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In Situ Treatment Performance Monitoring: Issues and Best Practices

Index

1. INTRODUCTION

The utility of monitoring wells for performance or attainment monitoring is based on the premise that contaminant concentrations measured in the wells are representative of aquifer conditions. However, during in situ treatment, various biogeochemical and hydrogeological processes and sampling and analysis procedures may affect the representativeness of the monitoring well and sample quality, which may not be adequately considered in current remediation practice.

A properly designed monitoring network that anticipates the distribution of amendments after injection would minimize impacts to monitoring wells. However, predicting amendment distribution prior to injection is challenging such that impacts to monitoring wells are likely.

The purpose of this issue paper is to:

- describe how in situ treatment technologies may impact sampling and analysis results used to monitor treatment performance; and
- provide best practices to identify and mitigate issues that may affect sampling or analysis.

This paper discusses eight potential sampling or analytical issues associated with groundwater monitoring at sites where in situ treatment technologies are applied. These issues are grouped under three topic areas:

- Issues related to monitoring wells (Section 2).
- Representativeness of monitoring wells (Section 3).
- Post-sampling artifacts (Section 4).

The paper presents issues that pertain to collecting water samples directly from a monitoring well and does not discuss the use of other sampling techniques, such as passive diffusion bags or direct push groundwater sampling.

The in situ technologies addressed in this paper are listed in Table 1.

This issue paper does not address in situ technology selection, design or implementation, or effects resulting from combined remedies.

A quick-reference table in the Appendix can help identify potential sampling issues related to the six technologies and the best practices for monitoring or preventing and mitigating these issues.

Table 1. In Situ Groundwater Treatment Technologies Addressed

Technology	Acronym	General Resources
Activated Carbon-Based Injectate	CBI	Remediating Petroleum Contaminants with Activated Carbon-Based Injectates
Enhanced In Situ Bioremediation	EISB	CLU-IN Bioremediation Overview; ITRC Technical and Regulatory Requirements for Enhanced In Situ Bioremediation of Chlorinated Solvents in Groundwater
In Situ Chemical Oxidation	ISCO	CLU-IN In Situ Oxidation Overview; ITRC Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater
In Situ Chemical Reduction	ISCR	CLU-IN In Situ Chemical Reduction technology area
In Situ Thermal Treatment	ISTT	CLU-IN Thermal Treatment: In Situ Overview; In Situ Thermal Treatment of Chlorinated Solvents
In Situ Solidification	ISS	CLU-IN Solidification Overview; ITRC Development of Performance Specifications for Solidification/Stabilization

2. ISSUES RELATED TO MONITORING WELLS

2.1 Biofouling of Monitoring Wells

2.1.1 Overview

Technologies Affected					
EISB	ISCO	CBI	ISCR	ISTT	ISS
✓					

Mechanism – The addition of nutrients and amendments during EISB can create conditions favoring microbial growth in the vicinity of well screens and filter packs (ESTCP, 2005). Biofouling of groundwater monitoring wells occurs when enough biomass forms so that water in the well no longer represents the aquifer (Smith and Comeskey, 2009).

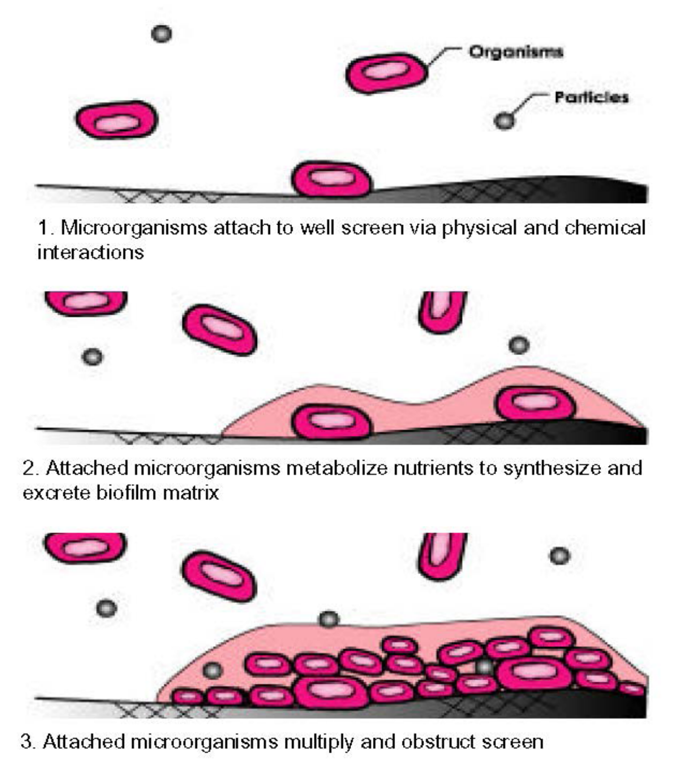
Impact – Biofouling of monitoring wells deposits slimes and excretions, sometimes called a biofilm, on well screens, which reduces groundwater flow into monitoring wells. Biofilms may appear as foams, pastes or gummy/slimy accumulations on well screens and sampling equipment. Figure 1 shows how a biofilm can form on an injection well screen.

Approximately 17 of 20 sites EISB surveyed reported some level of biofouling in injection wells, with most reporting at least a significant loss of injection well efficiency (ESTCP, 2005). Blocked monitoring wells and filter packs hinder sample collection or result in stagnant water in a monitoring well. Biofouling of well screens may also modify the flow of groundwater around a monitoring well and result in samples that may not be representative of the well screen interval. In addition, biofilms may trap and degrade contaminants reducing concentrations in the well (Smith and Comeskey, 2009).

Monitoring for Biofouling – Monitoring changes in well hydraulic performance, such as reduced well production or excessive water level drawdown and physiochemical water quality parameters (e.g., dissolved oxygen [DO], oxidation-reduction potential [ORP] and specific conductivity), can provide an indication of biofouling. Inspecting wells, submerged equipment and purge water for biofouling deposits during sampling can help diagnose biofouling. Biofouling also may be observed directly using borehole video cameras. Review of the well purging history after each sampling event to identify reductions in purge rate can help identify that biofouling is occurring. Conducting slug or pumping tests periodically can provide a quantitative measure of changes over time (Barcelona et al., 1985). Limiting the potential impacts of biofouling depends on regular monitoring for these changes and promptly mitigating any problems that arise (Smith, 1995).

2.1.2 Prevention and Mitigation

Prevention of biofouling in wells used to monitor EISB performance is best achieved by understanding site hydrogeology and contaminant distribution. This site characterization information is necessary for anticipating amendment distribution after injection and limiting amendment volumes to meet the site-specific electron acceptor demand (ESTCP, 2010). With this information, monitoring wells can be selected or installed so



1. Microorganisms attach to well screen via physical and chemical interactions

2. Attached microorganisms metabolize nutrients to synthesize and excrete biofilm matrix

3. Attached microorganisms multiply and obstruct screen

Figure 1. Schematic of Biofilm Formation Adapted from ESTCP, 2005.

that they are not anticipated to be influenced by the amendments or biological growth. Given that biofouling often is observed during EISB, it is recommended that remedial plans include well monitoring and maintenance to identify when biofouling is occurring and have agreed-upon procedures in place for mitigation. Mitigation procedures include both physical and chemical methods. Physical mitigation typically includes over-pumping, surging, jetting, or by injecting air in the casing (or vibratory methods, metal specific only). Manual brushing of well materials, followed by well redevelopment, can also remove material from the well screen and casing. However, brushing is not effective for cleaning filter packs (ESTCP, 2005, Smith and Comeskey, 2009). Chemical treatment with solutions of hypochlorite, hydrogen peroxide, chlorine and non-oxidizing biocides can mitigate biofouling by disinfecting the well. Chemicals are added to the well, left for varying treatment times depending on the chemical, and then surged within the well and pumped out (ESTCP, 2005). The use of chlorine will increase the concentration of chloride in groundwater, which should be considered if monitoring chloride to indicate the degradation of chlorinated compounds. Chemical treatment can result in byproducts. While these byproducts are not likely to affect existing contaminants, they may be toxic and harmful and will need to be handled carefully prior to disposal. It is important to review the available chemical treatment options to determine which is best suited for a specific site (Smith, 2011 and ESTCP, 2005). Bacteria usually regrow on the well materials in a few weeks or months after well treatment. Deeper well screens require more resources to mitigate biofouling. Mitigation of biofouling can be a significant operation and maintenance cost at sites using EISB.

Prevention and Mitigation

- Limit amendment volumes to meet the site-specific electron acceptor demand.
- Apply cleaning processes.

  Physical processes: Surging, over-pumping, jetting, air injection.

  Chemical processes: Hypochlorite, hydrogen peroxide, chlorine, non-oxidizing biocides.

2.2 Metal Precipitation on Monitoring Well Screens

2.2.1 Overview

Technologies Affected					
EISB	**ISCO**	**CBI**	**ISCR**	**ISTT**	**ISS**
✓	✓		✓		

Mechanism – Changes in groundwater chemistry due to amendment introduction can cause metal precipitation on well screens (Figure 2). In situ treatments can cause changes in pH, ORP, pressure, temperature, or levels of oxygen, carbon dioxide, manganese, methane or other chemicals. These changes can cause metals in saturated groundwater solutions to change to less soluble species that precipitate.

Impact – Precipitation of metals on well screens can reduce groundwater flow into the well and potentially hinder sample collection (Huling and Pivetz, 2006), or result in stagnant water in the well.

Monitoring for Metal Precipitation on Well Screens – Monitoring changes in well hydraulic performance, such as reduced well production or excessive water level drawdown, can provide an indication of metal precipitate fouling. Review of the well purging history after each sampling event to identify reductions in purge rate can help identify that metal precipitate fouling is occurring. Conducting slug or pumping tests periodically can provide a quantitative measure of changes over time (Barcelona et al., 1985). In addition, regular visual inspection of wells, submerged equipment and purge water is important to monitor for the presence of metal precipitates (Smith, 1995).

2.2.2 Prevention and Mitigation

Metal precipitation, can be anticipated through the completion of pilot-scale treatability studies (Huling and Pivetz, 2006). Precipitation is more likely to occur in water that is high in calcium and low in manganese. Activities that cause redox and pH shifts toward oxidizing and alkaline conditions may promote precipitation of iron, manganese and carbonates (Smith and Comeskey, 2009). Geochemical modeling with free software (e.g., Phreeqc or Minteq) can also predict or assess the impact of an amendment on metal precipitation. Mitigation for metal precipitate fouling of monitoring wells include physical and chemical methods. The physical methods are identical to those discussed in Section 2.1.2. In addition to the chemical methods discussed in Section 2.1.2., treatment with acid solutions can remove metal precipitates. Sulfamic acid can be effective for carbamate scales, and hydrochloric acid (HCl) for metal oxides (Smith and Comeskey, 2009). Glycolic acid, polymaleic acid and citric acid have also been used to rehabilitate wells impaired by metals precipitation. Chemicals are added to the well, left for varying treatment times depending on the chemical, and then surged or mixed within the well and pumped out (ESTCP, 2005). They may also be used in combination with jetting, surging or other physical methods (Smith and Comeskey, 2009).

Prevention and Mitigation

- Complete pilot-scale treatability study and perform geochemical modeling to anticipate metal precipitation.
- Apply cleaning processes.

  Physical Processes: Surging, over pumping, jetting, air injection, sonic and vibratory methods.

  Chemical Processes: Acid cleaning.

Mitigation may require more resources as the depth of the well screen increases. The use of chlorine will increase the concentration of chloride in groundwater, which should be considered if monitoring chloride to indicate the degradation of chlorinated compounds.

Chemical treatment can result in byproducts or oxidizing conditions. While these byproducts are not likely to affect existing contaminants, they may be toxic and harmful and will need to be handled carefully. In addition, they may have special disposal requirements. It is important to review the available chemical treatment options to determine which is best suited for a specific site (Smith, 2011).

Figure 2. Well Screen Plugged with Metal Precipitates (Scherer, 2013).

2.3 Reactions with Well Materials and Equipment

2.3.1 Overview

Technologies Affected					
EISB	ISCO	CBI	ISCR	ISTT	ISS
✓	✓	✓	✓	✓	✓

Mechanism – Well casing material and sampling equipment may be incompatible with contaminants, amendments and heat. High or low pH conditions resulting from the injection of strong oxidants and other reagents may corrode metal-based materials (Barcelona et al., 1985; Llopis, 1991). Further, oxidants may deteriorate piping and plumbing materials unless specialized oxidant-resistant materials are used (Huling and Pivetz, 2006), and materials may leach, sorb or react with contaminants (Llopis, 1991). Excessive temperatures may deteriorate materials such as PVC.

Table 2. Potential Reactions with Materials

Material	Potential Reactions with Materials
Teflon®	• PFOA may leach.
Stainless Steel	• Corrosion can release iron and chromium. • May leach metals under anoxic conditions. • May adsorb minor amounts of trace-level organic compounds.
Low-Carbon, Galvanized and Carbon Steel	• Corrosion can release iron, manganese, zinc and cadmium. • Weathered steel may present active adsorption sites for organics and inorganics.
PVC	• May release organic compounds from degradation. • May release tin or antimony. • May adsorb trace-level organic compounds. • May melt or compromise well casing and screen.
Flexible Polymers	• May adsorb chlorinated volatile organic compounds. • May adsorb trace-level organic compounds.

Adapted from Barcelona et al., 1985; McCaulou, Jewett and Huling, 1995; Smith and Comeskey, 2009; and Llopis, 1991.

Impact – Corrosion and degradation of steel materials can lead to leaching of metals (Table 2) and increased metal concentrations in samples. Elevated temperatures may damage materials (e.g., melt and deform plastic, and facilitate corrosion of stainless steel screens), which can inhibit sample collection. Contaminant sorption to or reaction with materials can result in a false trend of contaminant concentrations (Barcelona et al., 1985). Fenton and related reactions are exothermic, resulting in heat release and elevated temperatures during in situ Fenton oxidation. Heat accumulation near the injection well is common due to rapid decomposition of hydrogen peroxide and the slow dissipation of heat. Injection wells and nearby monitoring wells constructed of PVC have melted during in situ Fenton oxidation. Since the melting point of PVC is 200 °C, this suggests that very high localized temperatures have occurred under some conditions (Huling and Pivetz, 2006).

Monitoring for Reactions with Well Materials and Equipment – Regular inspection of wells and equipment for signs of corrosion, degradation or discoloration may reveal incompatibility. Monitoring subsurface conditions such as pH, dissolved solids, temperature and redox potential can also help detect conditions that might promote corrosion, and warrant further inspection. Reduction in well production may indicate corrosion has occurred. Review of the well purging history after each sampling event to identify reductions in purge rate can help identify corrosion and degradation. Conducting slug or pumping tests periodically can provide a quantitative measure of changes over time (Barcelona et al., 1985). Wells can also be checked using wellbore video cameras to ensure that they are physically intact and capable of providing water samples as intended. Monitoring for increases in metals concentrations can help identify leaching of metals.

2.3.2 Prevention and Mitigation

Select materials that are compatible with the amendments and target contaminants (Huling & Pivetz, 2006) and will resist changes in subsurface conditions that could cause corrosion or degradation. Decisions about which materials to use can be based on a number of factors, including structural integrity, long-term durability, minimization of the secondary effects of sorption or leaching, and anticipated temperatures (Barcelona et al., 1985). Cathodic protection may reduce corrosion of steel wells (Smith and Comesky, 2009). Also, Teflon®-coated well and sampling materials may be a source of perfluorooctanoic acid (PFOA) in groundwater well samples (Begley et al., 2005).

Choosing appropriate filter pack material can also help mitigate well degradation. Filter pack materials should be inert, such as glass or ceramic beads,

Prevention and Mitigation

- Select compatible materials.
- Use cathodic protection for metal wells and equipment.
- Choose inert filter pack material.
- Replace, restore or line corroded components.

silica sand, or gravel (preferably quartz sand) that has been cleaned (Barcelona et al., 1985). If corrosion or degradation occurs, wells may be restored by adding cathodic protection, replacing the well or corroded parts, or lining corroded parts with a more compatible material (Smith and Comeskey, 2009). Monitoring wells damaged by elevated temperatures may require repair or replacement.

3. REPRESENTATIVENESS OF MONITORING WELLS

3.1 Displacement of Contaminants During Amendment Injection

3.1.1 Overview

Technologies Affected					
EISB	ISCO	CBI	ISCR	ISTT	ISS
✓	✓	✓	✓		✓

Mechanism – The injection of large volumes of amendment solution can potentially displace contaminated water to regions outside the treatment zone (Payne et al., 2008 and Huling and Pivetz, 2006). Displacement of contaminants can potentially occur when amendments are injected in large volumes or reactions of amendments produce large volumes of gas in the subsurface, (e.g., Fenton reagents for ISCO). In addition, increasing subsurface temperature during in situ Fenton oxidation will increase contaminant mobility and cause groundwater to volatilize and expand potentially displacing contaminants. Contaminants may move downgradient or be displaced along preferential pathways of groundwater flow.

Impact – If contaminants are displaced away from the injection zone they could spread or move beyond the treatment zone (Figure 3). Displacement could spread contamination to areas that were previously not contaminated. Displacement may also affect the concentration of contaminants in monitoring wells. Changes in concentrations may represent the movement of contaminants rather than treatment and lead to inaccurate evaluation of treatment performance. The impact of displacement would be more significant where flowpaths are narrow, such as fractures in bedrock or thin sand lenses in a clay formation (Simpkin et al., 2011).

Monitoring for Displacement of Contaminants – Decreasing concentrations of contaminants in monitoring wells adjacent to an injection point coupled with increasing contaminant concentration in distal wells can indicate potential movement of contaminants outside the treatment zone. If displacement of contaminants is suspected, then the wells should also be monitored for amendments. If a well is used for injection, there are issues associated with its use to monitor performance (*See Section 3.2 Use of Injection Wells for Monitoring*.).

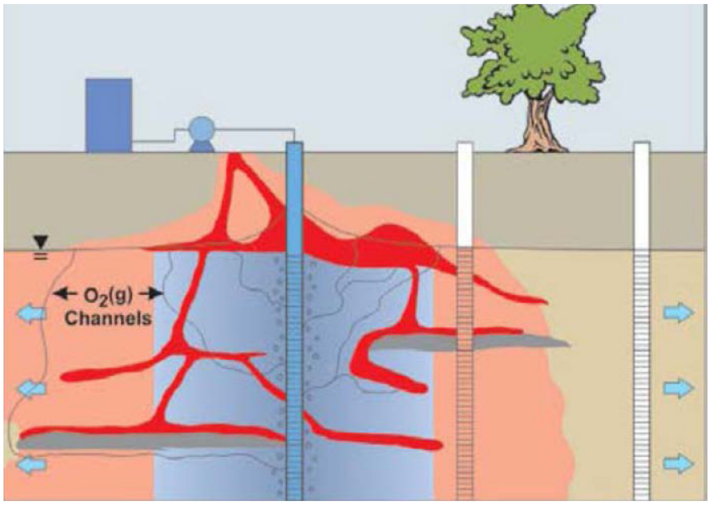


Figure 3. Model of Displacement of Contamination. *The pneumatic pressure from injection of oxidant (blue) results in mounding and displacement of groundwater and potential displacement of contaminants (orange) and DNAPL (red) away from the injection point. Adapted from Huling and Pivetz, 2006.*

3.1.2 Prevention and Mitigation

To assess the likelihood of displacement, the pore volume of the permeable formation can be estimated and compared with the injection volume. If this evaluation shows that a large fraction of the pore volume will be occupied or a large volume of liquid is being injected, then prevention and mitigation measures may be necessary. However, in general, significant displacement of contaminant mass is not expected during amendment injection (Simpkin et al., 2011 and Payne et al., 2008).

If displacement is likely, then prevention strategies such as groundwater recirculation or outside-in delivery should be considered. Groundwater recirculation, where groundwater is extracted mixed with amendments and reinjected, minimizes the potential for displacing contaminants (NAVFAC, 2013 and Borden et al., 2008). For example, the five-spot pattern consisting of a central permanganate injection well surrounded by four extraction wells achieved a 97% decrease in trichloroethene concentrations (Lowe et al., 2002). However,

Prevention and Mitigation

- Consider groundwater recirculation.
- Consider outside-in delivery.
- Treat areas contaminated by displacement.

recirculation systems have limitations where they may require an underground injection permit, have higher capital costs, and can be subject to fouling of injection wells (NAVFAC, 2013 and Borden et al., 2008). Using an outside-in delivery approach for amendment injections could minimize the impact from the lateral displacement of contaminants within a treatment area. With this method, injection points are located surrounding the contaminated area and amendments are injected from the outside (Huling and Pivetz, 2006). If monitoring indicates that contaminants have migrated outside the treatment zone, additional treatment and monitoring may be needed in the newly contaminated area. Mitigation of displaced contamination may involve expanding the treatment zone and installing additional monitoring wells if necessary.

3.2 Use of Injection Wells for Monitoring

3.2.1 Overview

Technologies Affected					
EISB	**ISCO**	**CBI**	**ISCR**	**ISTT**	**ISS**
✓	✓	✓	✓		

Mechanism – After injection, amendments will likely remain in and near the injection well (Figure 4).

Impact – Samples collected from injection wells may not be representative of the site as a whole because optimal treatment performance will likely occur near the injection well (Huling and Pivetz, 2006). Contaminant concentrations in an injection well may also be biased due to displacement of contaminants by the injected amendments (See Section 3.1.).

3.2.2 Prevention and Mitigation

Remedy performance monitoring is best achieved by having a thorough understanding of site hydrogeology and contaminant distribution. This site characterization information is necessary for anticipating amendment distribution after injection and determining if an adequate performance monitoring network exists (NJDEP, 2017). Remedy performance monitoring will require use of monitoring wells that are strategically placed to determine impacts to the contaminant source area, contaminant plume and potential receptors (Figure 5). Within this context, samples from injection wells may be useful for monitoring injection constituents and estimating the maximum rate of contaminant degradation (NJDEP, 2017). Although water quality samples from injection wells can be useful, they should not comprise the entire data set (Huling and Pivetz, 2006).

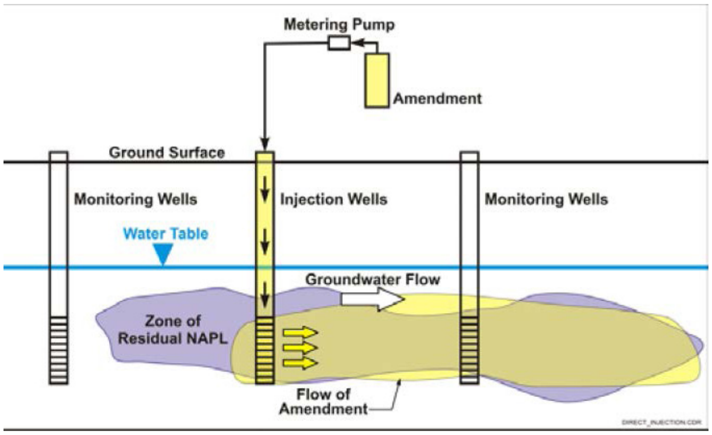


Figure 4. Use of Separate Injection and Monitoring Wells Adapted from NAVFAC, 2013.

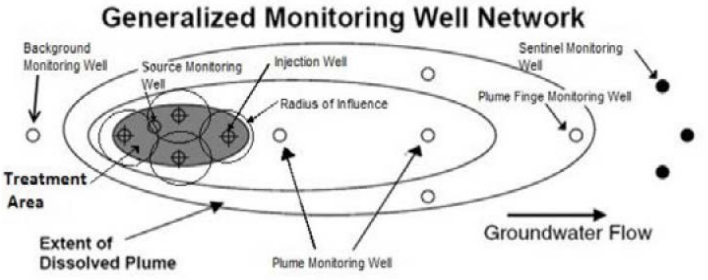


Figure 5. Generalized Monitoring Well Network (NJDEP, 2017).

Prevention and Mitigation

- Use a monitoring well network to determine impacts to the contaminant source, plume, and receptors.
- Use injection wells to monitor injection constituents and estimate the maximum rate of contaminant degradation

3.3 Preferential Accumulation of Amendment in Monitoring Wells

3.3.1 Overview

Technologies Affected					
EISB	**ISCO**	**CBI**	**ISCR**	**ISTT**	**ISS**
✓	✓	✓	✓		✓

Mechanism – Accumulation of amendment in monitoring wells may occur when they are located close to injection wells or high-pressure injection is used in low permeability formations (Figure 6). Under these circumstances, a monitoring well is more likely to intercept injection pathways and accumulate amendments. Existing preferential pathways (e.g., utility lines) between the injection and monitoring wells can also act as conduits leading to the accumulation of amendment in monitoring wells.

Impact – The extent of amendment distribution in an aquifer may be overestimated when amendments preferentially accumulate within monitoring wells. For example, it has been suggested that high-pressure injection of powdered CBI into low-permeability formations creates random fractures, which may result in amendments accumulating in nearby monitoring wells (Figure 6). Another impact is that samples from a monitoring well containing amendment may no longer be representative of the aquifer because the contaminant will partition to or be degraded by the amendment (See Section 4.1.). As a result, the low contaminant concentration measured from the impacted well may not reflect the true extent of aquifer treatment. For example, organic contaminants are known to strongly partition from water to carbon and can also partition to the vegetable oil used for EISB (Pfeiffer et al., 2005). Another example is with in situ ozonation where ozone channels intercept monitoring wells and treat the water in the monitoring wells instead of in the aquifer (See Figure 3.).

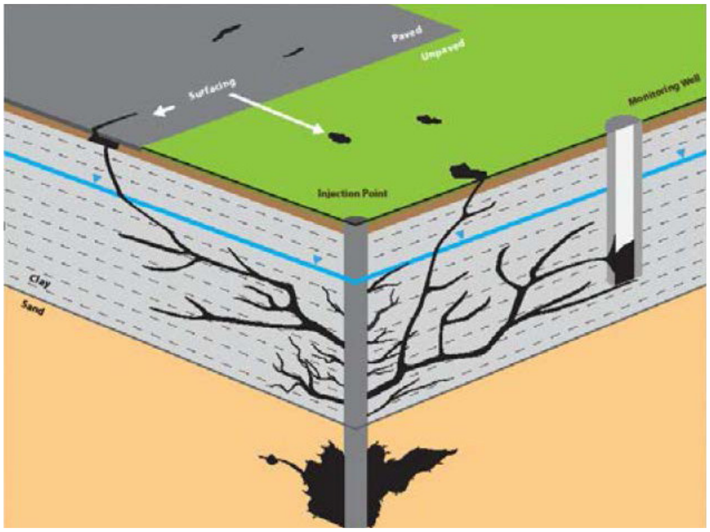


Figure 6. Uneven Distribution of CBI in Clay and Sand Introduced by High-Pressure Injection.

Monitoring for Amendment Distribution – Visual inspection of samples for color, particulates or a cloudy suspension may indicate the presence of amendments. For example, a light pink to deep purple color may indicate permanganate, and black particles may indicate the presence of carbon. The emulsified oil used in EISB can accumulate in monitoring wells where it will be visible as a cloudy suspension or detected by total organic carbon and dissolved organic carbon analysis (AFCEE, 2007).

3.3.2 Prevention and Mitigation

One method for minimizing amendment accumulation is to exercise best practices during injection. Controlling injection pressure, temperature, and flow rates can help prevent uncontrolled hydraulic fracturing (NAVFAC, 2013). The rate an aquifer can accept fluids and the lateral migration of these fluids before reaching structural failure is significantly influenced by the vertical acceptance rate (LARWQCB, 2009). Maximum injection pressure can be estimated using Equation 1 found in LARWQCB (2009) as long as the following are known: the density of the dry soil and saturated soil, the thickness of the vadose zone, and the height of the saturated zone above the injection point. When fracturing is needed in low-permeability formations, injection points should be carefully chosen to minimize potential impacts to monitoring wells. Additionally, it is important to note and consider existing preferential pathways that may impact monitoring wells.

Prevention and Mitigation

- Control injection pressure, temperature, and flow rate to prevent uncontrolled hydraulic fracturing.

4. POST-SAMPLING ARTIFACTS

4.1 Post-Sampling Transformation of Contaminants

4.1.1 Overview

Technologies Affected					
EISB	**ISCO**	**CBI**	**ISCR**	**ISTT**	**ISS**
✓	✓		✓		

Mechanism – Organic contaminants and amendments can be commingled in groundwater samples collected from sites where amendments have been injected, resulting in contaminants being transformed in the time between sample collection and analysis (Ko, Huling and Pivetz, 2012). Examples of amendments that may persist in samples include oxidants, such as permanganate for ISCO, or reductants such as micron or nano zero valent iron for ISCR. In addition, microbes contained in groundwater samples may continue to degrade contaminants between sample collection and analysis, particularly when amendments have been added for EISB. Changes in ORP between the aquifer and sample bottle may also facilitate chemical transformation.

Impact – If amendment is present and abiotic or biotic degradation is possible, and the samples are not preserved correctly, the results may indicate lower concentrations of contaminants than are actually present in the groundwater (Ko, Huling and Pivetz, 2012).

Monitoring for Post-Sampling Transformations of Contaminants – Post-sampling transformation can be monitored by checking for the presence of oxidative or reductive amendments in the sample. Groundwater samples can be collected and analyzed in the field specifically to determine the presence of these amendments. If the groundwater sample contains both amendments and organic contamination, then there is a high risk of contaminant transformation. Field tests for permanganate and persulfate oxidants include colorimetry test kits and field-based spectrophotometric analysis (Ko, Huling and Pivetz, 2012).

4.1.2 Prevention and Mitigation

Prevention and Mitigation

- Preserve samples.
  - Neutralize amendments.
  - Cool samples.
- Allow sufficient time for amendments to fully react before taking samples for performance monitoring.

Mitigation can be done by ensuring that the correct sample preservation and quenching procedures are used (Table 3). For ISCO applications, proper sample handling and preservation depend on the oxidant being used (Huling and Pivetz, 2006). In the case of permanganate and persulfate, ascorbic acid can be added to the groundwater sample in order to neutralize the oxidant and reduce the impact of the oxidant on sample results (Ko, Huling and Pivetz, 2012). Recommendations for preservative amounts can be found in references such as Ko, Huling and Pivetz, 2012. Notifying the analytical laboratory that the aqueous samples may contain residual persulfate or permanganate, and the volume of preservative solution added to the sample will allow the lab to correct for dilutions. Other preservatives have been used to successfully neutralize these oxidants but may negatively impact the quality of the sample (Huling, Ko and Pivetz, 2011). Applications using ozone or Fenton's reagent typically do not require preservation to prevent post-sampling oxidative transformation because of their short persistence. In lieu of preservation, delaying sampling until the oxidant has been fully consumed and is no longer detected in screening samples minimizes post-sampling transformation. However, permanganate may persist for long periods and, therefore, may require neutralization prior to complete reaction (Huling and Pivetz, 2006).

Table 3. Persistence and Preservatives for Common Oxidants

Oxidant	Persistence	Preservative
Permanganate	>3 months	Ascorbic acid
Persulfate	Hours - weeks	Ascorbic acid
Ozone	Minutes - hours	Not applicable
Fenton's reagent	Minutes - hours	Not applicable

Adapted from Huling and Pivetz, 2006 and Ko, Huling and Pivetz, 2012.

Methods for eliminating or slowing biodegradation in samples with volatile organics include cooling to between 0 and 6 °C and adjusting the pH to less than 2 (U.S. EPA, 2016). For fuel oxygenates, base may be added to samples to prevent biodegradation and minimize ether hydrolysis (U.S. EPA, 2003).

4.2 Loss of Volatiles when Sampling High-Temperature Groundwater

4.2.1 Overview

Technologies Affected					
EISB	**ISCO**	**CBI**	**ISCR**	**ISTT**	**ISS**
	✓			✓	✓

Mechanism – Where remedy application results in elevated temperature, it may trigger a phase change from liquid to gas for volatile contaminants. Volatile compounds may escape from the sample, resulting in contaminant losses, especially where groundwater samples are exposed to the atmosphere (USACE, 1998). ISTT heats the subsurface and increases sample temperatures, which may result in loss of volatiles. Technologies that cause exothermic reactions, such as ISCO and ISS, can also heat the subsurface and lead to a loss of volatile contaminates during sample collection. High temperatures may also cause contaminants to react after sampling.

Impact – Volatilization and reactions of contaminants from samples could result in an underestimate of contaminant concentrations (USACE, 2014).

4.2.2 Prevention and Mitigation

Evaluation of contaminant volatility at elevated temperatures can inform approaches to prevent or mitigate potential sampling or analytical issues associated with loss of volatiles.

Mitigation can involve using dedicated sampling ports or taps that can be accessed without opening the monitoring well cap (USACE, 2014). Groundwater extracted from the well should flow through a cooling coil to decrease the groundwater temperature before the sampling point (USACE, 2014). In addition, submerging samples in an ice bath immediately after collection and keeping them cool until analysis can reduce loss of volatiles (USACE, 2014).

If dedicated sampling ports are not available, then waiting until the subsurface has cooled before sampling may be necessary.

Prevention and Mitigation

- Use dedicated sampling ports and cooling coil to decease groundwater temperature before sample collection.
- Allow subsurface temperature to cool before sampling for performance monitoring.

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6. NOTICE AND DISCLAIMER

This paper was prepared for the EPA Office of Superfund Remediation and Technology Innovation (OSRTI), Technology Innovation and Field Services Division and the Ground Water Forum, a component of the U.S. EPA Superfund Technical Support Project, under EPA Contract Number EP-W-14-001. This information has received technical EPA review and does not necessarily reflect the views of EPA or other participating organizations, and no official endorsement should be inferred. The information is not intended, nor can it be relied upon, to create any rights enforceable by any party in litigation with the United States or any other party. Use or mention of trade names does not constitute an endorsement or recommendation for use.

A PDF version of *Ground Water Forum Issue Paper: In Situ Treatment Monitoring Issues and Best Practices* is available to view or download at https://www.epa.gov/remedytech/technical-support-project-cleaning-contaminated-sites-issue-papers and http://www.cluin.org.

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APPENDIX: Quick Reference Table: In Situ Treatment Monitoring Issues and Best Practices for Monitoring, Prevention and Mitigation

Potential Sampling Issue	Technology						Best Practices
	EISB	ISCO	CBI	ISCR	ISTT	ISS	
Issues Related to Monitoring Wells							
Biofouling of monitoring wells • ***Mechanism:*** Enhanced microbial activity leads to growth of biomass on well screen and in filter pack. • ***Impact:*** Impedes groundwater entry to well, potentially hindering sample collection or resulting in stagnant water in well. Changes groundwater flow around well and adsorption or degradation of contaminants, potentially resulting in samples not representative of aquifer.	✓						***Monitoring*** • Monitor changes in well hydraulic performance, such as reduced well production. • Inspect monitoring wells, submerged equipment and purge water for signs of biofouling. ***Prevention and Mitigation*** • Limit amendment volumes to meet the site-specific electron acceptor demand. • Apply cleaning processes followed by well redevelopment: – Physical processes: surging, over-pumping, brushing, jetting or air injection. – Chemical processes: cleaning with hypochlorite, hydrogen peroxide, chlorine (will increase chloride in groundwater) or non-oxidizing biocides.
Metals precipitation on monitoring well screens • ***Mechanism:*** Change in groundwater chemistry due to addition of amendments can cause metal precipitation on monitoring well screens. • ***Impact:*** Damages or fouls well screen impeding groundwater entry. Potentially hinders sample collection or results in stagnant water in well that is not representative of the aquifer.	✓	✓		✓			***Monitoring*** • Monitor changes in well hydraulic performance, such as reduced well production. • Inspect monitoring wells, submerged equipment and purge water during sampling for signs of precipitates. ***Prevention and Mitigation*** • Complete pilot-scale treatability study and perform geochemical modeling to anticipate metal precipitation. • Apply cleaning processes followed by well redevelopment: – Physical processes: surging, over-pumping, jetting, air injection, sonic or vibratory methods. – Chemical processes: acid cleaning.

Potential Sampling Issue	Technology						Best Practices
	EISB	ISCO	CBI	ISCR	ISTT	ISS	
Reactions with well materials and equipment • ***Mechanism:*** Well casing material and sampling equipment incompatible with contaminants, amendments and heat may cause corrosion or deterioration of casing or equipment. • ***Impact:*** May hinder sample collection or foster adsorption or desorption of contaminants, resulting in samples not representative of the aquifer.	✓	✓	✓	✓	✓	✓	***Monitoring*** • Monitor changes in well hydraulic performance, such as reduced well production. • Inspect monitoring wells, submerged equipment, and purge water during sampling for signs of corrosion or degradation. ***Prevention and Mitigation*** • Select compatible materials. • Use cathodic protection for metal wells and equipment. • Choose inert filter pack material. • Replace, restore or line corroded components.
Representativeness of Monitoring Wells							
Displacement of contaminants during amendment injection • ***Mechanism:*** Injection of large volumes of amendments or reactions of amendments that produce large volumes of gas can displace contaminated groundwater. • ***Impact:*** Displaces contaminated groundwater, possibly to uncontaminated areas. May yield non-representative sampling results if sampling is limited to original area of contamination.	✓	✓	✓	✓		✓	***Monitoring*** • Monitor wells adjacent to or downgradient from injection wells for increasing contaminant concentrations. ***Prevention and Mitigation*** • Consider groundwater recirculation. • Consider outside-in delivery. • Treat areas contaminated by displacement.
Use of injection wells for performance monitoring • ***Mechanism:*** Amendments will likely remain in and near the injection well. • ***Impact:*** Samples collected from injection wells may not be representative of the site as a whole because optimal treatment performance will likely occur near the injection well.	✓	✓	✓	✓			***Prevention and Mitigation*** • Use monitoring well network to determine impacts to contaminant source, plume and receptors. • Use injection wells to monitor injection constituents and estimate maximum rate of contaminant degradation.

Potential Sampling Issue	Technology						Best Practices
	EISB	ISCO	CBI	ISCR	ISTT	ISS	
Preferential accumulation of amendment in monitoring wells - ***Mechanism:*** Injection of amendments near monitoring wells or use of high-pressure injection. - ***Impact:*** Causes hydraulic fracturing that creates pathways for amendment to flow to wells. Results in overestimate of distribution of amendments. Also, contaminant concentrations in wells no longer represent treatment zone.	✓	✓	✓	✓		✓	***Monitoring*** - Visually observe amendments in monitoring wells for color, particulates or cloudy suspension. - Analyze total organic carbon or dissolved organic carbon for EISB amendments. ***Prevention and Mitigation*** - Control injection pressure, temperature and flow rate to prevent uncontrolled hydraulic fracturing.
Post-Sampling Artifacts							
Post sampling transformation of contaminants - ***Mechanism:*** Amendments and microbes are commingled in groundwater samples. - ***Impact:*** Transforms contaminants after collection but prior to analysis, resulting in unrepresentative samples.	✓	✓		✓			***Monitoring*** - Monitor presence of amendment and/or microbes. ***Prevention and Mitigation*** - Preserve samples. – Neutralize amendments. – Cool samples. - Allow sufficient time for amendments to fully react before taking samples for performance monitoring.
Loss of volatiles when sampling high-temperature groundwater - ***Mechanism:*** Increased temperature of groundwater samples through application of in situ thermal or chemical technologies that result in elevated temperatures. - ***Impact:*** Potential loss of volatile contaminants during sample collection, resulting in samples not representative of aquifer.		✓			✓	✓	***Monitoring*** - Evaluate contaminant volatility. - Monitor groundwater temperature during all stages of sample collection. ***Prevention and Mitigation*** - Use dedicated sampling ports and a cooling coil to decrease groundwater temperature before sample collection. - Allow subsurface temperatures to cool before collecting samples.