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Radioactive Materials Division

Guidelines for Treatment and Management of Injected Water at Aquifer Storage and Recovery Sites to Minimize the Potential Release of Arsenic

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1. Introduction

Population growth, land use changes, and prolonged droughts are motivating cities, municipalities, water utilities, groundwater conservation districts, and regional water planners in Texas to increasingly consider aquifer storage and recovery (ASR) as a strategy for supplementing drinking water supplies. For example, as shown in **Table 1**, there are three fully-operational ASR sites in Texas, and numerous exploratory ASR efforts are either in progress or have been performed. Most of these ASR sites have reported the occurrence of arsenic in groundwater, and thus far reported arsenic levels have been below the maximum contaminant level (MCL) of 10 µg/L. The lack of elevated arsenic concentrations observed to date at these sites may be considered encouraging for expanding ASR as an integral part of the state water plan, but the occurrence of arsenic also raises concerns about how to best manage ASR sites to reduce the risk of this pollutant being released to groundwater. This document provides basic information on water quality conditions leading to arsenic release at ASR sites, and guidelines for implementing injection water treatment and management alternatives that may mitigate this release. The intended audience for this document includes water utilities, municipalities, groundwater conservation district personnel, the regulated community, and environmental professionals.

Table 1. ASR Sites in Texas

Fully Operational:	San Antonio Water System, City of Kerrville, Ruby Ranch Water Supply Corporation
Exploratory Efforts in Progress or Performed:	Cities of Kerrville, Bandera, Brownsville, Bryan, Buda, Corpus Christi, New Braunfels, Laredo, and Victoria.

A main concern with ASR is that when injection water quality is different from native groundwater quality, injection of the former into a groundwater formation during ASR may promote the release of arsenic from mineral and sorbed phases to groundwater. This report provides guidance on characterization of ASR sites to evaluate the potential for arsenic release to groundwater, and on treatment and management options for injected water to minimize the potential risk of arsenic release to groundwater.

2. Characterization of Aquifer and Injected Water Quality

Key water quality parameters that affect arsenic release to groundwater during ASR are listed in Table 2. The primary concern is that concentration levels of one or more of these parameters will be different between native groundwater and injected water being used for recovery. Among the key parameters, the most important is dissolved oxygen, in some cases represented by the oxidation-reduction potential or pE of solution as shown in Figure 1. This is because the dominant form of arsenic, as well as the minerals available for it to associate with, change with oxygen availability. For example, under aerobic conditions (i.e., high pE) arsenic is in the +5 oxidation state as arsenate, and it strongly adsorbs to iron (hydr)oxides. Under anaerobic conditions (i.e., low pE) arsenic is in the +3 oxidation state as arsenite, and it is incorporated into iron sulfide minerals. Two related parameters are nitrate and dissolved organic matter (DOM). The former acts similarly to oxygen by increasing the pE, while the latter reacts with oxygen and nitrate to reduce their concentrations and lower the pE.

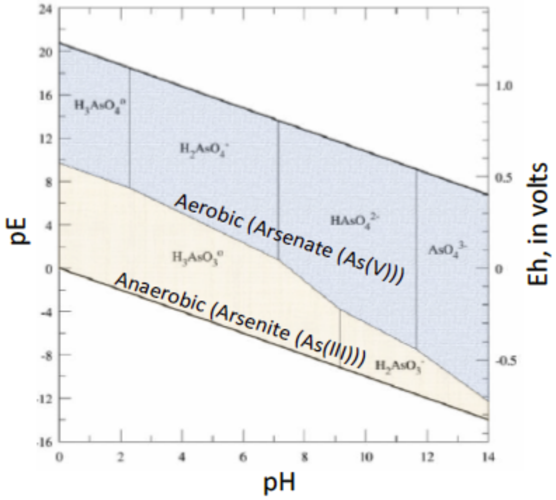


Figure 1. Impact of oxygen (indicated by pE or Eh) and pH on arsenic speciation (modified from Akter et al., 2005).

The second most important key parameter is pH, provided dissolved oxygen levels do not appreciably change, and it has the largest impact when both injection water and native groundwater are aerobic. For example, when injection water has a higher pH than native groundwater, then injection will promote the release of arsenate adsorbed to iron (hydr)oxides, especially above pH 8.5 (Fakhreddine et al., 2021; Smedley & Kiniburgh, 2002; McNab et al., 2009; Rathi et al., 2017). This is because the dominant arsenate species becomes more negatively charged with increasing pH (**Figure 1**), and the mineral surface charge becomes more negative; this results in greater electrostatic repulsion.

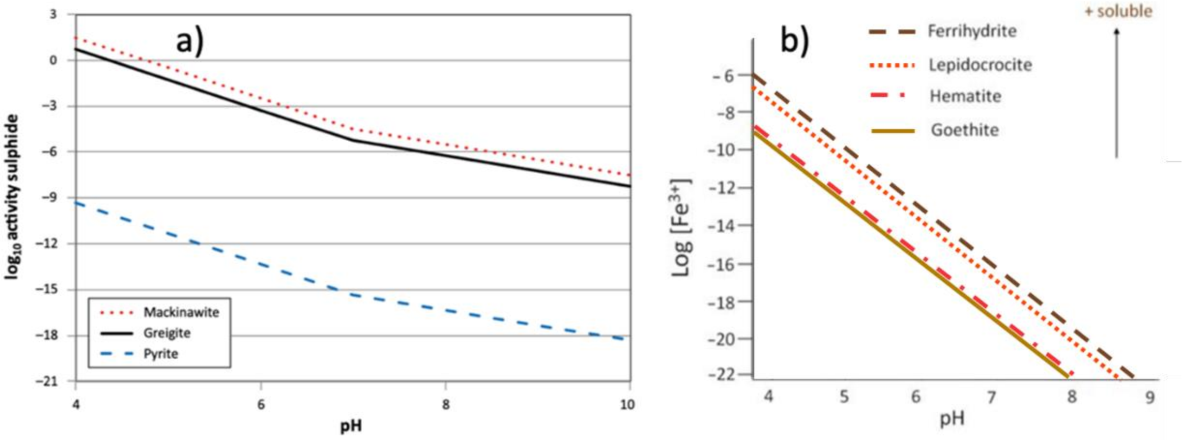


Figure 2. a) Aqueous sulfide concentration in equilibrium with iron sulfide minerals as a function of pH (King, 2013). b) Aqueous concentration in equilibrium with iron (oxyhdr)oxide minerals as a function of pH (Claudio et al., 2017).

Alternatively, when injection water has a lower pH than native groundwater, mineral solubility increases and this can also result in the release of arsenic. This is illustrated in **Figure 2**, where the solution concentrations of sulfide in equilibrium with three sulfide minerals (**Figure 2a**), and the solution concentrations of Fe^{3+} in equilibrium with four iron (oxyhydr)-oxide minerals (**Figure 2b**), all increase with decreasing pH; this means that more of the sulfide or Fe^{3+} is released into solution due to mineral dissolution with decreasing pH, and as a result arsenic adsorbed to these dissolved mineral phases is released into solution. Alkalinity is related to pH because it is usually dominated by carbonate species that buffer changes in pH. The remaining parameters, phosphate, divalent cations, and sulfate, can affect arsenic release to groundwater, but their effects are less pronounced and have not been directly attributed to arsenic release at field sites.

Table 2. Key Water Quality Parameters that Affect Arsenic Release to Groundwater during ASR.

Water Quality Parameter	Changes That May Affect Arsenic Release	References
Dissolved Oxygen (DO)	Arsenic in reduced iron minerals can be released to groundwater when aerobic surface water is injected into an anoxic aquifer. This effect is mitigated when iron (hydr)oxides form and adsorb the released arsenic. Arsenic adsorbed to iron (hydr)oxides can be released to groundwater when anoxic water is injected into an aerobic aquifer.	Corkhill & Vaughan, 2009; Mirecki et al., 2013
Nitrate	Nitrate acts similar to dissolved oxygen, but in some cases with a lag time because unlike oxygen, microorganisms are required to couple the release of arsenic from reduced iron minerals with nitrate consumption.	Fakhreddine et al., 2020; Seibert et al., 2016; Kiskira et al., 2017
Dissolved Organic Matter	Dissolved organic matter (DOM) reacts with oxygen (preferentially) and nitrate to reduce their levels in groundwater.Therefore, elevated DOM in aerobic injected water (e.g., from surface water) promotes anoxic conditions.	Greskowiak et al., 2006; Vanderzalm et al., 2010; Mirecki et al., 2013
Oxidation-Reduction Potential (ORP)	The ORP provides an overall measurement of the extent that water is oxidizing or reducing, and this is determined by concentrations of oxidants (e.g., oxygen, nitrate) and reductants (e.g., sulfide, ferrous iron) in solution. Measuring ORP accurately is challenging, so concentrations of oxidants and reductants are often used instead.	Eshel and Banin, 2007
pH	Injection water with a higher pH than native groundwater will promote the release of arsenate adsorbed to iron (hydr)oxides. The effect of pH in anoxic waters is less pronounced.	Dixit and Hering, 2003; McNab et al., 2009; Rathi et al., 2017

Water Quality Parameter	**Changes That May Affect Arsenic Release**	**References**
Alkalinity	Alkalinity is related to pH. It is often dominated by carbonate species, and these provide buffering capacity to prevent changes in pH.	Seibert et al., 2016
Phosphate	Phosphate competes with arsenic for adsorption sites on iron (hydr)oxides under aerobic conditions. Relatively high phosphate concentrations in injected (e.g., >1 mg/L) water can promote arsenic release.	Zeng et al., 2008; Stollenwerk, 2003
Divalent Cations (Ca^{2+},Mg^{2+})	Divalent cations can enhance arsenate adsorption to phyllosilicate clays. Their relative decrease in injected water can promote arsenic release.	Fakhreddine et al., 2015
Sulfate	Given sufficient DOM, sulfate is reduced to sulfide which can form iron sulfide minerals under reducing conditions.	Mirecki et al., 2013

A flow chart illustrating changes in key water quality parameters and their effect on arsenic release to groundwater is shown in **Figure 3.** Please note that the effects of nitrate are not included in the flow chart; it is anticipated to affect arsenic release similarly to oxygen but to a lesser extent, and it is not often present at problematic levels at Texas ASR sites. Also, please note that the effects of divalent cations are not included because, to the author's knowledge, their effects on arsenic release have not been observed at field sites. Each series of steps in the flow chart is grouped according to the risk of arsenic release to groundwater, and further explained, in **Tables 3** and **4**.

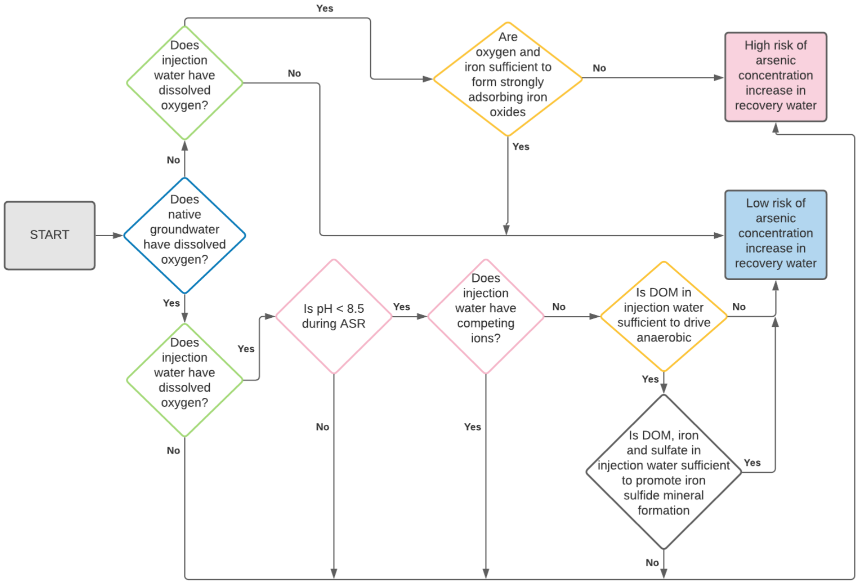


Figure 3. Flow chart indicating anticipated effects of different aquifer and injection water quality parameters on arsenic release to solution (DOM=dissolved organic matter) (Created using Lucid).

Table 3. Identification & explanation of low-risk arsenic release pathways in Figure 3 flow chart.

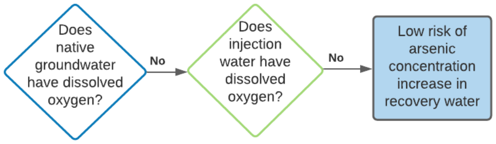
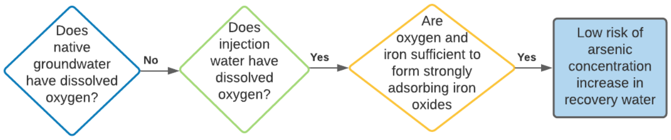
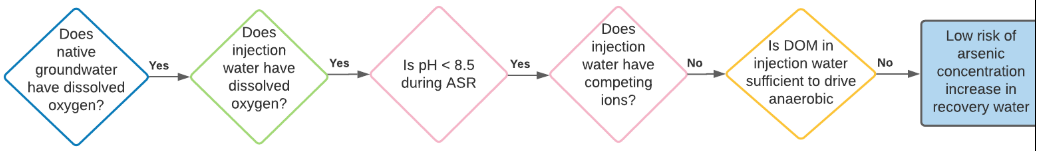
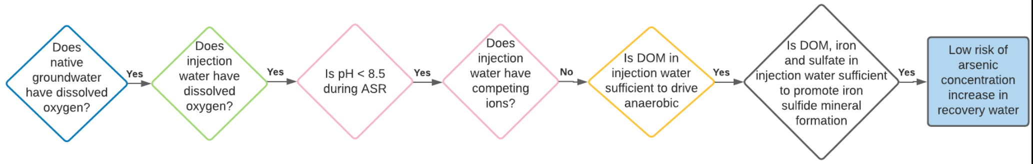
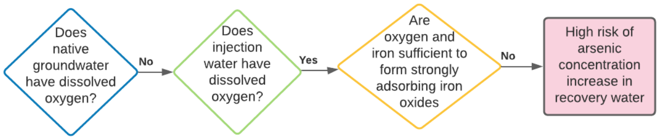
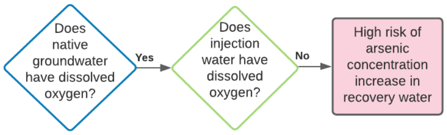
Pathway 1	
Explanation	Arsenite dominates in anaerobic groundwater, and is often incorporated into iron sulfide minerals such as pyrite (FeS_2) and arsenopyrite (FeAsS). These minerals remain stable under anaerobic conditions.
Pathway 2	
Explanation	Iron sulfide minerals (e.g., FeAsS) are oxidatively dissolved when aerobic injection water is introduced to anaerobic groundwater, causing the release of arsenite and its subsequent oxidation to arsenate ($H_2AsO_4^-$), as well as the oxidation of Fe^{2+} to an iron (hydr)oxide mineral (e.g., $Fe(OH)_3$). $$4FeAsS + 14O_2 + 16H_2O \rightarrow 4H_2AsO_4^- + 4Fe(OH)_3 + 4SO_4^{2-} + 12H^+$$ Iron (hydr)oxide minerals (e.g., $Fe(OH)_3$) can strongly adsorb aqueous arsenate (e.g., $2Fe(OH)_3 \equiv H_2AsO_4^-$). $$2Fe(OH)_3 + HAsO_4^{2-} + H_2O \rightarrow 2Fe(OH)_3 \equiv H_2AsO_4^- + OH^-$$ Arsenate can also adsorb to aluminosilicates and phyllosilicate clays.
Pathway 3	
Explanation	When both native groundwater and injection water are aerobic, near circumneutral pH, and lack ions like phosphate that compete for arsenate adsorption sites, arsenic concentrations are unlikely to increase.
Pathway 4	
Explanation	When dissolved organic matter (DOM) is present in aerobic injection water, it can consume dissolved oxygen, promote reductive dissolution of iron (hydr)oxide minerals, release adsorbed arsenate to pore water, and convert arsenate to arsenite. $$2Fe(OH)_3 \equiv H_2AsO_4^- + CH_2O \rightarrow 2Fe^{2+} + HCO_3^- + H_3AsO_3 + 2H_2O$$ If conditions are sufficiently reducing and if sulfate is present, sulfate will be reduced to sulfide, and iron sulfide minerals can incorporate the arsenic. $$4H_3AsO_3 + 3CH_2O + 4Fe^{2+} + 4HS^- \rightarrow 4\mathrm{FeAsS} + 3HCO_3^- + 6H_2O + 7H^+$$

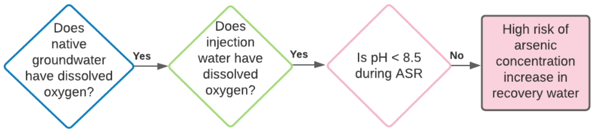
Table 4. Identification & explanation of high-risk arsenic release pathways in Figure 3 flow chart.

<table>
<tr><td>Pathway 5</td><td>


</td></tr>
<tr><td>Explanation</td><td>
Arsenite dominates in anaerobic groundwater, and can be incorporated into iron sulfide minerals such as pyrite (FeS_2) and arsenopyrite (FeAsS). These minerals oxidatively dissolve when aerobic injection water is introduced to anaerobic groundwater, causing the release of arsenite and its subsequent oxidation to arsenate ($H_2AsO_4^-$).

$$4FeAsS + 14O_2 + 16H_2O \rightarrow 4H_2AsO_4^- + 4Fe(OH)_3 + 4SO_4^{2-} + 12H^+$$
</td></tr>
<tr><td>Pathway 6</td><td>


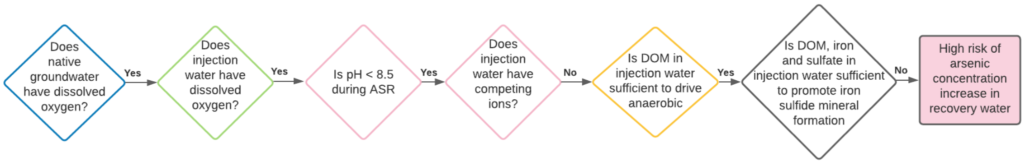
</td></tr>
<tr><td>Explanation</td><td>
Arsenate is the dominant form of arsenic in aerobic groundwater, and it can strongly adsorb to iron (hydr)oxide, aluminosilicate, and phyllosilicate minerals. When anaerobic injection water is introduced to the aquifer, the iron (hydr)oxide minerals reductively dissolve (e.g., with trace NOM), and arsenate is reduced to arsenite. This results in the release of arsenite to solution.

$$2Fe(OH)_3 \equiv H_2AsO_4^- + CH_2O \rightarrow 2Fe^{2+} + HCO_3^- + H_3AsO_3 + 2H_2O$$
</td></tr>
<tr><td>Pathway 7</td><td>


</td></tr>
<tr><td>Explanation</td><td>
The dominant arsenate species becomes more negatively charged with increasing pH (e.g., $H_2OsO_4^- \rightarrow H_2AsO_4^{2-}$), as do iron (hydr)oxide minerals. This results in electrostatic repulsion, leading to the desorption of arsenate into groundwater.

$$2Fe(OH)_3 \equiv H_2AsO_4^- + OH^- \rightarrow 2Fe(OH)_3 + HAsO_4^{2-} + H_2O$$
</td></tr>
<tr><td>Pathway 8</td><td>


</td></tr>
<tr><td>Explanation</td><td>
Phosphate (e.g., $H_2PO_4^-$) competes with arsenate for adsorption sites. When it is present at high concentrations it can displace arsenate from adsorption sites and cause it to be released to groundwater.

$$2Fe(OH)_3 \equiv H_2AsO_4^- + H_2PO_4^- \rightarrow 2Fe(OH)_3 \equiv H_2PO_4^- + H_2AsO_4^-$$
</td></tr>
<tr><td>Pathway 9</td><td>


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</table>

Explanation	Dissolved organic matter (DOM) in the injection water can result in the consumption of oxygen, driving the groundwater anaerobic and promoting reductive dissolution of iron (hydr)oxide minerals and the release of adsorbed arsenic (e.g., see Pathway 6 equation)

3. Water Treatment Technologies and ASR Management Strategies That Can Affect Key Water Quality Parameters

Possible water treatment technologies that may affect key water quality parameters are shown in **Table 5**. In general, groundwater used for injection is rarely treated at ASR sites, while surface water is typically used only after treatment at a conventional water treatment plant. The few cases where groundwater was treated before injection at ASR sites involved oxygen removal via a gas-liquid membrane contactor (e.g., **Figure 4**). This technology proved effective in providing de-oxygenated injection water, but came with the additional expense for treatment.

Figure 4. Images of (left) 3M-Liqui-Cel® membrane contactor, (middle) hollow-fiber configuration within contactor, and (right) gas removal process within a single hollow fiber (Images from 3M™).

Conventional water treatment of surface water often involves coagulation, flocculation, and precipitation, followed by media filtration and disinfection. This approach removes particles, dissolved organic matter, some metals, and microorganisms. Depending on surface water conditions, other potential treatment processes used with some or all of the aforementioned processes include ion exchange (to remove problematic anions, cations, or DOM), activated carbon filtration (to remove DOM or lower molecular weight organic pollutants), or microfiltration (to remove DOM and microorganisms).

Figure 5. Examples of dynamic mixing tank options (from Dynamix and Polyprocessing).

Groundwater used for drinking is often treated using these same processes if it contains problematic ions or organic pollutants. Surface water treatment processes do not generally remove oxygen, and the oxidant chlorine (or chloramine) is often added as a residual disinfectant. Therefore, further treatment is required to remove chlorine, oxygen, and possibly nitrate to create reducing conditions.The reductant bisulfite has been added to remove residual chlorine, followed by oxygen removal using the aforementioned gas-liquid membrane contactor. Addition of bisulfite or other amendments can be done post-conventional treatment in a mixing tank (e.g., **Figure 5**) just prior to injection. Other possible treatment approaches are listed in **Table 5**, and have not been intentionally performed at an ASR field site; their anticipated effects are based on laboratory measurements, theoretical calculations, and/or observations of reactions occurring at field sites without intentional intervention.

Table 5. Water treatment technologies to alter key water quality parameters in Table 2.

Gas-liquid membrane contactor (e.g., 3M-Liqui-Cell®)	Removes dissolved oxygen from injection water. Can also be used to add dissolved oxygen.	Prommer et al., 2018; Rathi et al., 2017; Fischler et al., 2015; Norton, 2011
Sodium bisulfite addition	Reacts to consume residual chlorine and oxygen.	Fischler et al., 2015; Norton, 2011
Oxidant addition (nitrate, potassium permanganate)	Added in mixing tank to water prior to injection to promote aerobic conditions.	Antoniou et al., 2012; Harvey et al., 2002; Antoniou et al., 2014

Coagulation, flocculation, settling/flotation, followed by media filtration	Water is treated before injection to remove particles, DOM, microorganisms and some metals from injection water. This treatment can also be done with or augmented by membrane treatment.	Matilainen et al., 2010
Ion exchange, activated carbon filtration, or microfiltration, with or without coagulant addition	Water is treated prior to injection to remove problematic ions (e.g., nitrate, sulfate), DOM, organic pollutants, and/or microorganisms.	Odegaard et al., 2010
Dissolved organic matter (DOM) addition (e.g., molasses, fatty acids)	Added in mixing tank to water prior to injection to promote oxygen depletion in aquifer.	Harvey et al., 2002
pH buffer addition (e.g., bicarbonate)	Added in mixing tank to water prior to injection for buffering near a desired pH.	Antoniou et al., 2017
Acid or base addition (e.g., HCl, KOH)	Added in mixing tank to water prior to injection to increase or decrease pH.	No known work where acid or base was added or inadvertently provided at an ASR site
Sulfate addition	Added in mixing tank to water prior to injection for reduction to sulfide in anaerobic aquifers, and subsequent trapping of arsenic in newly formed iron sulfide minerals.	Mirecki et al., 2013
Phosphate addition	Added in mixing tank to water prior to injection to promote adsorbed arsenic release from iron (hydr)oxide minerals in aquifer.	Vandenbohede et al., 2019
Ca^{2+} or Mg^{2+} addition	Added in mixing tank to water prior to injection to enhance arsenic adsorption to phyllosilicate clays.	Fakhreddine et al., 2015

There are two management strategies commonly used at ASR sites to reduce the risk of arsenic release to groundwater. The first strategy is illustrated in **Figure 6**, where a storage zone bubble (zone 1) is created by displacing native groundwater away from the injection well to maintain a permanent buffer of injected water (zone 2) between the native groundwater (zone 3) and zone where water is repeatedly injected and extracted (zone 1). The rationale for this strategy is that easily mobilized arsenic is displaced with the injected groundwater and remains in the native groundwater and buffer zone. The second strategy is to pre-flush the ASR zone by discarding the first several pore volumes of water that are injected and extracted in zone 1, allowing easily displaced arsenic to be withdrawn and discarded with little risk of human exposure. A third potential management strategy that may not be intentionally used, but is a result of operational requirements at ASR sites, is to control the residence time of injected water to either prevent or allow undesired or desired reactions, respectively, to occur.

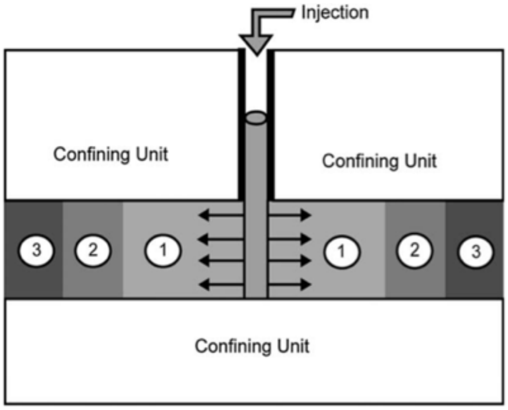


Figure 6. Model aquifer storage and recovery scenario with idealized storage zone bubble (Vacher et al., 2006).

For example, if native groundwater is anaerobic and injected water is aerobic and contains sufficient DOM to consume oxygen, then a longer residence times (weeks) may allow this reaction to go to completion. These strategies are listed in **Table 6** with potential effects on arsenic in groundwater.

Table 6. ASR management strategies to reduce potential arsenic release to groundwater.

Management Strategy	Purpose	References
Create storage zone bubble	Displace easily mobilized arsenic with injection water outward away from the active storage zone, creating a buffer zone of injected water that is not recovered.	Goyal et al., 2008; Vacher et al., 2006
Preflush ASR zone	Discard the first several cycles of injection and extraction water to remove easily displaced arsenic from the storage zone to minimize risk of human exposure.	Mericki et al., 2013
Control injection water residence time	Prevent reactions with short residence times or promote reactions with longer residence times.	Goyal et al., 2008; Mericki et al., 2013

A flow chart illustrating the most commonly considered water treatment technologies (bold dark red boxes) and ASR management strategies to control key water quality parameters is provided below in **Figure 7**. Each series of steps in the flow chart that includes use of a new water treatment approach is further explained in **Table 7**, along with more detailed steps on how to design a treatment approach. Water treatment approaches that have little field data to support them, such as adding DOM and/or sulfate, removing nitrate, adding phosphate, or adding divalent cations, are not included in **Figure 7**. We note that for any series of steps that results in a high risk of arsenic mobilization in groundwater, the aquifer management strategies of creating a storage bubble zone or pre-flushing the storage zone are identified. These aquifer management strategies can also be practiced when there is a lower risk of arsenic release, as they are generally considered low cost and/or low risk relative to water treatment options.

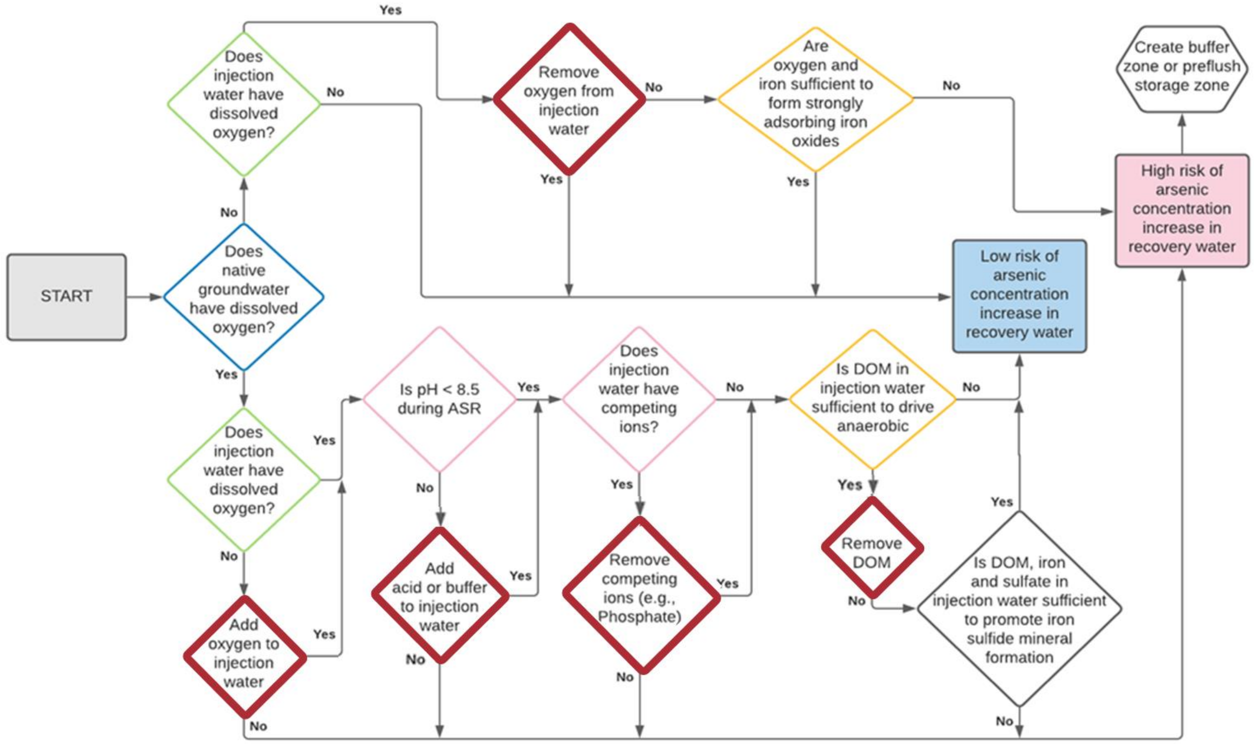
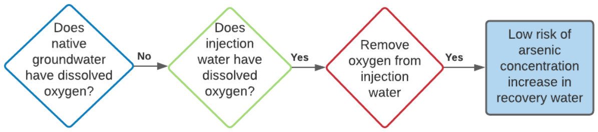
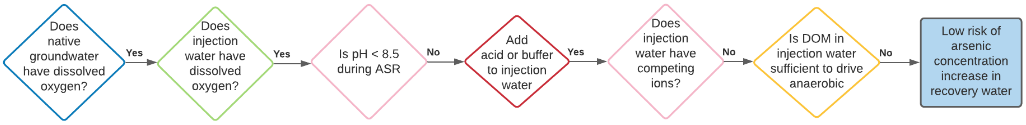


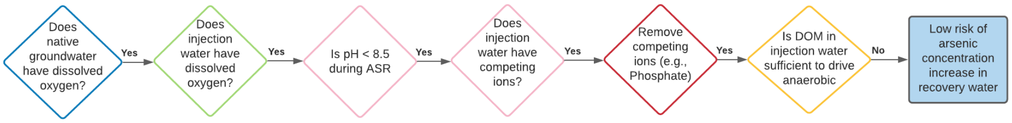
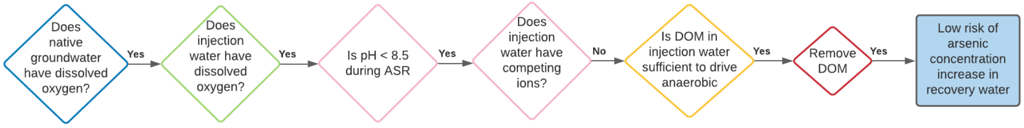
Figure 7. Flow chart indicating anticipated effects of differing aquifer and injected water quality parameters, and differing water treatment and ASR management decisions, on arsenic release to recovery water (Created using Lucid).

Table 7. Identification, explanation, and design of water treatment approaches to lower the risk of arsenic release to groundwater as identified in Figure 7.

Pathway 10	

Explanation	When the native groundwater is anaerobic, removing oxygen from the injection water maintains anaerobic conditions so that arsenic remains complexed in one or more reduced iron minerals such as pyrite and arsenopyrite.
Design Approach (O_2 Removal)	a) Determine maximum injection water treatment flow rates and dissolved oxygen concentrations b) Select gas-liquid contactor membrane module or modules from a vendor to treat desired flows and oxygen removal levels (e.g., two-log removal or greater) c) Determine if pretreatment is required to remove residual chlorine, or potential membrane foulants such as DOM or mineral precipitates (e.g., remove Ca^{2+} to prevent calcite precipitation) d) Determine membrane cleaning protocols to reverse fouling e) Will likely need to perform a pilot study to verify anticipated performance of oxygen removal, membrane cleaning effectiveness and intervals, and if applicable pretreatment system performance f) Install gas-liquid contactor membrane module(s) and if necessary a pretreatment system. g) Monitor (at a minimum) oxygen and arsenic levels in recovered water to determine efficacy
Pathway 11	
Explanation	When the native groundwater is aerobic, adding oxygen to anaerobic injection water may help maintain aerobic conditions so that arsenate remains adsorbed to mineral surfaces.

Design Approach (O_2 Addition)	a) Determine maximum injection water treatment flow rates, dissolved oxygen concentrations, and chemical oxygen demand b) Select gas-liquid contactor membrane module or modules from a vendor to treat desired flows and add oxygen to >4 mg/L c) Determine if chemical oxygen demand will consume added oxygen such that pretreatment is required d) Chemical oxygen demand likely comes from DOM, so pretreatment would target this e) Determine if pretreatment is required to remove potential membrane foulants such as DOM or mineral precipitates (e.g., remove Ca^{2+} to prevent calcite precipitation) f) Determine membrane cleaning protocols to reverse fouling g) Will likely need to perform a pilot study to verify anticipated performance of oxygen addition, membrane cleaning effectiveness and intervals, and if applicable pretreatment system performance h) Install gas-liquid contactor membrane module(s) and if necessary a pretreatment system i) Monitor (at a minimum) oxygen and arsenic levels in recovered water to determine efficacy of approach
Pathway 12	
Explanation	Reducing the injection water pH below 8.5 will promote arsenate adsorption to iron (hydr)oxide and other minerals surfaces, thereby inhibiting arsenic partitioning to water.
Design Approach (Acid Addition)	a) Determine maximum flow rates, pH, and buffering capacity of injection water b) Determine equilibrium pH and buffering capacity of aquifer sediments c) Calculate the amount of strong acid required to consume buffering capacity and change pH to desired level d) Select the desired acid (e.g., HCl) e) Determine the minimum pH allowed in the injection water, and then the number of injection zone pore volumes required to consume buffering capacity f) If the number of injection zone pore volumes is reasonable (e.g., <5), proceed with acid addition. g) Using a mixing tank or in-line mixer, add acid to the injection water at the minimum pH allowed until buffering capacity is consumed, and then add acid at the desired pH thereafter. h) Monitor (at a minimum) pH and arsenic concentrations in recovered water to adjust acid addition, and to determine efficacy of approach

Design Approach (Buffer Addition)	a) Determine maximum flow rates, pH, and buffering capacity of injection water b) Determine equilibrium pH and buffering capacity of aquifer sediments c) If natural buffering capacity is insufficient to hold pH at the desired level, calculate the amount of a specific buffer needed based on anticipated reactions occurring during injection and storage that create or consume protons, or based on measurements of protons consumed in water during injection and storage d) The most likely buffers are bicarbonate or phosphate e) If sufficient buffering capacity can be added to the injection water, then proceed with adding this in a mixing tank or in-line mixer prior to injection f) Monitor (at a minimum) pH, buffering capacity, and arsenic concentrations in recovered water to adjust buffer addition and determine efficacy of approach
Pathway 13	
Explanation	Competing ions like phosphate in injection can displace arsenate adsorbed to iron (hydr)oxide and other minerals into solution. Removing these competitive ions will ensure arsenate remains adsorbed to mineral surfaces.
Design Approach (Phosphate Removal)	a) Determine the maximum flow rates and concentrations of competing ions (most likely phosphate) in injection water b) Design ion exchange system to remove phosphate, recognizing that other anions compete with phosphate for ion exchange resin sites and will decrease system performance c) Will need to determine concentrations of anions that compete with phosphate for ion exchange resin sites d) Will likely need to perform a pilot study to verify anticipated performance of ion exchange for phosphate removal to enable final design e) Determine ion exchange system regeneration approach, characteristics of waste brine, and how to dispose of waste brine f) Monitor (at a minimum) arsenic concentrations in recovered water so that if phosphate removal is discontinued, the effects can be evaluated
Pathway 14	
Explanation	DOM in injection water can react to consume oxygen. When native groundwater is aerobic, this DOM can be removed from the injection water so that injected water remains aerobic and arsenate remains adsorbed to iron (hydr)oxides and other minerals.

Design Approach (DOM Removal)	a) Determine maximum flow rates and DOM concentrations of injection water b) Design activated carbon, ion exchange, or microfiltration system to remove DOM, depending on costs and other desired water quality outcomes c) Will likely need to perform a pilot study to verify anticipated performance of the selected technology to enable final design, as there are different water constituents that can compete with DOM for ion exchange and activated carbon adsorption sites, and that can foul microfiltration membranes d) Determine residual waste and handling procedures, such as disposal or regeneration of activated carbon, regeneration of ion exchange resins, or cleaning of microfiltration membranes e) Monitor (at a minimum) arsenic concentrations in recovered water, DOM, and oxygen concentrations to evaluate efficacy of approach

4. Final Summary and Points of Emphasis

Water quality conditions determine the speciation and mobility of arsenic. The biggest risk for arsenic mobilization occurs when the quality of native groundwater and injection water differ. Among the water quality parameters, changes in oxygen concentration have the largest effect, followed by changes in pH. Other water quality parameters that have been shown to affect arsenic mobilization include nitrate, sulfate, DOM, divalent cations, and phosphate concentrations, as well as pH and alkalinity.

There are both water treatment and management strategies to mitigate the potential for mobilization of arsenic during ASR. When groundwater is used as injected water, oxygen removal has been demonstrated at ASR sites through the use of gas-liquid contactor membrane modules. When surface water is used as injected water, it may first be routed through a conventional water treatment plant, and at some ASR sites this includes removal of residual chlorine and oxygen prior to injection. Conventional water treatment plant processes often include coagulation, flocculation, settling/flotation, followed by media filtration. Other conventional options include ion exchange, activated carbon adsorption, and membrane filtration. Sodium bisulfite has also been used to remove residual chlorine.

Treatment beyond that already in place at existing water plants may present an added expense for ASR operations, with the risk of realizing no benefits. Water treatment approaches that have been demonstrated to work at ASR sites tend to represent lower risk options. These include removing residual chlorine and/or oxygen from injection water. Approaches that are similar to those already being performed at conventional water treatment plants may also be lower risk. These include adding oxygen or removing DOM from injection water. Approaches that are less tested carry a higher risk of not showing benefits; these include adding phosphate, acid, or buffer to the injection water.

Aquifer management strategies can be used to mitigate risks at ASR sites, and these are expected to be inexpensive relative to additional water treatment technologies. Specifically, pre-flushing the storage zone may be attempted to displace easily mobilized arsenic during the first several pore volumes of flushing. These methods either leave this arsenic in groundwater away from the zone of injection and extraction, or extract the released arsenic for disposal during early stages of operation. Regardless of the options selected for minimizing the potential for arsenic release and mobilization at ASR sites, they should be complemented by 1) a site conceptual model, 2) knowledge of water quality conditions, aquifer geochemistry, and anticipated arsenic reactions, and 3) monitoring to evaluate efficacy and the need for further water treatment or aquifer management strategies.

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