples can be collected and immediately stored in air-tight containers (e.g., mason jars) with oxygen scrubbing packets like those used in the food industry. Even when sediments are not preserved properly, there is still value in analyzing samples for mineralogy and total concentrations of redox-active elements. Pyritic minerals are known to oxidize slowly and may persist in sediments even when stored in oxic conditions though this must be considered when interpreting results of geochemical analyses. Additionally, total concentrations of metal(loid)s including arsenic, iron, and manganese will not change; rather, their speciation and mineralogical association may change.

Common sediment analyses include X-ray diffraction (XRD) and X-ray fluorescence (XRF). XRD can provide information on crystalline minerals present in the sediments controlling arsenic mobility including pyrite. XRD instruments often have high detection limits (~ 5% wt), and

pyritic minerals can often be present at lower concentrations and cause the mobilization of arsenic. Additionally, XRD only detects crystalline minerals which includes crystalline iron (oxyhydr)oxides (e.g., goethite, hematite) but not amorphous forms like ferrihydrite which is commonly formed after pyrite oxidation and has a strong adsorption affinity for arsenic. XRF provides information on total bulk concentrations of elements in sediments. While total arsenic concentrations in sediments is not necessarily an indicator of the likelihood of arsenic mobilization (Section 2), total concentrations of key redox-active elements (e.g., iron, manganese, arsenic, sulfur) in combination with other analyses including XRD can provide complementary information for assessing mineralogical associations of arsenic in the aquifer. Comparison of these values to reported, natural concentration ranges in aquifer sediments can help identify the presence of anomalies or areas with elevated concentrations of naturally occurring contaminants.

6. Geochemical compatibility assessments

Methods for assessing potential interactions between injected water and aquifer sediments include both laboratory and modeling approaches. The ability to use a specific method depends on the availability of data and sediment samples which may be more limited at initial stages of ASR planning relative to later project stages when more information has been gathered.

6.1. Laboratory experiments

When sediment samples are available, laboratory experiments can provide valuable information regarding potential reactions between injection water and aquifer solids. Sediment samples used for laboratory experiments include core samples and drill cuttings as described in Section 5.1. Mineralogical analyses of sediments can help prioritize sediment samples containing reactive minerals (e.g., pyrite) for experiments. Given the spatial variability of subsurface properties, small-scale experimental studies serve only as a guide to potential field-scale processes and cannot always reliably capture field-scale complexities (NRMMC et al., 2008).

Laboratory experiments can also be used to support the development of geochemical models and estimate model parameters. Both laboratory and modelling studies can also be effective tools for evaluating the impact of management strategies including pretreatment of injection water.

6.1.1. Batch experiments

Batch experiments (also referred to as leaching experiments) involve mixing aquifer sediment samples (typically a few grams to a few hundred grams) with injection water (typically a few hundred milliliters). Sediments and injection water are placed in a vial and continuously stirred or shaken until no further changes are observed in dissolved concentrations of species including arsenic and other metals released from the sediments. While batch experiments can provide an initial assessment of potential release of arsenic or other metals from aquifer sediments, there are many important limitations to understand when interpreting results of batch experiments. First, solid-to-sediment ratios under batch experiments differ from those occurring in situ at ASR sites. Therefore, observed concentrations under experimental conditions will not be directly transferrable to predicting groundwater concentrations during ASR and are difficult to scale to field conditions. Additionally, batch experiments do not capture the complexity of field-scale processes. Batch experiments are typically conducted to reach equilibrium concentrations whereas at the field-scale kinetic limitations often occur due to fast porewater velocities occurring during injection which may not allow for local equilibrium with aquifer solids. These are important considerations for both interpreting experimental results and designing batch experiments.

The Florida Geological Survey conducted batch leachability analyses (Figure 8A) to assess potential arsenic mobilization at several ASR sites (Arthur et al., 2008, 2007; Arthur and Dabous, 2005; Arthur and Fischler, 2008). These experiments involved exposing core samples

to various solutions in order to simulate geochemical reactions occurring during ASR. For example, experimental conditions included switching between low and high dissolved oxygen conditions. Solutions were monitored over time for water quality changes and remaining core samples were analyzed for changes in solid-phase composition using sequential extraction procedures to better characterize reactions occurring during cycling of experimental conditions. Experimental results matched the general pattern of arsenic mobilization reported at ASR sites in which high initial concentrations of arsenic are released during the first cycle and peak arsenic concentrations decline with subsequent cycles. The Florida Geological Survey leachability study program was designed as a cost-effective testing program to evaluate geochemical behavior of ASR systems prior to operational testing (Maliva et al., 2006).

6.1.2. *Column experiments*

Continuous flow-through column experiments allow for the simulation of transport conditions to better represent field processes (Figure 8B). Columns are packed with sediments and solution is pumped from the bottom and eluted from the top of the column to prevent issues associated with air entrapment. Pumping rates are typically selected to match possible porewater velocities at a given ASR site. This allows for evaluation of potential kinetic limitations occurring under transport conditions and the associated impacts on water quality. Influent solutions can be altered and cycled to simulate various ASR conditions, and pumping can be halted to simulate storage phases of ASR. In comparison to batch experiments, column experiments allow evaluation of conditions better representing operational settings of ASR. Like batch experiments, the solid-to-solution ratios can vary from *in situ* conditions at the field scale and concentrations should be interpreted with an understanding of experimental-scale limitations.

Column studies have been used to simulate and evaluate AR and ASR under a number of potential geochemical conditions. For example, column experiments were used to evaluate arsenic release during infiltration of advanced treated wastewater amended with various lime treatments using sediments collected from recharge basins in California (Fakhreddine et al., 2015). Column experiments were used in combination with reactive transport modeling to evaluate causal mechanisms of arsenic mobilization from carbonate-rich sediments simulating ASR operations in Florida (Lazareva et al., 2015). Similarly, ASR operations were simulated using columns packed with sediments collected from an ASR site in the Netherlands. Influent solutions were modified to evaluate the impact of potassium permanganate addition on metals mobilization (Antoniou et al., 2014).

Figure 8A. Batch reactors with nitrogen gas lines (from Arthur et al., 2008)
Figure 8B. Continuous flow-through columns packed with sediments

6.2. Modeling studies

Modeling studies are an effective way to decipher geochemical processes occurring during ASR and test the impact of various combinations of injection water, ambient groundwater, and operational site conditions. These tools can be valuable for designing ASR projects including well configurations and operational parameters. Models vary greatly in complexity and the ability to effectively develop and utilize a model depends on the availability and quality of data.

6.2.1. *Equilibrium speciation and mineral saturation modeling*

Equilibrium speciation modeling is the simplest form of modeling used to conduct geochemical compatibility studies for ASR sites. It is often used during early stages of site feasibility assessments. Aqueous water quality data for ambient groundwater and injection water is input into a geochemical model to calculate the equilibrium speciation (e.g., speciation of arsenic) and mineral saturation indices for each solution. For example, if calcite is estimated to be oversaturated in the ambient groundwater and undersaturated in the injection water, it can be concluded that injection will likely result in dissolution of calcite if it is present in the aquifer matrix. Commonly used, publicly available geochemical modeling programs include PHREEQC (Parkhurst, 1999) and MINTEQ (US EPA, 2013). Understanding the range of potential water quality compositions is important for simulating the potential conditions occurring during ASR. Geochemical modeling can also be used to estimate concentration thresholds and water quality compositions which may result in shifts in saturation indices or other water quality impacts (e.g., alkalinity concentrations that result in over or under saturation with respect to calcite for a given pH, calcium, and CO_2 conditions). Examples of PHREEQC modeling for estimating mineral saturation indices can be found in several published initial feasibility assessments (e.g., CH2MHILL, 2017).

Equilibrium modeling has several limitations including that it does not represent the full complexity of processes occurring during ASR, such as kinetic limitations and transport conditions. Rather, it is intended to serve as a simplified initial assessment. Moreover, the reactivity of aquifer solids is inferred from aqueous groundwater data and modeling, but solid-phase analyses are required to constrain potential reactions. While limitations should be considered when interpreting results of equilibrium geochemical modeling, these methods can be a valuable first step for understanding potential geochemical processes and developing a site-specific conceptual model.

6.2.2. *Reactive transport modeling*

More rigorous numerical modeling approaches include developing reactive transport models (RTMs) of ASR sites. RTMs couple physical flow and transport processes with geochemical reactions occurring as water moves through porous media. RTMs can be developed for 1-D, 2-D, and 3-D representations of ASR sites and simulate a broad suite of potential reactions. While RTMs have been developed for a number of ASR sites, they are more data intensive and computationally demanding than simpler equilibrium batch models. Parameterizing and calibrating a field-scale RTM requires knowledge of a broad suite of physical and geochemical parameters which are often obtained from rigorous sampling and monitoring efforts. Additionally, given the small scale of biogeochemical processes, RTMs are often constructed at fine spatial resolutions, particularly surrounding the injection well, compared to numerical models of groundwater flow often used at ASR sites. However, coarser flow models can be refined for RTMs if sufficient data is available. Given the regulatory requirement for hydrogeologic modeling and related analyses (30 TAC §331.186), analyses and sampling efforts can be designed to support potential future development of RTMs at sites where more rigorous evaluation of water quality and management approaches is desired.

RTMs can be effective not only for evaluating causal mechanisms of arsenic mobilization or other shifts in water quality, but also for designing operational controls and pretreatment strategies. For example, the effect of deoxygenating and adjusting pH of injection water on

arsenic mobilization was evaluated at injection test sites in Australia (Prommer et al., 2018; Rathi et al., 2017). Similarly, the effect of calcium addition on injection water to prevent the mobilization of fluoride during injection was evaluated using RTMs (Schafer et al., 2020a). For additional information on the use of RTMs to understand and manage water quality, Yang et al. (2017) discusses various RTMs for ASR decision support.

7. Monitoring guidance

As described previously (Section 3.1), there are no specific UIC program regulations in Texas for developing monitoring programs for ASR projects, and water quality samples of recovered water are only required to be reported annually unless otherwise specified within the ASR authorization or other TCEQ program areas regulated under 30 TAC Chapter 290, which may have more stringent requirements if recovered water is directly used for public water supply systems. However, robust water quality monitoring programs are key to preventing arsenic mobilization which can result in abandoned ASR projects due to the cost prohibitive nature of treatment and remediation. Adequate monitoring of water quality parameters controlling arsenic mobilization is critical for (1) understanding the geochemical processes controlling contaminant mobility, (2) tracking water quality trends to anticipate shifts in contaminant concentrations, (3) selecting appropriate management strategies for limiting contaminant mobilization, (4) developing modeling tools, and (5) facilitating conversations with stakeholders and regulatory agencies. While detailed guidance for designing a robust monitoring, program is beyond the scope of this document, this section highlights important considerations related to water quality monitoring relevant to arsenic mobilization processes during ASR. Appendix A lists more specific guidance on developing groundwater monitoring programs. In practice, development of a groundwater quality monitoring network requires balancing multiple factors including (1) available resources, (2) existing monitoring programs, (3) the level of local groundwater use and development, (4) the hydrogeologic and geochemical complexity of the site, (5) current and proposed local groundwater management actions or projects, and (6) the proximity of the site to wells for domestic, irrigation, public water supply, or other uses (Moran and Belin, 2019).

Ideally, monitoring data should be collected at spatial and temporal resolutions sufficient to understand the extent of water quality impacts and capture short-term, seasonal, and long-term shifts. Table 1 (Section 5.1) lists key water quality monitoring parameters relevant to arsenic mobilization processes. To the extent possible, direct measurement of arsenic and other trace contaminants of concern should be sampled frequently as part of general water quality sampling. However, accurate measurement of arsenic at trace concentrations near the 10 µg L^{-1} MCL can be expensive and require laboratory instrumentation. If it is not feasible to directly measure arsenic and other trace contaminants on a regular basis, it may be possible to adapt by paying close attention to measurement of common water quality parameters that serve as proxies for geochemical conditions controlling arsenic mobility. DO, ORP, and pH are critical water quality parameters that should be monitored regularly in both the groundwater and injection water and can be monitored *in situ* with field probes at relatively low cost. If shifts in DO, ORP, and/or pH are observed in monitoring data, there is higher likelihood that changes in contaminant mobilization processes have occurred, and samples should be collected immediately to determine trace contaminant concentrations (Fakhreddine et al., 2019).

The spatial extent of monitoring depends on the scale of the project and requires understanding the flow and transport conditions induced by ASR. Groundwater flow models with particle tracking capability can help determine the spatial extent of ASR impacts on the aquifer. The TCEQ rules define the area of review for an ASR project as the area determined by a half-mile radius from the injection well. If an ASR project consists of multiple injection wells, the area of review is defined as the area determined by a half-mile radius from the centroid of the well field. If the extent of subsurface stored water will extend beyond a half-mile radius, then the area of review is calculated from site-specific hydrogeologic information (30 TAC §331.182). For the majority of ASR wells monitored to date, lateral arsenic movement within

the storage zone is typically limited to less than 60 m (200 ft) (ASCE, 2020). However, the movement of arsenic depends heavily on several site-specific hydrogeologic, geochemical, and operational conditions and should be evaluated for each site. In addition, a limited number of ASR sites globally provide information on water quality monitoring (Stefan and Ansems, 2018) rendering it difficult to evaluate the transferability of general rules of thumb.

In addition to capturing the spatial extent of water quality shifts, monitoring wells should be positioned between the project area and production wells or other groundwater users in locations that provide sufficient response time between detecting a problem and implementing a strategy to prevent contaminated water from reaching users should a problem be observed. If water quality issues are first observed in monitoring wells too close to groundwater users, there may not be an adequate response time for preventing contamination from reaching users. Additionally, monitoring wells should span impacted depth intervals. If the ASR well is screened at multiple depth intervals to recharge multiple hydrostratigraphic units, monitoring should be depth-resolved (e.g., nested monitoring wells) to capture water quality changes at each depth interval rather than only sampling mixed water from all depths. This is critical for pinpointing issues and targeting specific depth intervals to deploy management strategies (e.g., sealing the injection well at problematic depth intervals).

Temporal resolution of water quality sampling should capture the frequency of potential variations in water quality. Arsenic concentrations can vary throughout the duration of injection, storage, and recovery phases as each phase can cause a shift in geochemical and hydrologic conditions. It is important to capture variations in water quality occurring across different ASR phases and over subsequent ASR cycles. As described in Section 2, peak arsenic concentrations tend to decline when ASR cycles are operated consistently (e.g., without extended periods of inactivity). However, some sites do not observe this decline in peak arsenic concentrations for unknown reasons. Whenever there is a change in ASR operations (e.g., ASR activity resumes after a period of prolonged inactivity, a change in injection water quality), monitoring of groundwater, recovered water, and injection water becomes even more critical to capture potential perturbations in water quality. Injection water quality is more likely to vary seasonally than deep ambient groundwater quality. Monitoring and understanding variations in injection water quality (short-term, seasonal, or long-term) is critical to understand when geochemical shifts in the receiving aquifer may occur. Additionally, groundwater can have long lag times which emphasizes the importance of catching shifts in water quality before they become a problem (Moran and Belin, 2019).

8. Overview of management strategies

This section offers a summary of various management approaches that have been deployed or proposed at ASR sites to limit arsenic mobilization. Management approaches can broadly be categorized into strategies focused on (1) pretreating injection water to match the ambient geochemical conditions in the aquifer (Section 8.1) and (2) modifying physical or operational conditions to limit the extent of arsenic mobilization (Section 8.2).

The feasibility and efficacy of a given management strategy depend heavily on site-specific parameters including geochemical mechanisms of arsenic mobilization, project operational constraints, and cost effectiveness. Therefore, selection and deployment of a given management strategy should be done with the input of geochemical experts familiar with the site (Section 9.2).

8.1. Pretreatment of injection water

8.1.1. Deoxygenation

The most common example of pretreatment is removal of oxidants, primarily dissolved oxygen, from injection water when recharging into anoxic aquifers to prevent oxidation of sulfidic minerals. Removal of nitrate or residual oxidants (e.g., hydrogen peroxide, free chlorine, ozone)

may be required in order to prevent all potential oxidation of sulfidic minerals. Deoxygenation using membrane contactors has been investigated at sites in Florida and Australia (Fischler et al., 2015; Prommer et al., 2018; Rathi et al., 2017). While proven highly effective at minimizing arsenic release, deoxygenating injection water has high operational costs, requires additional capital, and continuous operations during injection phases of ASR (Maliva, 2020; Maliva and Missimer, 2010).

8.1.2. *Organic carbon removal*

Deep aquifers are typically thermodynamically limited systems, and injection water containing organic carbon can stimulate microbially-mediated reactions in the aquifer. Excessive concentrations of organic carbon in injection water can have deleterious impacts to groundwater quality. For example, reductive dissolution of iron (oxyhydr)oxides (previously residing in aquifer sediments or freshly formed during the injection of oxic water) can occur if organic carbon causes iron reducing conditions. This can result in the release of dissolved iron and mobilization of arsenic and other contaminants adsorbed to iron (oxyhydr)oxide surfaces. If there is sufficient organic carbon in the injection water, it is possible that reducing conditions will cause sulfate reduction. Under sustained sulfate-reducing conditions, if appreciable dissolved hydrogen sulfide concentrations are sustained, sulfidic minerals can precipitate thereby removing dissolved arsenic concentrations from groundwater (Mirecki et al., 2013). However, this requires sustained dissolved hydrogen sulfide concentrations (O'Day et al., 2004) which also degrades water quality. Additionally, it is difficult to determine *a priori* if organic carbon concentrations in the injection water are sufficient to cause coprecipitation of arsenic in sulfidic minerals. Therefore, caution should be exercised when injection water contains organic carbon, and pretreatment to remove organic carbon is generally the most advisable option.

8.1.3. *Ionic composition and pH control*

Pretreatment options include polishing steps (e.g., lime addition) to modify the ionic composition and/or adjust pH. If the goal is to prevent pH shifts during ASR, adjusting pH of the injection water may have limited impact as groundwater pH is more likely controlled by the buffering capacity of the injection water and aquifer sediments. Modifying ionic composition to target specific concentrations of calcium, magnesium, and/or alkalinity can impact the buffering capacity of the injection water and carbonate precipitation/dissolution reactions within aquifer sediments that control groundwater pH. For example, the addition of lime to treated injection water has been used to increase saturation with respect to calcite and limit calcite dissolution during ASR. Where arsenic mobilization is attributed to pH-promoted desorption or associated with dissolution of aquifer minerals, polishing steps may help mitigate mobilization.

While arsenic mobilization is not commonly directly attributed to dissolution of carbonate minerals owing to the low abundance of arsenic in carbonates, this mechanism can be modified to inhibit the mobilization of fluoride. Modifying ionic composition of injection water has been proposed as a mechanism to limit fluoride mobilization during ASR by preventing dissolution of carbonate-rich fluorapatite minerals (Schafer et al., 2020a).

8.1.4. *Pre-oxidation of target storage zone*

It has been proposed that accelerating the oxidation of sulfidic minerals by pre-oxidizing the aquifer can limit arsenic mobilization by conditioning the aquifer prior to ASR operations. Conceptually, this is analogous to several cycle tests of oxic injection water conditioning the aquifer by oxidizing pyritic minerals and precipitating iron (oxyhydr)oxides which increases the adsorption capacity of the aquifer sediments. Pre-oxidation can be achieved by injecting strong oxidants in the target storage zone. A test ASR cycle was conducted at a field-scale pilot site in the Netherlands using injection water with elevated nitrate concentrations through the addition of sodium nitrate as a potential method for enhancing oxidation of aquifer sediments. However, increased oxidation rates were not observed at most sampling locations (Antoniou et al., 2012).

Similarly, Antoniou et al. (2014) conducted laboratory column experiments on anoxic, siliciclastic sediments from an ASR site in the Netherlands using synthetic injection water with potassium permanganate as a strong oxidant. The pre-oxidized columns were then flushed with oxic tap water to simulate ASR cycling. Results indicated that permanganate pre-treatment can reduce pyrite oxidation during subsequent cycles. However, oxidized conditions must be maintained. If reducing conditions return, it may be necessary to retreat the aquifer. Given the limited field-scale studies of pre-oxidation, further analysis is required to determine the efficacy of this management approach at limiting arsenic concentrations during long-term ASR operations.

8.2. Physical

8.2.1. Buffer zone maintenance

The concept of forming and maintaining a buffer zone was initially developed to limit recovery of saline water at ASR sites injecting freshwater into brackish aquifers. The term "bubble" refers to the zone of recharge during ASR (National Research Council, 2007). The target storage volume consists of both the injected, stored water and the buffer zone (Figure 1). The stored water volume typically extends several hundred feet (100 ft = ~ 30 m) from the ASR well. With each injection cycle as water flows through the pore spaces of the aquifer, the injection water reacts with aquifer sediments and, in the case of injection of oxic water into a previously anoxic aquifer, gradually oxidizes the aquifer. During formation of the buffer zone, mobilized arsenic is adsorbed to iron (oxyhydr)oxide surfaces in the stored water zone or displaced to the buffer zone. In the buffer zone, mixing between injection water and native groundwater can promote additional mobilization of arsenic and other geochemical interactions. While the buffer zone is expected to have potentially elevated arsenic concentrations, the volume of water in the buffer zone is not recovered. Only stored water is extracted during the recovery phases of ASR cycles. This prevents the recovery of mixed water with degraded quality (e.g., elevated concentrations of arsenic, total dissolved solids, chloride). In some cases, it is necessary to replenish the buffer zone where migration or mixing occur beyond acceptable thresholds or if there are plans to increase the storage volume for recovery.

Values of target storage volumes are determined based on hydrogeologic properties and mixing criteria. The volume of the buffer zone usually ranges from 0 – 50% of the target storage volume. If local experience or previous geochemical studies indicate that no water quality issues are expected, then smaller buffer zones may be sufficient. Determining the target storage and buffer zone volumes required to ensure water quality may be an iterative process (ASCE, 2020). Determination of the appropriate target storage volume can be an iterative process that depends on the quality of the recovered water. Preliminary estimates of the buffer zone are typically 30 – 50%, depending on total dissolved solids (TDS) concentrations and anticipated shifts in arsenic concentrations (D. Pyne, personal communication, August 5, 2021).

Cycle testing in combination with frequent water quality monitoring can help evaluate the efficacy of the buffer zone approach at a given site. Early cycle testing typically injects a small volume while successive cycles can have larger injection volumes and leave an increasingly larger volume of water stored in the aquifer to progressively build and maintain the buffer zone. This leads to the gradual development of a target storage volume while limiting the spatial extent of arsenic mobilization in early testing cycles and recovery of potentially mobilized concentrations. The aquifer is gradually conditioned to attenuate arsenic in the storage zone. When the buffer zone volume has been achieved, full recovery of stored water may occur in subsequent cycles. Operational experience in Florida suggests that this is an effective approach for Floridan sites which typically involve municipal water storage in carbonate aquifers containing trace pyrite concentrations.

Unlike pretreatment methods, this approach does not focus on addressing causal geochemical mechanisms of arsenic mobilization. Rather, the buffer zone approach acknowledges that arsenic mobilization may occur within the buffer zone and seeks to prevent recovery of

contaminated water. A regulatory concern is that arsenic concentrations may persist in the storage zone and potentially migrate to other wells (Maliva, 2020).

This approach is based on operational experience and has not been evaluated with modeling or laboratory studies to rigorously understand geochemical mechanisms controlling arsenic mobility and sensitivity of the approach to site-specific parameters including injection water composition, ambient geochemical conditions, and operational controls. Therefore, it is difficult to assess the direct transferability of this approach to other sites without further investigation. Many proposed sites in Texas have similar settings to Floridan sites (i.e., treated surface water injection in carbonate-rich formations with trace pyrite concentrations) suggesting potential transferability of this approach. In all cases, robust monitoring and evaluation of water quality during ASR testing will be key to understand the potential for arsenic mobilization.

8.2.2.   *ASR variants or multi-well systems*

ASTR and/or multi-well injection systems may allow for more control over maintenance of oxic zones surrounding the injection area rather than a single ASR well where recharge water migrates back and forth potentially shifting redox conditions in the aquifer. However, at present, there are no published studies comparing ASR and ASTR for the effects on arsenic mobilization. ASTR, particularly if continuously operated, does not cause shifting redox conditions as with ASR. Rather recharge and recovery occur along a continuous flow path instead of alternating directions as with a single dual-purpose ASR well. Therefore, when metals mobilization does occur, ASTR often results in a single, transient peak concentration of arsenic that is attenuated over time if injection is consistently operated and maintains oxic conditions. Additionally, hybrid approaches may offer more flexibility in managing water quality. Artificial recharge via infiltration generally occurs in oxic, well-aerated environments and is typically considered less vulnerable to arsenic mobilization due to arsenic retention on aquifer solids generally being more favorable under oxic conditions. A recently completed peer-review report evaluating ASR operations at the Comprehensive Everglades Restoration Project in Florida encouraged future study of hybrid approaches that use bank filtration, ASTR, and emerging well configurations and operational strategies (Arthur et al., 2020). Additional work is needed to better understand how ASR (or ASTR) configuration and hybrid approaches differ in their potential impacts on metals mobilization.

8.2.3.   *Modifying operational controls*

Arsenic mobilization is influenced by operational parameters including timing and frequency of injection, storage, and recovery phases, injection and recovery volumes, injection and recovery rates. The physical movement of water is inherently intertwined with the geochemical reactions occurring in the aquifer, particularly the time that water has to react with the aquifer solids as it moves through the aquifer. Kinetically limited reactions can be further limited or enhanced by using operations controls to increase or decrease porewater velocities, respectively. Examples of kinetically limited reactions that have been evaluated in multiple site-specific studies include (1) the kinetic oxidation of pyrite by dissolved oxygen and/or nitrate and (2) degradation of organic carbon. While operational controls are a potential cost-effective method for optimizing geochemical processes occurring during ASR to limit arsenic mobilization, no sites have evaluated and deployed this as a management approach. It requires a comprehensive understanding of site-specific geochemical conditions and further evaluation (e.g., reactive transport modeling studies) for use as a management approach.

9.   Additional management considerations

9.1. Consistent operations and long-term planning

There is evidence that attenuation of arsenic concentrations during ASR depends on consistent operations (Section 2) though this has not been mechanistically evaluated and requires additional research. A shift in injection water chemistry or operational conditions (e.g.,

injection volumes, timing, periods of inactivity) may cause new pulses of arsenic release even following previous cycle with low or no arsenic mobilization. Therefore, a key consideration for new ASR sites is the ability to consistently operate ASR cycles. ASR planning efforts should involve long-term assessment of future availability and quality of injection source waters being considered for ASR. Operators should evaluate how ASR operations may change in the future in response to climatic factors, land use changes, population growth, and interactions with other groundwater management projects and uses. For example, project needs may evolve from seasonal storage to multiyear drought planning.

Changes in climatic factors may result in periods of inactivity, switching to alternate water sources, project abandonment, and/or variations in storage times. These can have significant impacts on arsenic mobilization, water quality, and project goals, more broadly. For example, a number of ASR wells in California have not been operational for several years due to lack of excess water available for recharge (Bloetscher, 2015). Australia's guidance for managed aquifer recharge (AR) projects states that climate change is expected to lead to longer average residence times in storage which may result in lower recovery efficiencies due to total dissolved solids in the recovered groundwater, particularly where the ambient groundwater has a higher salinity than the injection water (NRMMC et al., 2008). Potential long-term changes in ASR operations should be evaluated and incorporated into initial geochemical assessments during project planning.

9.2. Technical advisory panels for ASR planning

Additional recommendations from experience in Florida include the development of technical advisory panels that include geochemists for future ASR projects. The use of technical advisory panels with domain knowledge on arsenic mobilization was found to be helpful during implementation of several ASR projects in Florida (J.D. Arthur, personal communication, November 18, 2020). Experienced geochemists with knowledge of metals mobilization processes can help develop a site-specific conceptual model, design cycle tests including robust monitoring, interpret water quality data, and evaluate potential management strategies if needed based on site-specific conditions. Technical advisory panels can also be used to design laboratory or modeling studies beyond simplified geochemical equilibrium modeling to better understand local geochemical shifts occurring during ASR. A technical advisory panel for each project would allow ASR operators access to directed expertise for protecting groundwater quality at their sites beyond broad, general guidance.

9.3. Contingency plans and mitigation programs

While all necessary precautions should be taken to prevent degradation of water quality during ASR, a contingency plan should be developed in case arsenic mobilization occurs, particularly if groundwater supplies are used for drinking water or other beneficial uses. Contingency plans should account for protocols to (1) increase or augment monitoring, (2) assess potential impacts to end users, (3) notify users, and if necessary, (4) provide alternate, safe water supplies, (5) discontinue use of impacted water supplies as needed, (6) address contamination by remediation or discontinuing use, and (7) develop targeted future monitoring once the problem has been resolved to ensure it does not occur again. Having a plan in place a priori will help improve response times and protect groundwater users (Fakhreddine et al., 2019).

In addition to contingency plans, proactive mitigation programs can help preemptively address stakeholder concerns and ensure continuous access to safe water supplies should an ASR project have deleterious impacts. For example, during development of the H2Oaks ASR system, the San Antonio Water Systems (SAWS) established a policy to mitigate potential impacts to private wells. H2Oaks consists of 29 ASR wells with a planned total storage volume of approximately 200,000 acre-feet (SAWS, n.d.). The SAWS well mitigation program focused primarily on impacts to groundwater levels. Individual wells in the vicinity of the ASR site were assessed for potential impacts, and mitigation options included (1) lowering pumps, (2) connecting to a water system, and (3) drilling of a new replacement well. SAWS mitigated

impacts to 166 wells, including lowering 53 pumps and developing 83 new wells (Thompson, 2019). Occasionally, the well mitigation program addressed water quality issues when replacement wells produced water of lesser quality than the original well. This was primarily attributed to the steel casings initially used in replacement wells (later switched to polyvinyl chloride, PVC). Elevated iron was the most common water quality issue, and some PVC replacement wells produced water with higher iron concentrations than the original wells. For those wells, modifications were made to storage tanks to help remove iron from solution (C. Langston, personal communication, January 8, 2021). Development of contingency plans and mitigation programs can also help facilitate discussions with stakeholders and regulatory agencies in order to improve likelihood of project success.

10.   Summary

The mobility of arsenic and other naturally occurring contaminants during ASR is controlled by a broad suite of site-specific conditions. Accordingly, this document provides general guidance for developing site-specific conceptual models of arsenic mobilization processes in order to assess risks and determine potential management approaches. In cases where high risk of arsenic mobilization is determined, project viability may depend on the ability to effectively deploy management approaches for limiting arsenic mobilization. Selecting a management approach requires site-specific studies to ensure feasibility and desired impacts for protecting water quality.

This document highlights the need for continuous data collection and updating site-specific conceptual models of hydrological and geochemical processes occurring during ASR. Developing a rigorous understanding of water quality shifts and appropriate management strategies may require an iterative approach as additional information becomes available during later stages of project development. To effectively anticipate water quality impacts and select appropriate management strategies, projects should (1) evaluate long-term operations which likely depend on future water availability, (2) form technical advisory panels to provide site-specific geochemical guidance, and (3) develop contingency plans or mitigation programs to limit adverse impacts and ensure a rapid response should unintended water quality degradation occur.

Appendix A. Table of additional resources relevant to ASR and water quality

Title	Author	Description and URL
Texas Aquifer Storage and Recovery Applet	Werth et al. (University of Texas at Austin; prepared for TCEQ)	User-friendly interactive web app for assessing feasibility of ASR based on physical aquifer properties and operational parameters. https://txasr.tceq.texas.gov/
Statewide Survey of Aquifer Suitability for Aquifer Storage and Recovery Projects or Aquifer Recharge Projects	HDR (prepared for TWDB)	Statewide site-suitability study including interactive story map and data (e.g., water demand, excess water, aquifer properties) related to ASR suitability. https://www.twdb.texas.gov/innovativewater/asr/projects/Statewide/index.asp
Texas Water Development Board Groundwater Database	TWDB	Statewide database of water quality monitoring data which can help in initial ASR site assessment. https://www.twdb.texas.gov/groundwater/data/gwdbrpt.asp
An Excel Workbook for Identifying Redox Processes in Groundwater	Jurgens et al. (USGS)	Excel workbook for estimating predominant redox processes based on water quality measurements. https://pubs.usgs.gov/of/2009/1004/
API Groundwater Arsenic Manual: Attenuation of Naturally Occurring Arsenic at Petroleum Impacted Sites	Brown et al. (American Petroleum Institute)	Focused on petroleum-impacted sites, but contains general information on monitoring of arsenic and other naturally occurring contaminants that may be applicable to ASR sites. https://www.api.org/-/media/Final%20API%20Pub%204761%20Feb2011%20Arsenic%20GW%20site%20management.pdf
Standard Guidelines for Managed Aquifer Recharge	American Society of Civil Engineers	Recent description of guidelines for planning, design, construction, operation, monitoring and closure of MAR projects. Includes description of formation and maintenance of buffer zones. https://doi.org/10.1061/9780784415283
M63 Aquifer Storage and Recovery	Bloetscher et al. (American Water Works Association)	Manual for general understanding of ASR principles. Includes state by state assessment of ASR wells. https://www.awwa.org/Store/Product-Details/productId/26636

Title	Author	Description and URL
Aquifer Storage and Recovery	Pyne, R., David G. (ASR Systems)	General guide to ASR topics including case studies and suggested future directions for research and applications. https://my.ngwa.org/NC_Product?id=a18500 0000BYub2AAD
Australian Guidelines for Water Recycling: Managing Health and Environmental Risks (Phase 2) Managed Aquifer Recharge	Natural Resource Management Ministerial Council, Environment Protection and Heritage Council, National Health and Medical Research Council	Risk-based framework for developing MAR sites. Includes risk assessments for metals mobilization including arsenic and iron https://www.waterquality.gov.au/sites/default /files/documents/water-recycling-guidelines-mar-24.pdf
Decision Support System for Aquifer Recharge and Aquifer Storage and Recovery Planning, Design, and Evaluation: Principles and Technical Basis	Yang et al. (prepared for US EPA)	Provides overview of framework for a decision support system for ASR planning. Includes some information related to developing reactive transport models of ASR sites and understanding arsenic mobilization. Describes relevant examples and case studies https://cfpub.epa.gov/si/si_public_record_rep ort.cfm?Lab=NRMRL&dirEntryId=335408
Protecting Groundwater Quality in California: Management Considerations for Avoiding Naturally Occurring and Emerging Contaminants	Fakhreddine et al. (Environmental Defense Fund, Stanford University, Lawrence Berkeley National Lab, Green Science Policy Institute)	Focuses on California, but contains general information on water quality considerations and mobility of naturally-occurring contaminants (arsenic, uranium, chromium, manganese, iron, vanadium, selenium) and emerging contaminants (TCP, PFAS) in actively managed aquifers https://www.edf.org/sites/default/files/docu ments/groundwater-contaminants-report.pdf
A Guide to Water Quality Requirements Under the Sustainable Groundwater Management Act	Moran and Belin (Stanford University)	A guide for water quality considerations under California's Sustainable Groundwater Management Act. Contains generally applicable information on active management and groundwater quality including frameworks for assessing groundwater quality impacts and ensuring regulatory compliance https://purl.stanford.edu/dw122nb4780
Mobilization of Arsenic and Other Naturally Occurring Contaminants during Managed Aquifer Recharge: A Critical Review	Fakhreddine et al.	In-depth review of hydrological and geochemical processes controlling arsenic and other naturally-occurring contaminants at MAR sites. Includes descriptions of specific sites and management considerations https://dx.doi.org/10.1021/acs.est.0c07492?r ef=pdf

Title	Author	Description and URL
Guidelines for Preparing a Groundwater Sampling and Analysis Plan	TCEQ	Technical guidance for groundwater monitoring of municipal solid waste facilities—contains general information on groundwater sampling procedures https://www.tceq.texas.gov/downloads/permitting/waste-permits/publications/rg-074.pdf
Guideline on: Groundwater Monitoring for General Reference Purposes	International Groundwater Resources Assessment Centre (IGRAC)	General guidance document on groundwater monitoring programs, including groundwater quality sampling https://www.un-igrac.org/sites/default/files/resources/files/WG1-7-Guideline-v12-03-08.pdf
Injection Wells: A Guide to Their Use, Operation and Regulation	Groundwater Protection Council	Introductory information about groundwater and Underground Injection Control (UIC) program and concepts https://www.gwpc.org/sites/gwpc/uploads/documents/publications/UIC_Guide_June_2021_Update1.pdf
Central and Southern Florida Project Comprehensive Everglades Restoration Plan	South Florida Water Management District and U.S. Army Corps of Engineers	Technical report on large-scale ASR project for ecosystem restoration. Includes case studies of pilot wells and data for arsenic mobilization https://www.saj.usace.army.mil/Portals/44/docs/Environmental/ASR%20Regional%20Study/Final_Report/ASR_RegionalStudy_Final_2015.pdf.pdf
Review of the Everglades Aquifer Storage and Recovery Regional Study	National Research Council of the National Academy	Technical review of large-scale ASR project in Florida. Evaluates arsenic and water quality impacts observed in technical report with recommendations for future management https://www.nap.edu/catalog/21724/review-of-the-everglades-aquifer-storage-and-recovery-regional-study
A Review of Selected Florida Aquifer Storage and Recovery Sites and Their Geochemical Characteristics	Fischler et al. (Florida Geological Survey)	Overview of analysis of thirteen ASR sites across Florida for arsenic mobilization and other water quality shifts. Provides example case studies https://ufdc.ufl.edu/AA00038434/00001
Bench-scale Geochemical Assessment of Water-Rock Interactions: City of Sanford Aquifer Storage and Recovery Facility	Arthur et al. (Florida Geological Survey)	Example of batch experiments used to assess arsenic leaching potential from sediments at ASR sites in Florida http://publicfiles.dep.state.fl.us/FGS/FGS_Publications/FGS%20Library%20Documents/GreyLit/ASR/Bench_SanfordASR_Final.pdf

References

Antoniou, E.A., Hartog, N., van Breukelen, B.M., Stuyfzand, P.J., 2014. Aquifer pre-oxidation using permanganate to mitigate water quality deterioration during aquifer storage and recovery. Appl. Geochem. 50, 25–36. https://doi.org/10.1016/j.apgeochem.2014.08.006

Antoniou, E.A., van Breukelen, B.M., Putters, B., Stuyfzand, P.J., 2012. Hydrogeochemical patterns, processes and mass transfers during aquifer storage and recovery (ASR) in an anoxic sandy aquifer. Appl. Geochem. 27, 2435–2452. https://doi.org/10.1016/j.apgeochem.2012.09.006

Arthur, J. D., 2020. Personal Communication.

Arthur, J.D., Dabous, A.A., 2005. Bench scale Geochemical Assessment of Water-Rock Interactions: Seminole County ASR Core Samples: Final report submitted to Camp, Dresser and McKee, Inc.

Arthur, J.D., Dabous, A.A., Cowart, J.B., 2005. Water–Rock Geochemical Considerations for Aquifer Storage and Recovery: Florida Case Studies, in: Tsang, C.-F., Apps, J.A. (Eds.), Developments in Water Science, Underground Injection Science and Technology. Elsevier, pp. 327–339. https://doi.org/10.1016/S0167-5648(05)52024-0

Arthur, J.D., Dabous, A.A., Fischler, C., 2007. Bench-Scale Geochemical Assessment of Water-Rock Interactions: City of Sanford Aquifer Storage and Recovery Facility: Final report submitted to CDM and the St. Johns River Water Management District.

Arthur, J.D., Fischler, C., 2008. Bench-Scale Geochemical Assessment of Water-Rock Interactions: Rome Avenue Aquifer Storage and Recovery Facility: Final report submitted to the Southwest Florida Water Management District.

Arthur, J.D., Fischler, C., Dabous, A.A., 2008. Bench-Scale Geochemical Assessment of Water-Rock Interactions: Orange County Aquifer Storage and Recovery Facility: Final report submitted to Barnes, Ferland and Associates, Inc. Environmental Consultants.

Arthur, J.D., Hyle, R., Missimer, T.M., Price, R., Upchurch, S., 2020. Aquifer Storage and Recovery Peer Review Panel Final Report (Submitted to the South Florida Water Management District).

ASCE, 2020. Standard Guidelines for Managed Aquifer Recharge. American Society of Civil Engineers. https://doi.org/10.1061/9780784415283

ASR Systems, 2007. Evaluation of Arsenic Mobilization Processes Occurring During Aquifer Storage and Recovery Activities. SFWMD.

Battistel, M., Stolze, L., Muniruzzaman, M., Rolle, M., 2020. Arsenic release and transport during oxidative dissolution of spatially-distributed sulfide minerals. J. Hazard. Mater. 124651. https://doi.org/10.1016/j.jhazmat.2020.124651

Bloetscher, F., 2015. M63 Aquifer Storage and Recovery. American Water Works Association.

Bloetscher, F., Sham, C.H., Iii, J.J.D., Ratick, S., 2014. Lessons Learned from Aquifer Storage and Recovery (ASR) Systems in the United States. J. Water Resour. Prot. 06, 1603. https://doi.org/10.4236/jwarp.2014.617146

Bloetscher, F., Sham, C.H., Ratick, S.J., 2020. Aquifer Storage and Recovery: Can an Updated Inventory Predict Future System Success? J. AWWA 112, 48–55. https://doi.org/10.1002/awwa.1594

Brown, R., Lee, R., Patterson, K., Zimmerman, M., Hiebert, F., 2011. API Groundwater Arsenic Manual: Attenuation of Naturally-Occurring Arsenic at Petroleum Impacted Sites. American Petroleum Institute.

CH2MHILL, 2017. City of Buda ASR Feasibility Study (Technical Memorandum).

Descourvières, C., Hartog, N., Patterson, B.M., Oldham, C., Prommer, H., 2010. Geochemical controls on sediment reactivity and buffering processes in a heterogeneous aquifer. Appl. Geochem. 25, 261–275. https://doi.org/10.1016/j.apgeochem.2009.11.012

Fakhreddine, S., Babbitt, C., Sherris, A., Lopez, A., Wells, A., Holmes, R., Fendorf, S., Burton, T., Nico, P., 2019. Protecting Groundwater Quality in California: Management Considerations for Avoiding Naturally Occurring and Emerging Contaminants (No. White Paper). Environmental Defense Fund.

Fakhreddine, S., Dittmar, J., Phipps, D., Dadakis, J., Fendorf, S., 2015. Geochemical Triggers of Arsenic Mobilization During Managed Aquifer Recharge. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.5b01140

Fakhreddine, S., Prommer, H., Gorelick, S.M., Dadakis, J., Fendorf, S., 2020. Controlling arsenic mobilization during managed aquifer recharge: The role of sediment heterogeneity. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.0c00794

Fakhreddine, S., Prommer, H., Scanlon, B.R., Ying, S.C., Nicot, J.-P., 2021. Mobilization of Arsenic and Other Naturally Occurring Contaminants during Managed Aquifer Recharge: A Critical Review. Environ. Sci. Technol. 55, 2208–2223. https://doi.org/10.1021/acs.est.0c07492

Fendorf, S., 2010. Arsenic chemistry in soils and sediments. Lawrence Berkeley Natl. Lab.

Fischler, C., Arthur, J.D., 2014. Geochemical, mineralogical and petrographic characterization of rocks comprising the upper Floridan aquifer system in south Florida. Florida Geological Survey, Tallahassee.

Fischler, C., Hansard, P., Ladle, M., Burdette, C., 2015. A Review of Selected Florida Aquifer Storage and Recovery (ASR) Sites and Their Geochemical Characteristics (Florida Geological Survey Report of Investigation). Tallahassee.

HDR, 2020. Statewide Survey of Aquifer Suitability for Aquifer Storage and Recovery Projects or Aquifer Recharge Projects (Final Report). Texas Water Development Board.

Kolker, A., Nordstrom, D.K., 2001. Occurrence and micro-distribution of arsenic in pyrite, in: Proceedings of the USGS Arsenic Workshop. USGS, Denver.

Langston, C., 2021. Personal Communication.

Lazareva, O., Druschel, G., Pichler, T., 2015. Understanding arsenic behavior in carbonate aquifers: Implications for aquifer storage and recovery (ASR). Appl. Geochem. 52, 57–66. https://doi.org/10.1016/j.apgeochem.2014.11.006

Maliva, R.G., 2020. Anthropogenic Aquifer Recharge and Water Quality, in: Maliva, R.G. (Ed.), Anthropogenic Aquifer Recharge: WSP Methods in Water Resources Evaluation Series No. 5, Springer Hydrogeology. Springer International Publishing, Cham, pp. 133–164. https://doi.org/10.1007/978-3-030-11084-0_6

Maliva, R.G., Guo, W., Missimer, T.M., 2006. Aquifer Storage and Recovery: Recent Hydrogeological Advances and System Performance. Water Environ. Res. 78, 2428–2435.

Maliva, R.G., Missimer, T.M., 2010. Aquifer Storage and Recovery and Managed Aquifer Recharge Using Wells: Planning, Hydrogeology, Design, and Operation. Schlumberger.

Mirecki, J.E., Bennett, M.W., López-Baláez, M.C., 2013. Arsenic Control During Aquifer Storage Recovery Cycle Tests in the Floridan Aquifer. Groundwater 51, 539–549. https://doi.org/10.1111/j.1745-6584.2012.01001.x

Moran, T., Belin, A., 2019. A guide to Water Quality Requirements Under the Sustainable Groundwater management Act. Stanford Digital Repository.

National Research Council, 2007. Prospects for Managed Underground Storage of Recoverable Water. https://doi.org/10.17226/12057

Neil, C.W., Jason Todd, M., Jeffrey Yang, Y., 2018. Improving arsenopyrite oxidation rate laws: implications for arsenic mobilization during aquifer storage and recovery (ASR). Environ. Geochem. Health 40, 2453–2464. https://doi.org/10.1007/s10653-018-0111-2

Nordstrom, D.K., 2000. An overview of arsenic mass-poisoning in Bangladesh and West Bengal, India.

NRMMC, EPHC, AHMC, 2008. Australian guidelines for water recycling: Managing health and environmental risks (Phase 2): augmentation of drinking water supplies. Environment Protection and Heritage Council, National Health and Medical Research Council, Natural Resource Management Ministerial Council, Canberra.

O'Day, P.A., Vlassopoulos, D., Root, R., Rivera, N., 2004. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. Proc. Natl. Acad. Sci. U. S. A. 101, 13703–13708. https://doi.org/10.1073/pnas.0402775101

Paktunc, D., 2008. Speciation of arsenic in pyrite by micro-X-ray absorption fine- structure spectroscopy (XAFS), Australasian Institute of Mining and Metallurgy Publication Series.

Parkhurst, D.L., 1999. User's guide to PHREEQC (Version 2)-a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geol. Surv. Water-Resour. Investig. Rep. 312.

Pichler, T., Koopmann, S., 2019. Should Monitoring of Molybdenum (Mo) in Groundwater, Drinking Water and Well Permitting Made Mandatory? Environ. Sci. Technol. acs.est.9b06869. https://doi.org/10.1021/acs.est.9b06869

Pichler, T., Mozaffari, A., 2015. Distribution and mobility of geogenic molybdenum and arsenic in a limestone aquifer matrix. Appl. Geochem. 63, 623–633. https://doi.org/10.1016/j.apgeochem.2015.08.006

Pichler, T., Renshaw, C.E., Sültenfuß, J., 2017. Geogenic As and Mo groundwater contamination caused by an abundance of domestic supply wells. Appl. Geochem., Environmental and Health Roles of Geogenic Arsenic 77, 68–79. https://doi.org/10.1016/j.apgeochem.2016.03.002

Prommer, H., Stuyfzand, P.J., 2005. Identification of Temperature-Dependent Water Quality Changes during a Deep Well Injection Experiment in a Pyritic Aquifer. Environ. Sci. Technol. 39, 2200–2209. https://doi.org/10.1021/es0486768

Prommer, H., Sun, J., Helm, L., Rathi, B., Siade, A.J., Morris, R., 2018. Deoxygenation Prevents Arsenic Mobilization during Deepwell Injection into Sulfide-Bearing Aquifers. Environ. Sci. Technol. 52, 13801–13810. https://doi.org/10.1021/acs.est.8b05015

Pyne, D., 2005. Aquifer Storage and Recovery: A Guide to Groundwater Recharge through Wells. Second Edition, ASR Systems, Gainesville.

Rathi, B., Siade, A.J., Donn, M.J., Helm, L., Morris, R., Davis, J.A., Berg, M., Prommer, H., 2017. Multiscale Characterization and Quantification of Arsenic Mobilization and Attenuation During Injection of Treated Coal Seam Gas Coproduced Water into Deep Aquifers. Water Resour. Res. 53, 10779–10801. https://doi.org/10.1002/2017WR021240

Reedy, R., Scanlon, B.R., Walden, S., Strassberg, G., 2012. Naturally Occurring Groundwater Contamination in Texas (Prepared for Texas Water Development Board No. Contract Number 1004831125).

SAWS, n.d. Aquifer Storage and Recovery [www document]. San Antonio Water Systems. URL https://www.saws.org/your-water/management-sources/aquifer-storage-recovery/

Schafer, D., Sun, J., Jamieson, J., Siade, A., Atteia, O., Seibert, S., Higginson, S., Prommer, H., 2020a. Fluoride release from carbonate-rich fluorapatite during managed aquifer recharge: model-based development of mitigation strategies. Rev. Sci. Total Environ.

Schafer, D., Sun, J., Jamieson, J., Siade, A.J., Atteia, O., Prommer, H., 2020b. Model-Based Analysis of Reactive Transport Processes Governing Fluoride and Phosphate Release and Attenuation during Managed Aquifer Recharge. Environ. Sci. Technol. 54, 2800–2811. https://doi.org/10.1021/acs.est.9b06972

Seibert, S., Atteia, O., Ursula Salmon, S., Siade, A., Douglas, G., Prommer, H., 2016. Identification and quantification of redox and pH buffering processes in a heterogeneous, low carbonate aquifer during managed aquifer recharge. Water Resour. Res. 52, 4003–4025. https://doi.org/10.1002/2015WR017802

Smedley, P.L., Cooper, D.M., Lapworth, D.J., 2014. Molybdenum distributions and variability in drinking water from England and Wales. Environ. Monit. Assess. 186, 6403–6416. https://doi.org/10.1007/s10661-014-3863-x

Smedley, P.L., Kinniburgh, D.G., 2017. Molybdenum in natural waters: A review of occurrence, distributions and controls. Appl. Geochem. 84, 387–432. https://doi.org/10.1016/j.apgeochem.2017.05.008

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568. https://doi.org/10.1016/S0883-2927(02)00018-5

Stefan, C., Ansems, N., 2018. Web-based global inventory of managed aquifer recharge applications. Sustain. Water Resour. Manag. 1–10. https://doi.org/10.1007/s40899-017-0212-6

TCEQ, n.d. Texas Commission on Environmental Quality General Information on Aquifer Storage and Recovery [www document]. Tex. Comm. Environ. Qual. URL https://www.tceq.texas.gov/assets/public/permitting/waste/uic/ASR_Gen_Info.pdf

Thompson, D., 2019. A History of SAWS Aquifer Storage and Recovery.

US EPA, 2015a. National Primary Drinking Water Regulations [www document]. US EPA. URL https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

US EPA, 2015b. Aquifer Recharge and Aquifer Storage and Recovery [www document]. US EPA. URL https://www.epa.gov/uic/aquifer-recharge-and-aquifer-storage-and-recovery (accessed 5.20.20).

US EPA, 2013. MINTEQA2 Equilibrium Speciation Model [www document]. US EPA. URL https://www.epa.gov/ceam/minteqa2-equilibrium-speciation-model

US EPA, 2006. Arsenic Rule [www document]. URL http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations.cfm

Vacher, H.L., Hutchings, W.C., Budd, D.A., 2006. Metaphors and Models: The ASR Bubble in the Floridan Aquifer. Groundwater 44, 144–154. https://doi.org/10.1111/j.1745-6584.2005.00114.x

Vanderzalm, J.L., Dillon, P.J., Barry, K.E., Miotlinski, K., Kirby, J.K., Le Gal La Salle, C., 2011. Arsenic mobility and impact on recovered water quality during aquifer storage and recovery using reclaimed water in a carbonate aquifer. Appl. Geochem. 26, 1946–1955. https://doi.org/10.1016/j.apgeochem.2011.06.025

Verrastro, R.T., Kraft, N., 2018. Hillsboro Canal Aquifer Recharge, Storage, and Recovery System (Cycle Testing Summary Report No. Technical Publication WS-48hi). South Florida Water Management District, West Palm Beach, FL.

Wallis, I., Prommer, H., Pichler, T., Post, V., B. Norton, S., Annable, M.D., Simmons, C.T., 2011. Process-Based Reactive Transport Model To Quantify Arsenic Mobility during Aquifer Storage and Recovery of Potable Water. Environ. Sci. Technol. 45, 6924–6931. https://doi.org/10.1021/es201286c

Wallis, I., Prommer, H., Simmons, C.T., Post, V., Stuyfzand, P.J., 2010. Evaluation of Conceptual and Numerical Models for Arsenic Mobilization and Attenuation during Managed Aquifer Recharge. Environ. Sci. Technol. 44, 5035–5041. https://doi.org/10.1021/es100463q

Yang, Y.J., Neil, C., Neal, J., Goodrich, J.A., Simon, M., Jun, Y., Burnell, D.K., Cohen, R., Schupp, D., Krishnan, R., 2017. Decision Support System for Aquifer Recharge (AR) and Aquifer Storage and Recovery (ASR) Planning, Design, and Evaluation - Principles and Technical Basis (No. EPA/600/R-16/222). U.S. Environmental Protection Agency, Washington, DC.