**Assessing And Remediating Low Permeability Geologic Materials
Contaminated By Petroleum Hydrocarbons
From Leaking Underground Storage Tanks:
A Literature Review**

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Office of Underground Storage Tanks
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Notice: This document provides technical information to EPA, state, tribal, and local agencies involved in investigating and addressing petroleum releases from leaking underground storage tanks. We obtained this information by reviewing selected literature relating to the occurrence, investigation, behavior, and remediation of contaminants in low permeability geologic materials. This document does not provide formal policy or in any way affect the interpretation of federal regulations. EPA does not endorse or recommend commercial products mentioned in this document, and we do not guarantee performance of methods or equipment mentioned.

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INTRODUCTION

Many leaking underground storage tank (LUST) sites are located in areas underlain by low permeability (low-k) geologic materials, for example alluvial silts and clays that are characteristic of river floodplains and often overlie water supply aquifers (97). Such sites typically are difficult to remediate using conventional technologies for these reasons (59).

- It is difficult to accurately determine the location and extent of contamination.
- Due to the low permeability, flow through the contaminated zone is reduced and contact with contamination is limited.
- Source areas tend to be persistent and prolong remedial actions, thereby increasing costs.[1]

Consequently, sites such as these potentially represent a significant percentage of the LUST cleanup backlog.

Key Takeaways

Below are key takeaways in four main areas—diffusion, heterogeneity, site characterization, and remediation—from our review of literature pertaining to petroleum hydrocarbon contamination in low-conductivity soils.

Diffusion. Contaminant transport and fate, especially in low-k environments, is diffusion-dominated. Contaminants residing in low-k zones have the potential to cause persistence of plumes and increase the remediation timeframe, that is the time required to reach regulatory concentration goals, because of diffusion-controlled release of contaminants back into transmissive zones, that is matrix or back diffusion.

- Matrix diffusion processes should apply to almost any dissolved contaminant, including benzene and other aromatic compounds found in gasoline.
- The slow release of contaminants by back diffusion from low permeability zones into the higher permeability zones creates a persistent, secondary source of contamination that is difficult to remediate.
- Advection-dispersion models used to assess contaminant transport and remedial progress are likely to be overoptimistic if they do not accurately simulate releases of contaminants stored in low permeability zones.

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[1] Removing the source of contamination through excavation or remediating it *in situ* is a typical part of a LUST cleanup. 40 CFR Part 280.64 states that owners and operators whose underground storage tanks have had a release must remove free product to the maximum extent practicable as determined by the local implementing agency. A large number of state, local, and tribal regulatory agencies employ risk-based corrective action with site-specific cleanup standards. This approach guides the amount of cleanup activity at a given site.

Site Characterization. Contaminant transport in low-k zones is diffusion limited and relevant processes occur over small spatial scales; this means it helps to apply tools for these assessments at very fine spatial resolution. Conventional approaches to site characterization at LUST sites make it challenging to develop a detailed and robust conceptual site model. Collecting high-resolution characterization data to identify contaminant and stratigraphic heterogeneity can provide a more realistic understanding of contaminant transport and fate, as well as how contaminated sites will respond to remediation efforts.

- Traditional soil sampling may be unlikely to generate sufficiently detailed data for the purposes of characterizing low-k zones.
- Conventional monitoring wells with long screens are particularly poorly suited for low-k zone investigations; instead, shorter-screened wells at multiple levels that provide depth-discrete data for evaluating contaminant distribution may be more effective.
- Closely-spaced sampling is required to identify microbiological processes in contaminated aquifers.

Heterogeneity. Heterogeneity exerts control on solute transport pathways in any subsurface environment and contributes to the complexity of site characterization and remediation strategies. Thus, it is important to understand the heterogeneities at a site with a reasonable degree of accuracy in order to support selection and design of effective remedial systems.

- Low-k environments are not necessarily monolithic layers of clayey material; discontinuous clay stringers dispersed throughout alluvial sediments can effectively represent a low-k environment in terms of contaminant transport and fate.
- Heterogeneity within a natural aquifer can significantly lengthen the residence time of contaminants.
- Contaminant transport in heterogeneous media cannot be accurately simulated by models developed for homogeneous and isotropic media.

Remediation. Remediating sites where a significant portion of contaminant mass is present in lower permeability zones can be difficult using conventional technologies. Contaminants in low-k zones have the potential to sustain plumes for extended periods of time and limit the applicability of technologies that solely address contaminants in transmissive zones.

- Implementing source-zone remediation will ultimately result in accelerated site closure and reduced long-term site management costs.
- When UST releases occur, early detection and initiation of aggressive remediation are keys to minimizing the spread of contaminants and reducing the contact time with low permeability layers.

Purpose And Scope

During an annual research coordination conference call, EPA invited members of the Association of State and Territorial Solid Waste Management Officials (ASTSWMO) Leaking Underground Storage Tanks Task Force to share their research and technical assistance needs with EPA's Office of Underground Storage Tanks (OUST) and Office of Research and Development (ORD). One proposed topic area was how to effectively remediate LUST sites underlain by low permeability geologic materials, specifically silts and clays. EPA agreed to investigate this topic and divided the project into three phases.

1. Systematically search literature to obtain a general sense of the nature and volume of available, published materials.
2. Analyze the discovered literature to assess its relevance to remediating petroleum releases from leaking USTs in low-k geologic materials.
3. Develop a document to aid states in assessing and remediating such petroleum-contaminated sites.

The plan was to identify a sufficient amount of literature that discussed the effectiveness of various remediation technologies so we could develop a framework to help states in selecting appropriate technologies for their own low permeability sites.

Low permeability settings generally fall into one of two categories: unconsolidated silts and clays, and fractured or crystalline rock. Though there are some similarities between these two types of settings, the differences are significant; as a result, EPA focused our search solely on unconsolidated silts and clays. However, when discussion of similarities and differences between these settings is instructive, we include that. Additionally, Appendix A contains some summary material specifically pertaining to fractured rock settings.

Literature Search Methodology

EPA conducted a literature search to locate peer-reviewed sources describing case studies of LUST cleanups in low permeability settings. The literature search consisted of several phases.

- EPA searched the Web of Science database, EPA's National Service Center for Environmental Publications (NSCEP), the National Ground Water Association (NGWA) journals *Groundwater* and *Groundwater Monitoring & Remediation*, and Google. EPA used these search terms, singly and in combinations: low permeability, low-k, low hydraulic conductivity, petroleum hydrocarbons, underground storage tanks, and remediation.
- As we identified relevant literature, we scanned their lists of references for additional relevant literature. The vast majority of literature pertaining to remediation of contaminants in low permeability materials is concerned with dense

non-aqueous phase liquids (DNAPLs), generally chlorinated solvents[2] (34); few studies focus on petroleum-impacted aquifers (12).

- We read the literature and highlighted relevant passages to include in this document. EPA initially flagged more than 400 pieces of literature for closer inspection, but ultimately retained fewer than 100. None of the pieces of literature described detailed case studies of LUST cleanups in low permeability settings. Though chlorinated solvents and petroleum hydrocarbons have significant differences, for example physical properties and biodegradability, in theory, "matrix diffusion processes should apply to almost any dissolved contaminant, including benzene and other aromatic compounds found in gasoline, although the overall impacts may differ." (34)

This report of the literature review was produced between March and September 2018. Members of the ASTSWMO LUST Task Force reviewed a draft of the document and provided comments in April 2019, including notice of a recently-published journal article *Groundwater Remediation in Low-Permeability Settings: The Evolving Spectrum of Proven and Potential,* by Horst *et.al* (2019). This article is especially significant to this project as it provides an overview of a "selection of technologies that reflect both demonstrated and promising new approaches across a spectrum of strategies ranging from complete treatment to source reduction to flux control." This article examines 9 technologies and provides a "remedy selection framework" that states may find helpful at some leaking UST sites. As this article had not been published until the draft literature review had been finalized, it is summarized in Appendix C.

Report Composition

This document is primarily a compilation of excerpts that EPA cut-and-pasted from references compiled from our literature search. We developed a minimum of connecting text to transition between concepts because we show respect for the expertise of the various authors by presenting the authors' perspectives and maintaining nuances that could otherwise be lost in translation. We organized these excerpts in a logical sequence to explain the state of the science of contaminant transport and remediation effectiveness. EPA attributed each of the sources of information provided. To aid in readability, we provide most passages—whether one sentence or many—verbatim without quotation marks and each of the passages generally has a single attribution at the end of the passage. There are some exceptions, typically with shorter passages where connecting text blends with noteworthy passages; here we attribute quoted text to the particular reference source. In addition, we lightly edited for formatting and style consistency, to remove redundant acronyms, and for clarity.

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[2] In theory many of the processes at chlorinated solvent sites will be applicable to light non-aqueous phase liquid (LNAPL) sites. However, we are not aware of any detailed research studies where matrix diffusion at LNAPL source zones was evaluated. (34)

DIFFUSION

Diffusion has long been recognized as an important process in contaminant transport in unconsolidated deposits, or fractured porous media, or both (71, 94), though in some ways underappreciated (39). Over the past 20 years, the groundwater research community has developed the view that much of the inability to achieve cleanup to the level desired and required is the result of the failure to recognize the role of diffusion in the process, and that remediation technologies have not generally addressed the potential flux and mass of contaminants stored in the aquifer matrix and released to these pores by diffusion.[3] (91)

When contaminants are released into the subsurface they are preferentially transported along the most permeable pathways by flowing groundwater as a contaminant plume. These higher and lower permeability zones are typically interbedded and intertwined. (69a, 75) As contaminants advance through relatively permeable pathways in heterogeneous media, concentration gradients cause diffusion of contaminant mass into the less permeable media. Matrix diffusion is most likely to occur with dissolved contaminants that are not strongly sorbed, such as inorganic anions and some organic chemicals. (27) As the plume migrates through and past material of lower permeability, a portion of the contaminant mass diffuses into the lower permeability material—typically silts, clays, and fractured rock—where they may be stored for a long period of time. (69a, 75)

The rate at which the contaminant diffuses into the lower permeability material and how much is retained depends on several factors, including the concentration in the plume compared to the concentration in the lower permeability material, the sorptive capacity of the lower permeability material[4], and the length of time that the contaminants are in contact with the low permeability material. This process is referred to as forward diffusion. When the concentration gradient between the low permeability material and flowing groundwater is reversed, as in the case where the source has been eliminated and the plume has dissipated, diffusion proceeds in the reverse direction; this process is referred to as back diffusion (94). This process is illustrated by tailing or rebound, especially during pump-and-treat, or aquifer flushing, or both (30, 71).

Forward diffusion can result in the storage of substantial contaminant mass, and the storage capacity is generally increased by sorption attributable to higher organic carbon

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[3] While low permeability materials complicate cleanup, the low permeability of aquitards, coupled with high sorption capacity, confers importance to them as protective barriers keeping drinking water aquifers safe from contamination or in isolating wastes disposed in the subsurface (94). It is important during site characterization to assess whether low permeability zones in the subsurface could potentially be a benefit or a liability.

[4] The depositional environments that create low permeability zones often favor higher concentrations of organic carbon. As a result, low permeability layers may have large sorptive capacities, increasing the potential for diffusion into these materials, and enhancing their ability to sustain dissolved chemical plumes after the original chemical source…has been depleted, contained, or remediated. (75)

content characteristic of silts and clays (69a). The slow release of contaminants by back diffusion from low permeability zones into the higher permeability zones creates a persistent, secondary source of contamination that is difficult to remediate. (09, 69a, 69b, 97, 92, 71, 94, 75, 77, 91) Because forward and back diffusion are slow processes, delivery and subsequent penetration of injected materials intended to promote remediation is also slow and may be incomplete. (92, 49) Thin clay layers can cause appreciable tailing for decades, while the thicker aquitard or thicker clay layers can cause tailing for much longer periods. (20, 71, 76)

Even under unrealistic conditions where contaminants could be instantaneously transferred from storage in the low permeability materials to clean, flowing groundwater, it would take at least as long—and some estimates are twice as long or longer—to remove the contaminants as it took the contaminants to diffuse into the low permeability materials in the first place (91). Estimates of source longevity range from decades to centuries (76a). Advection-dispersion models that assess contaminant transport and remedial progress are likely to be overoptimistic if they do not accurately simulate releases of contaminants stored in low permeability zones (39).

SITE CHARACTERIZATION

The overall goal of site characterization is to support developing an accurate and defensible conceptual site model (CSM). (76) A conceptual site model is an organized set of ideas about a site. (39) This model is an invaluable component of the site management process because it integrates all available site information. It is critical that it be based on sound science and reflect all potentially-relevant processes. (76a) A comprehensive CSM should be created that incorporates the location and mass of all contaminants of concern (COCs), an understanding of the geology and hydrogeology, aquifer geochemistry, major migration pathways for the COCs, groundwater flow direction and gradient, and identification of surface and subsurface structures, underground utilities, and potential receptors in the area. (16)

Characterization objectives for the source area include determining the magnitude and extent of the spill, hydrological characteristics of the release, and the potential pathways the release could follow. This process of characterizing the released non-aqueous phase liquid (NAPL) and its subsequent migration has been challenging for scientists and engineers involved in soil cleanup and remediation. Two traditional detection and monitoring strategies are primarily used for site characterization. The first strategy is to use point sampling with monitoring wells or multilevel piezometers. The second strategy involves making indirect subsurface measurements using surface or borehole geophysical techniques (40). As both fuels and solvents are highly resistive fluids (~1010–1013 Ohm-m), when replacing water in a porous media (~100–102 Ohm-m) they provide a strong electrical contrast. This resistive contrast allows site characterization to rapidly obtain significant spatial coverage of sites. Electrical resistance surveys may be used to delineate the boundaries of an impacted area and allow more complete data coverage of the subsurface than drilling monitoring wells. (40)

Heterogeneity

Heterogeneity exerts an important control on solute transport pathways in any subsurface environment (41). Heterogeneity is now recognized as the rule in subsurface environments rather than the exception. Low permeability zones will serve as a major contributor to source and plume behavior at all but the most homogeneous of sites (69a). For example, abrupt contacts between highly transmissive and less transmissive zones are common in most geologic settings. Heterogeneity contributes to the complexity of site characterization and remediation strategies. (69b)

In contrast to the current paradigm that contaminant transport is the result of advection and dispersion, recent trends in groundwater characterization recognize that the subsurface is heterogeneity-dominated and, consequently, that contaminant transport is controlled by advection and diffusion. (39) The importance of diffusion compared with dispersion becomes apparent with startling concentration gradients reported between permeable, transmissive zones facilitating advective transport and adjacent low permeability, or non-transmissive, zones storing contaminants through diffusion.[5] (39)

In characterizing a site, distinguishing between transmissive and low permeability zones is extremely important because contaminants in transmissive zones are found in moving groundwater, while contaminated groundwater in a low permeability zone is largely stagnant. (75) Heterogeneity within a natural aquifer can significantly impact the residence time of contaminants. (20) The development of appropriate characterization methods for low-k zones is a key goal for understanding the impact of contaminants stored and released from low-k zones. (03)

Soil heterogeneities influence natural source zone depletion as light non-aqueous phase liquid (LNAPL) will have varying attenuation rates in lithologic units with differing permeability, hydraulic conductivity, grain size, and organic carbon content. (67) Due to the poor soil sample representativeness, a significant uncertainty may remain in plume delineation or estimated volumes of impacted soils. As a result, designing appropriate remediation plans remains difficult. This often leads to costly or failed attempts to minimize risks associated with the contamination. (18) An estimation of the amount of pollutants contained in low permeability regions would allow a better design and cost estimation of the remediation operation of the aquifer. (20) Consequently, it is important to understand the heterogeneities at a site with a reasonable degree of accuracy in order to support selection and design of effective remedial systems. (67)

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[5] Today [2014], however, after almost 40 years of inquiry, analysis, and debate, groundwater experts find themselves confronting the troubling possibility that the main conceptual and numerical transport models that have been employed for decades have serious conceptual problems, and may overlook the critical role that heterogeneities play in governing contaminant behavior in groundwater. (39)

Because aquifers have tremendous heterogeneity by orders of magnitude, there are enormous surface areas where contaminants in transmissive zones can pass in or out of low permeability zones. Although there will always be a role for source remediation at some sites, traditional thoughts about linkage between source and dissolved phase need serious re-thinking; if matrix diffusion is important in the plume, then at some point the plume becomes the source (39). Extra care should be taken to prevent releases from occurring and, in the event that a release occurs, early detection and initiation of aggressive remediation are keys to minimizing the spread of contaminants and reducing the contact time with low permeability layers. (39)

Heterogeneity of hydraulic properties in aquifers may lead to dissolved and sorbed contaminants residing in lower permeability zones, primarily due to diffusive mass flux from non-aqueous phase liquid source zones into low-k zones. (04) Heterogeneities limit mass transfer rates for contaminant recovery and reagent delivery[6]. (19) Contaminants residing in low-k zones have the potential to cause persistence of plumes and increase the remediation timeframe, that is the time required to reach regulatory concentration goals, because of diffusion-controlled release of contaminants back into transmissive zones, that is the matrix or back diffusion. (04)

In fine-grained sediments such as aquitards, molecular diffusion is usually the dominant solute transport mechanism. Hence, the interpretation and modeling of solute migration in these systems requires the characterization of both physical heterogeneity, or hydraulic properties, and chemical heterogeneity, or concentration gradients. The spatial resolution of physical or chemical characterization, or both, that most field-scale investigations require is, however, seldom achieved. This is because monitoring wells and piezometers, by their design, only provide short-interval data points in the investigation domain and the costs of drilling and installing them at the desired resolution are prohibitive. (41)

Sand deposits are common in many aquitards. These features can provide preferential pathways for solutes, including contaminants, to advect through what is otherwise a diffusion-dominated environment. (42) The migration of contaminants through porous conduits, for example sand layers, in aquitards or any preferential flow feature within a low permeability matrix, can be significantly retarded via diffusion into the matrix and processes such as sorption and decay. (42)

Indicators Of Biodegradation

Heterogeneities in physical and chemical properties of aquifer sediments can constrain not only the possibilities for hydrologic contaminant transport, but also biogeochemical reactions (17).

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[6] For more information about mass transfer limitations, see *Soil Flushing And Surfactants*, page 23.

Depletion of the hydrocarbons in the oil pool is controlled by: the lack of oxygen and nutrients, differing rates of recharge, and the spatial distribution of oil in the aquifer…the composition of LNAPL changes over time and that these changes are spatially variable. This highlights the importance of characterizing the temporal and spatial variabilities of the source. (05)

The biogeochemical reactions and the resulting chemical composition of shallow groundwater are affected by: 1) microbially mediated reactions that occur at a small spatial scale and 2) heterogeneity in the physical composition of the aquifer that results in two different hydrologic regimes (17). Regarding 1, it has been demonstrated that closely spaced sampling is required to identify microbiological processes in contaminated aquifers (17). Regarding 2, hydrocarbons were more persistent over time in the low permeability layer due to the limited availability of electron acceptors for degradation. (17) This is because the majority of the degradation activity, which contributed the formation of significant amounts of by-products at downgradient locations, generally occurs in the high-K zones and not the low-k zones. (69a) However, even very slow rates of degradation in low-k zones can substantially impact aqueous concentrations in transmissive portions of plumes. (76)

Several lines of evidence can be used to assess whether biotic or abiotic degradation is occurring, but these are generally focused on aquifers, not aquitards. Contaminant transport in low-k zones is diffusion limited and relevant processes occur over small spatial scales, meaning that it is necessary to apply tools for these assessments at very fine spatial resolution. Since sampling of groundwater in low-k zones presents challenges and issues, methods should primarily focus on use of high quality sediment or rock cores collected across the aquifer-aquitard interfaces and into the low-k zones, with high-frequency sub-sampling of these cores on the order of 10s of centimeters or less. (76)

Examples of lines of evidence that can be used to support contaminant degradation in low-k zones include:

1. ***Distribution of parent compounds and degradation products.*** Patterns favoring low-k zone degradation include: i) higher ratios of degradation products occurring in low-k zones away from the aquitard-aquifer interface, especially relative to those observed in adjacent transmissive zones and ii) lower penetration of contaminants into low-k zones compared to expectations, based on diffusion and sorption processes without transformations. Note that obtaining a representative contaminant distribution requires high resolution sampling across interfaces and into low-k zones as well as appropriate extraction and analytical techniques to ensure that mass is accurately quantified.
2. ***Analytical data showing favorable geochemical and redox conditions.*** Conditions within the low-k zone should be conducive to the targeted degradation reaction. Positive indicators for biotransformations include:
   a. presence of electron donors, for example natural organic carbon, or electron acceptors, such as dissolved oxygen, nitrate, and sulfate, that can be used as redox indicators or serve as lines of evidence for microbial degradation;

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b. reduced mineral species, for example ferrous iron, that may promote abiotic reactions;

c. presence of metabolic by-products indicative of degradation, for example methane.

Note that establishing geochemical conditions within lower permeability zones can be challenging given that groundwater sampling is problematic in such zones.

3. ***Microbiological data supporting presence of appropriate microbial communities in the low-k zones.*** Typically, these efforts involve microbial characterization of core samples. Depth-specific subsamples can be analyzed to identify and quantify genetic signatures associated with various microbial species. The presence of these biomarkers within lower permeability zones is taken as a positive indicator of the potential for microbial activity and, hence, degradation of contaminants. Microcosm studies can also be used to provide supporting evidence of degradation in low-k zones, but these are likely to have restricted application due to the time and expense involved in completing them. Further drawbacks to microcosm studies are that they rarely reproduce the in situ conditions and heterogeneity of the sediments they contain, and the rates of degradation they produce are either too slow to measure in reasonable time frames or compare poorly to field rates.

4. ***Compound specific isotope analyses.*** Greater shifts in isotopic ratios are expected in lower permeability zones, or across interfaces, or both when degradation is occurring.

5. ***Contaminant distributions that match modeled distributions affected by simulated degradation.*** This can include 1-D modeling showing lower contaminant penetration observed in low-k zones than expected based on diffusion and sorption processes without transformations, or more detailed 2-D numerical modeling to compare observed and predicted contaminant distributions. (76)

Soil, Stratigraphy, Lithology

Soil sampling is typically undertaken during the initial stages of the site characterization process. Therefore, it does not suffer from the same inherent problem as groundwater sampling, where monitoring methods have been misapplied as characterization methods. In soil sampling, the primary investigative method—collecting material from the locations and intervals of interest—remains the same regardless of whether standard or high-resolution characterization principles are considered. The primary differences lie in the way these various methods are applied, particularly the scale and level of detail associated with the investigative approaches. Simply, soil sampling has traditionally not been used to generate sufficiently detailed data for the purposes of characterizing low-k zones. (76)

Soil sampling has frequently focused on the unsaturated zone during traditional site characterization. This is largely a function of the overreliance on groundwater monitoring wells as the primary method for measuring contaminants within saturated zones. Under this conceptual model, soils are collected from the vadose zone to identify contaminant sources and potential migration routes, but the investigation is often not extended to the underlying aquifer. Cleanup objectives for a site may be based solely on concentrations from groundwater

wells, such that there is little interest from regulators or stakeholders in collecting soil data from this zone. There is also the general perception that soil coring and analysis within the saturated zone is technically challenging, and that collecting groundwater data provides a more comfortable route for everyone involved. (76)

Characterization often focuses on soil classifications based on visual inspection that may not be representative of the true lithology. A geologic log generated without the use of information from supporting physical property analyses or stratigraphic logging methods may miss subtle changes. Similarly, soil analyses may include contaminant concentrations, but ignore parameters such as the organic carbon fraction which greatly influence transport of these contaminants. (76)

Even one thin clay bed, less than 0.2m thick, can cause plume persistence due to back diffusion for several years or even decades after the flux from the source is completely isolated. Thin clay beds, which have a large storage capacity for dissolved and sorbed contaminant mass, are common in many types of sandy aquifers. However, without careful inspection of continuous cores and sampling, such thin clay beds, and their potential for causing long-term back-diffusion effects, can easily go unnoticed during site characterization. (71, 76)

The problem is further compounded at sites where lower K zones make up a significant portion of the soil matrix. There is little reason to expect that low-k soils will be adequately characterized if groundwater monitoring data is the primary method used to investigate the saturated zone. (76)

Collectively, conventional approaches for collecting and analyzing soil samples represent a missed opportunity for characterizing sites, particularly for those with low-k zones. (76)

Groundwater

Groundwater wells provide no stratigraphic information unless cores were logged and sampled when the well was installed. In some cases, groundwater is sampled blindly, with only limited knowledge of the specific intervals that may be contributing most to the measured concentration. It is a much different situation than soil sampling, where the contaminant concentration can be tied directly to the soil type sampled. (76)

Groundwater monitoring wells are the most widely-used tool for environmental site investigations, but their role—particularly as part of the site characterization process—is often out of proportion to the information that they provide. This is related to two factors: 1) wells are constructed with little attention to identifying and characterizing small-scale heterogeneities; and 2) sampling groundwater, in the absence of soil sampling, provides an incomplete picture of contaminant concentrations and the influence of hydrostratigraphy on contaminant distribution. Because of these limitations, wells are more appropriately categorized as a monitoring tool, not a characterization tool. (76)

The primary problem is that conventional long-screened monitoring wells do not provide depth-discrete information, and thus do not provide information at a scale that is relevant to understanding important fate and transport processes at a site. As noted above, the concentration obtained from these monitoring wells is a flow-weighted average that preferentially draws from the most transmissive zones within the screened interval. If those transmissive zones are lower in concentration than adjacent finer-grained soils, then the well will not identify the peaks or the overall distribution. (76)

Conventional monitoring wells typically have a long screen of 10-feet or longer, and this is particularly poorly-suited for low-k zone investigations. Even if the screen covers the lower permeability interval of interest, groundwater will be sampled from soil layers that represent a distribution of hydraulic conductivities, and the most transmissive layers will be over-represented in the measured groundwater concentration. While this can be useful in water supply evaluations because it mimics the concentration that would be measured within a water supply well, which necessarily uses longer screens to maximize yield, it is problematic at late stage sites where the more transmissive zones, due to extended advective flushing, might be cleaner than the less transmissive zones where inward diffusion may have led to significant mass storage. (76) Further, the historical consequence of this practice within the environmental field is that groundwater data from monitoring wells end up being used not only to satisfy the needs of the regulatory community, but also became the primary means to characterize a site. This failure to appreciate the differences between characterization and monitoring can hinder the development of an appropriate conceptual site model. (76)

Collectively, these factors mean that it is very difficult to characterize groundwater with long-screened monitoring wells unless there is basically negligible heterogeneity at a site—a condition that may not actually exist in nature. More effective groundwater characterization should focus on shorter screens installed at multiple levels that provide depth-discrete data for evaluating contaminant distribution. However, even if properly constructed, groundwater wells still have significant limitations as a primary site characterization tool. Specifically, they provide information on aqueous phase concentration but do not address contaminant mass present in other aquifer compartments. This includes sorbed-phase, non-aqueous phase, and vapor-phase mass, none of which can be quantified via groundwater well sampling. The contaminant mass present in these compartments can be considerable at many sites, and their persistence may be a major contributor to the time required to achieve cleanup objectives. (76)

Contaminant Plumes

The key concerns with contaminants in low permeability zones are their potential to sustain plumes for extended periods of time and their constraining effects on the benefits of technologies that solely address contaminants in transmissive zones. (75) Matrix diffusion from one or a few thin clayey beds in a sand aquifer could result in persistent plume concentrations above drinking water standards long after isolation or removal of the original NAPL source zone. (04)

Flushing out the plume, that is, pump-and-treat, is a slow, inefficient process when there are contaminants in the low permeability compartment. Over the past decade the effects of source control measures, that is, depletion or containment, on plumes has been the focus of rigorous debate and research. It is now clear that source treatment will reduce the ultimate total mass in downgradient plumes, and will likely result in reduced plume extent or longevity, or both. However, in most instances it is likely that contaminants will remain and persist for extended periods, leading to a sense that no action will get a site to closure. Reconciling these perspectives is critical to moving forward in risk management and site remediation. A pragmatic approach is to strike a balance between what can be done and living with the inevitable imperfections that remain. (75)

Characterizing a contaminant plume based on contaminant mass flux or mass discharge is a potentially useful approach that places concentration data in context with groundwater flow within the region being characterized. Mass discharge in units of mass per time represents the total contaminant mass transported across a plane located transverse to groundwater flow, meaning that in the simplest terms, it can be calculated by multiplying the Darcy velocity by the concentration. However, a heterogeneous aquifer contains soil layers with permeabilities that may span several orders of magnitude, resulting in concentration of the groundwater flow within the highest permeability channels. Therefore, all distinguishable zones should be included in the calculation to reduce uncertainty in mass discharge estimates. This is accomplished by high-resolution, multi-level groundwater sampling across a transect, combining the measured concentration with a known or estimated Darcy velocity for each of the sampled depths. Sampling across multiple transects in the direction of groundwater flow can help document attenuation processes and rates within the system, such as contaminant mass degraded or stored in lower permeability units. (76)

While there are multiple methods for estimating mass discharge, collecting data across a transect is an effective tool for quantifying source strength, investigating plume boundaries, and documenting remediation performance because it is consistent with our current understanding of contaminant transport in heterogeneous porous media. Specifically, most plumes are characterized by laminar groundwater flow within preferential flow channels represented by mobile porosity and do not expand significantly in the transverse direction. This allows plumes to maintain a high concentration core structure that can decrease significantly when moving relatively short distances in the transverse and vertical directions. Because of this, it is possible to miss the plume core if high-resolution transects are not included in the investigation. (76)

As plumes advance, dissolved phase solvents are lost through sorption, diffusion into low permeability layers, and degradation. (75) Small-scale permeability contrasts are increasingly understood to play a significant role in the evolution of source zones and contaminant plumes. (69a) As a rule of thumb, if a plume within a transmissive zone is in contact with an adjacent zone or zones that have permeabilities that are lower than a factor of 100 or more, then matrix diffusion can be an important process. For example, if a contaminant plume moving in a 10^{-3} cm/sec sand is in contact with a 10^{-5} cm/sec silt, then the silt can be

charged up with contaminants during a loading period when concentrations in the sand are higher than the silt and then slowly discharge contaminants into the sand via diffusion when the silt has higher concentrations than the sand. (34)

Understanding the effects of back diffusion of groundwater contaminants from low permeability zones to aquifers is critical to making site management decisions related to remedial actions. (95)

The lack of information provided by conventional monitoring wells can contribute to a false confidence that conditions at the site are well understood. Or, even worse, a sense of large dilute plumes where, in fact, contaminants occur in tight plume cores (76).

LNAPL

Assessing the potential for removal or containment of free product may be the first priority at NAPL-contaminated sites, followed by assessment of the extent of residual NAPL contamination. Typically, for LNAPLs most residual contamination is located in the vadose zone, but it may also extend to the depth of the seasonal low water table. Pumping to remove free LNAPL product, which lowers the water table, can cause residual NAPL to move deeper into the saturated zone. Consequently, when removing free-product LNAPL that is floating on the water table, take steps to avoid or minimize movement of residual NAPL deeper into the saturated zone. Evaluation of the relative importance of the degree of heterogeneity in hydraulic conductivity and mass transfer processes reveals that the rate of mass transfer and the extent to which contaminants are sorbed on aquifer solids are the most important parameters that affect predicted cleanup time. (27) In addition, some LNAPL components may persist for a long period of time, making it difficult to understand whether the hydrocarbon plume is being sourced by matrix diffusion or from the persistent LNAPL phase. (34)

Characterization of hydrocarbon-impacted soils and groundwater remains one of the most challenging problems when dealing with the restoration of contaminated sites, especially on industrial waste lands. Typical characterization includes determining the magnitude and extent of the spill, hydrological characteristics of the release, and the potential pathways the release could follow. The task of delineating and quantifying the amount of NAPL present in soils and groundwater has presented significant challenges to engineers and scientists involved in soil and groundwater remediation. (40)

Two traditional detection and monitoring strategies are primarily used for site characterization. The first strategy is to use point sampling with monitoring wells or multilevel piezometers, from which soil and groundwater samples are collected and analyzed. (40, 18) The second strategy involves making indirect subsurface measurements using surface or borehole geophysical techniques (40). Detailed evaluation of the vertical distributions at individual locations of LNAPL, and soil properties throughout the vertical soil profile with LNAPL impact, is critical to understand the LNAPL conceptual site model. Useful stratigraphic and LNAPL impact

assessment tools that are available and commonly used to provide detailed vertical distribution data that include (55):

1. continuous soil core sampling in conjunction with visual observation and organic vapor meter readings during well installation;
2. continuous cone penetrometer testing;
3. laser-induced fluorescence; and
4. fluid gauging data approximating equilibrium conditions.

Additional tools that are available but less common include soil core photography under visible and ultraviolet light, natural gamma ray logging, and soil core and total petroleum hydrocarbon analysis for determination of LNAPL saturation. The use of LNAPL baildown testing can also be used as a method for evaluating the distribution of mobile LNAPL in the formation. (55)

Rigid-matrix multiphase theory typically assumes that the intrinsic permeability of a soil is independent of the fluid type. This assumption allows the estimation of the potential transport and recovery of various petroleum products and dense or light oils in the presence of water and vapor (06). However, little research has been done to evaluate the applicability of theories developed for LNAPL behavior in coarse-grained porous media to describing LNAPL behavior in fine-grained soil.[7] (02) If certain soils exhibit different permeability characteristics to oil versus water, as has been observed in many settings, then certain fundamental assumptions about plume movement and recovery in fine-grained media need to be re-evaluated. (06)

Contaminant plumes are inextricably linked to their sources. Given this linkage it follows that decisions regarding management of plumes are likely to involve decisions regarding management of sources. A common perception has been that removing the source will result in removing the plume after several years of flushing similar to a smoke plume disappearing once the source of the smoke is extinguished (75). Many remediation strategies endeavor to remove subsurface NAPL in order to reduce NAPL mass flux, contaminant plume concentrations, and plume longevity. However, subsurface heterogeneity and complex NAPL distributions make complete NAPL removal challenging (31). Unfortunately, experience has made it clear that the relationship between sources and plumes is much more complicated, and that plumes can persist at lower concentrations long after their sources are depleted or contained. The degree to which plumes can persist is governed by site-specific attributes, for example, geologic setting, hydrology, contaminant properties, biogeochemistry, and release volume, and the fact that contaminant plumes and subsurface geochemical conditions more generally evolve with time. (75)

Where leaking underground storage tank sites are considered to have met regulatory standards and are, therefore closed, the residual NAPL can continue to release benzene and

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[7] API Soil & Groundwater Research Bulletin (September 1996) summarizes a series of 10 papers on the topic of LNAPL in low permeability soils. (90)

less mobile hydrocarbons, such as naphthalene, into groundwater. (31) Commonly, when hydrocarbons reach the water table, the fluid head gradients cause LNAPLs to spread laterally on top of the water table, but LNAPL may also migrate below the water table, creating a smear zone. As far as electrical properties, NAPLs are generally highly resistive fluids. Hydrological studies have shown LNAPLs do not dissipate uniformly in a homogeneous manner; they move through the unsaturated zone in discontinuous accumulations creating NAPL blobs or pools (40). When two poorly miscible fluids such as water and oil are present within a clay rock, the high capillary pressure at narrow pore throats can shut down the mobility of the non-wetting phase, that is, NAPL. (13)

Some common observations of petroleum hydrocarbon behavior in low-k settings include (06):

- Many petroleum releases in fine-grained materials exhibit more extensive distribution of NAPL than would otherwise be anticipated based on the theoretically small effective hydraulic conductivity.
- The non-polar nature of petroleum hydrocarbons as compared to the polar nature of water is the root cause for observations of higher oil permeability in fine-grained and clayey soils.
- Petroleum products can travel much faster in clayey soils during the spreading stages of a release than would be anticipated by theory. This would be particularly true in unsaturated clayey soils. Homogeneous saturated expansive clays would still be expected to hold water tightly and have a high entry pressure toward oil, thereby limiting oil movement in these specific materials. But in heterogeneous soils…this higher permeability toward oil is observed even in the saturated zone.

Impact Of Ethanol-Blended Gasoline On Soil Permeability

Clay soils have low hydraulic conductivities in the presence of high polarity pore fluids, such as water. Low polarity fluids, including hydrocarbon fuels and halogenated organic solvents, typically cannot migrate into clay pores because they cannot displace water. Oxygenated additives in gasoline, such as alcohols and methyl-tert-butyl ether (MTBE), have been used to control air pollution emissions. These relatively polar and water-soluble compounds may facilitate displacement of pore water and enhance migration of fuels and solvents through clay-rich soil strata. (83)

Some research suggests that alcohol added to hydrocarbon fuels can enhance their migration through clays. Gasoline did not migrate into water saturated clay, even after 14 days under pressure, but the gasohol mixture migrated readily into the clay in only 20 minutes. Increased hydraulic conductivity of the clay in the presence of gasohol is hypothesized to be due to the collapse of the clay's pores thereby creating larger pores. Increasing pore diameter decreases the capillary pressure needed for the alcohol-blended fuel to replace water and allows alcohol-blended fuel to migrate through the clay. (83)

High Resolution Site Characterization (HRSC)

A relatively new approach in site characterization that relies on detailed mapping of contamination in both transmissive and non-transmissive zones at a very fine scale, is referred to as high resolution site characterization (HRSC). This strategy, and the technologies that make it possible, derive from understanding that heterogeneity and anisotropy are the controlling features in contaminant transport and remediation. (39) The effectiveness of soil, groundwater, and tracer based characterization methods may be site and technology specific. Employing multiple methods can improve characterization. (61)

In the case of highly heterogenous sites, HRSC tools can be used to refine the CSM and better understand the LNAPL distribution and the variability in the soil and bedrock structure. Tools that are useful to understand highly heterogeneous sites include the use of cone penetrometer testing or hydraulic profiling tools to understand the lithology (41, 67). When used along with laser induced florescence or membrane interface probe (MIP)[8], these technologies will aid in understanding the variability of the LNAPL source term and how to best apply the remedial approach. (67) The only limitation with using these methods in very fine-grained sediments is that depths of tool penetration may be considerably less than those currently achievable in sand and silt deposits. (41)

Collecting high-resolution characterization data to identify contaminant and stratigraphic heterogeneity can provide a more realistic understanding of how contaminated sites will respond to remediation efforts. This information is critical in developing a more accurate CSM to inform remedial decisions. This is particularly important at sites where a significant portion of contaminant mass is present in lower permeability zones because treatment of these zones can be difficult using conventional technologies. (03)

For highly-heterogeneous sites, an improved understanding of the LNAPL distribution can increase the likelihood of remedy success. A summary of the various tools available to characterize unconsolidated media is provided in Interstate Technology Regulatory Council (ITRC) (2009) and Contaminated Land: Applications in Real Environments (CLAIRE) (2014). (67) Examples of the use of direct push technologies for site characterization are provided in (78a) and (78b), which both used electrical conductivity logging for high resolution hydrostratigraphic characterization. Reference 78b provides an example for an MTBE plume. Reference 100 provides a recent review of a variety of direct push technologies.

Triad

The U.S. EPA developed a framework for a dynamic and adaptive site investigation and characterization process called Triad. It includes several features that U.S. EPA identified as necessary for successful investigation and remediation programs. Among the potential benefits of this approach are a reduction in the level of data uncertainty, more successful remedial

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[8] For additional information on MIP, see Appendix B.

outcomes, and lower life-cycle costs. ITRC published technical and regulatory guidance for the Triad process (2003), along with a framework for implementing the approach at a site (2007). While these documents do not explicitly address sites with significant low-k zones, the approach is wholly consistent with recommended methods for these zones because they typically use high-resolution stratigraphic data generated in near real-time. (76)

Key features of the Triad approach as documented in ITRC's (2007) TechReg, are:

1. Systematic planning. Develop a conceptual site model and determine any data gaps in this model that need to be addressed. Identify all key personnel and stakeholders to ensure that they are involved in a well-defined decision-making framework throughout the project lifetime.
2. Real-time measurements. Employ techniques that generate data that permit real-time and near real time decision-making.
3. Dynamic work strategies. Use on-going data collection efforts as an opportunity to update the conceptual site model.

Recommendations For Site Characterization (From Reference #76)

Unfortunately, the path to embracing the importance of contaminants in low-k zones is not simple. First it requires rethinking our conceptualization of contaminant transport in heterogeneous porous media. This includes:

- Recognizing that the long-standing principle of homogeneous-isotropic aquifers employed in groundwater supply hydraulics are inappropriate for contaminant transport;
- Embracing diffusion and slow advection as fundamental governing processes at contaminated sites;
- Abandoning dispersion as a basis for accounting for local heterogeneities in aquifers and as an explanation for dilute concentrations in wells;
- Recognizing that sorption and reactions in low-k zones are critical fate and transport processes;
- Developing dynamic site conceptual models that evolve with time, for example, the problem begins with nonaqueous phase liquids and ends with contaminants in low-k zones; and
- Employing contaminant transport models that can address governing processes that occur at a small scale, such as centimeters to millimeters, over large domains, such as kilometers. (76)

Secondly, we need to recognize the limitations of long screen monitoring wells for site characterization. Conventional monitoring wells leave us largely ignorant of contaminant in nonaqueous, sorbed phases in transmissive zones and are blind with respect to all contaminant phases in low-k zones. Herein lies a root of our frequent lack of success with remediation; far

too often we only see the tip of the iceberg through the lens of a conventional groundwater monitoring network based on long-screened wells, while the bulk of the problem remains unseen. Reflecting the limitation of conventional wells for site characterization, newer second generation, or 2G, site characterization tools that have been developed over the past three decades should be employed routinely. These include:

- Multiple level sampling systems;
- High resolution of subsamples from cores for total contaminant concentrations; The Membrane Interface Probe; and
- The Waterloo Advance Profiling System[TM]. (76)

However, these tools are not themselves without limitations and, consequently, they should be employed in combinations with the anticipation that collectively they will provide the data needed to build accurate, comprehensive CSMs and facilitate the design and performance monitoring of effective, efficient site remediation technologies. Though critics may perceive this approach as being impractical or costly, the counter argument is that proceeding with remedies based on flawed understanding of the problem is even more impractical and wasteful. (76)

REMEDIATION TECHNOLOGIES

Engineered and natural remediation processes in heterogeneous environments may preferentially remove contaminants from the most transmissive subsurface zones due to the reliance on advective flow to deliver reactants and remove contaminants partitioned to mobile groundwater and vapor phases. As a result, residuals may remain in lower permeability layers following treatment, with these serving as decades long persistent sources of groundwater impacts, especially if nonaqueous phase liquid is present. (12)

Removal of contaminants is hindered in soils with low hydraulic conductivity (10^{-5} cm/s or less) due to two main factors. The first factor is that pathways to remove the contaminants are not as abundant as in permeable soils. Since most in situ technologies require sufficient pathways for contaminant remediation, this poses a problem. The second factor is that the primary transport processes are governed by diffusion. Diffusive transport times are much greater than for advective flow. (49)

Several treatment processes are typically used to remove volatile organic compounds (VOCs) from the subsurface. These technologies, which require some permeability to effectively access the contaminated zone, include:

- Soil vapor extraction;
- Free-product recovery;
- Soil flushing;
- Steam stripping;
- Air sparging; and

- Pump and treat methods in saturated soils.

These technologies are most appropriate in permeable media. In low permeability media, competing technology includes the baseline of excavation and ex-situ treatment or containment. (19)

Resolving whether source remediation would be effective for a given site requires a determination of its relative costs and benefits.[9] The key set of questions to address in determining cost-benefit are: 1) what degree of source reduction is expected to be accomplished with the selected remedial technology for the given site conditions, that is, mass removal; 2) what impact would this level of mass reduction have on the amount of contaminant emanating from the source zone, that is, contaminant mass discharge; and 3) would this reduction in mass discharge result in a significant reduction in risk, or remedial costs, that is, plume response, or both. (09)

An argument for source-zone remediation, even when only partial source reduction is expected, is that the reduction in source-zone mass will result in reduced mass discharge to the plume over the long term, thus reducing the time-scale required for pump and treat. Another argument for implementing source-zone remediation involves the concept of integrated remedial strategies wherein aggressive source-zone remediation is combined with low-cost methods for managing the contaminant plume. A prime example of this approach is combining source-zone treatment with monitored natural attenuation. If the mass discharge of contaminant from the source zone is too large, the attenuation capacity of the system will be exceeded and the contaminant plume will not be contained. However, implementing source reduction may reduce the mass discharge such that the attenuation processes can affect plume containment. In either case, it is hypothesized that implementing source-zone remediation will ultimately result in accelerated site closure and reduced long-term site management costs. (09)

Injection And Extraction

It is often difficult to accurately assess the performance of injection and extraction systems for remediating soils and groundwater. This is due in part to the complexity and heterogeneous nature that exist in the subsurface at each site. (26)

Pump And Treat. Fine-grained sediments contaminated with organic solvents are pollution sources, slowly diffusing dissolved contaminants into adjacent high permeability zones, leading to groundwater contamination. Since hydraulic pumping in a heterogeneous matrix draws water primarily through the coarse grained zones, circumventing finer grained zones with higher contamination, mechanical pump and treat technology is not effective in the cleanup of clayey, fine grained zones. (14)

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[9] Note: Compliance with applicable laws and regulations is also a necessary consideration.

The U.S. EPA presented many of the concepts related to forward and backward diffusion in an October 1989 review of pump and treat systems that found that pump and treat cleanups were going slower than expected. (39) The primary effect of pump and treat is to deplete aqueous phase solvents in transmissive zones. A secondary effect is the slow release of solvents stored in other impacted compartments, for example, dissolved and sorbed contaminants in low permeability zones. Unfortunately, slow release of solvents from compartments that are not directly addressed can create a need to extract groundwater from source zones for decades or even centuries. (75)

Studies consistently show that contaminant concentrations are generally higher within the laterally extensive lower permeability units compared to the more permeable units, suggesting that pump and treat is ineffective at flushing the lower permeability units. Assessment of the historic integrated plume-scale contaminant mass discharge, along with the results of mathematical modeling, indicated that the plume would persist for many decades even with the isolation or removal of the source zones, primarily due to back diffusion of contaminant associated with the lower permeability units. (09)

During a pump and treat operation, dissolved contaminant concentrations in the relatively permeable zones are reduced by advective flushing, causing a reversal in the initial concentration gradient and slow diffusion of contaminants from the low to high permeability media. The significance of matrix diffusion increases as the length of time between contamination and cleanup increases. In heterogeneous aquifers, matrix diffusion contributions to tailing and rebound can be expected, as long as contaminants have been diffusing into less permeable materials. (27)

The number of pore volumes of contaminated water to be removed during a remediation depends on the sorptive tendencies of the contaminant. The number of pore volumes to be removed also depends on whether groundwater flow velocities during remediation are too rapid to allow contaminant levels to build up to equilibrium concentrations locally. (52) Hence, continuous operation of pump and treat remediations may result in steady releases of contaminants at substantially less than their chemical equilibrium levels. With less contamination being removed per volume of water brought into contact with the affected sediments, it is clear that large volumes of mildly contaminated water are recovered, where small volumes of highly contaminated water would otherwise be recovered. (52)

A promising innovation in pump and treat remediations is pulsed pumping. Pulsed operation of hydraulic systems is the cycling of extraction or injection wells on and off in active and resting phases. The resting phase of a pulsed pumping operation can allow sufficient time for contaminants to diffuse out of low permeability zones and into adjacent high permeability zones, until maximum concentrations are achieved in the higher permeability zones. (52)

During the resting phase of pulsed pumping cycles, peripheral gradient control may be needed to ensure adequate hydrodynamic control of the plume. In an ideal situation,

peripheral gradient control is unnecessary. Such might be the case where there are no active wells, major streams, or other significant hydraulic stresses nearby to influence the contaminant plume while the remedial action wellfield is in the resting phase. (52)

When significant hydraulic stresses are nearby, however, plume movement during the resting phase may be unacceptable. Irrigation or water supply pumpage, for example, might cause plume movement on the order of several tens of feet per day. It might then be impossible to recover the lost portion of the plume when the active phase of the pulsed pumping cycle commences. In such cases, peripheral gradient control during the resting phase is essential. (52)

Determining realistic objectives for a pump and treat system requires sufficient site characterization to define the complexity of the hydrogeologic setting and the subsurface distribution of contaminants. Such information makes it possible for the system operator to assess whether conditions at the site will result in tailing and rebound and to evaluate the extent to which these conditions are likely to increase the time needed to attain health based cleanup standards. The sorption characteristics of contaminants can be assessed using batch sorption tests with aquifer materials, although aquifer heterogeneity increases the difficulty of interpreting test results. For organics, the potential effects of sorption can be assessed based on a literature review of contaminant properties and on site specific data on organic carbon in aquifer materials. Geochemical computer codes can be used to assess the potential for tailing and rebound effects from precipitation-dissolution reactions. Evaluation of the relative importance of the degree of heterogeneity in hydraulic conductivity and mass transfer processes reveals that the rate of mass transfer and the extent to which contaminants are sorbed on aquifer solids are the most important parameters that affect predicted cleanup time. (27)

Soil Vapor Extraction And Air Sparging. Silt and clay sediments are not considered appropriate for air sparging (AS) and soil vapor extraction (SVE). The low permeability characteristics of clayey soil inhibit air flow through the subsurface, thus lowering contaminant removal efficiencies by reducing mass exchange rates of volatile contaminants to the vapor phase. Air flow patterns are affected by hydraulic conductivity, soil permeability, and soil structure with less permeable sediments causing the formation of distinct air flow channels up to the unsaturated zone and producing poor air distribution. Silty and clayey sediments generally require higher air injection pressures to achieve air flow through the saturated zone. Excessive pressure can result in destruction of the soil formation and promote soil fracturing which reduces AS and SVE effectiveness. (54)

Generally, soil hydraulic conductivity should be greater than 10^{-3} cm s^{-1} for effective use of AS and SVE. Thus, the term low permeability generally refers to sediments with hydraulic conductivities less than 10^{-3} cm s^{-1}. Numerous studies have suggested that AS and SVE efficiency may be reduced in low permeability sediments. (54)

Pulsed operation of AS and SVE was more effective than continuous AS and SVE in this short term study and suggested that pulsed operation may optimize mass removal while reducing the electrical cost of operation. (54)

Vacuum data tend to present a picture of the flow field that is much more uniform than is generally the case. Thin layers of lower or higher permeability can have profound effects on flow patterns, and these effects may not be reflected in the vacuum data. At many sites, there is more flow from the surface than is commonly assumed, and at many sites there is less flow near the water table than is commonly assumed. As a consequence, at many sites the time required for soil cleanup using soil vapor extraction and bioventing is much longer than predicted, based on simple calculations or analytical models. (26)

Soil venting efficiency becomes limited by diffusion of the contaminant vapors from the low permeability zone to the air flowing in the high permeability zone. (43) The reason for this can often be traced to nonuniform air flow due to soil characteristics, such as heterogeneity, high water content, and others. (26)

Due to the heterogeneous nature of the porous matrix over a broad range of pore sizes, from 1 nm to 1 mm, the rate of intrinsic biodegradation within the matrix is limited. The main pollutant removal mechanism was the ventilation in which most volatile hydrocarbons vaporized and diffused toward the gas phase that was flowing along the preferential flow pathways. Hydraulic fractures facilitated and accelerated the pollutant remediation rate by enhancing the interconnectivity of the porous matrix with natural fracture systems or any other type of natural preferential flow pathway. (86)

When trapped NAPL exists in low permeability zones, decreasing the water content can markedly improve the overall mass removal rate due to enhanced gas flow, faster mass transfer, and conversion of trapped to free NAPL. Possible strategies to reduce water saturation in low permeability zones include thermal venting, high gas flow rate injection and extraction coupled with dry air, surface capping to prevent water infiltration, and water table lowering in the capillary fringe. (96)

Some vendors of soil venting services have begun to inject heated air, or heat enhanced soil ventinq, to accelerate the process and extend treatment to less volatile or semivolatile organics. The cost of energy to heat the soils is moderately high, depending of course on the targeted temperature. (64)

Soil Flushing And Surfactants. Diffusion limitations are primarily the result of diffusion-dominated contaminant transport that is characteristic of low-permeability soils. Low permeability clays with hydraulic conductivities on the order of 10^{-4} cm/s may significantly increase the time for solutes to permeate through the contaminated zone.(63)

Recent studies have elucidated the importance of even small scale heterogeneities on remediation effectiveness, and thus fomented the recent flurry of research on enhanced-

delivery methods. A particularly important hypothesis that was developed based on these studies was that most removal occurs in high hydraulic conductivity zones, which is where most of the contaminant resides, yet complete removal, and thus long term site cleanup, is limited by contaminant mass stored in low hydraulic conductivity zones or isolated in hydraulically inaccessible regions (*i.e.*, flow field specific). It was demonstrated that even in the relatively homogeneous systems, significant contaminant mass may be hydraulically inaccessible likely due to small variations in flow through the heterogeneous subsurface. Push-pull remediation schemes implemented in heterogeneous zones may be helpful to overcome the influence of heterogeneities.(61)

In massive clays, where contaminants have diffused into clay blocks, surfactant flushing would be ineffective unless the permeability was increased.(49) For remediation processes such as in situ bioremediation, delivery of remediation amendments using traditional injection approaches distributes amendments primarily to higher-permeability zones. Back diffusion of contaminants from low-k zones has been reported to inhibit the success of site remediation as reported in pump-and-treat systems, surfactant-enhanced aquifer remediation, and injection of amendments for bioremediation. In particular, bioremediation is a promising source zone treatment technique, but like many technologies, it is most effective at treating the mass present in transmissive zones.(04)

As extensively discussed earlier in this report, low-k zones can serve as a long-term secondary source of contamination because transport may be diffusion controlled, yet they are difficult to target using standard injection-based treatment approaches.(04)

One method commonly employed to enhance recovery of contaminants from the subsurface is through the introduction of surfactants, which lower the surface tension of the contaminants so that they become more soluble and thus more mobile. A major concern with the use of surfactant flushing to mobilize nonaqueous phase liquids in aquifers is specific mineral-surfactant interactions that may effect significant permeability changes in the soil formation—specifically permeability reduction. (36) Fixed-gradient step tests are an appropriate methodology to assess the global effect of surfactant-LNAPL-soil groundwater interactions and that such tests should be used routinely during the selection process of surfactant solution formulations.(73)

Another method is to use a shear-thinning fluid to distribute a bioremediation amendment, for example lactate[10] around an injection well such that the solution is able to better penetrate and deliver the amendments to both high and low-permeability zones. The shear-thinning nature of the solution allows it to flow more readily and cross-flow from high to low-permeability zones is promoted. It is anticipated that permeability contrasts of 1-2 orders of magnitude are amenable to this technology, for example improving distribution to silt layers within a sand matrix, but not clay layers.(04)

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[10][NOTE: Lactate would be used for anaerobic biodegradation of chlorinated compounds such asTCE through reductive dechlorination.]

Shear-thinning fluids are typically water-soluble organic polymers, such as xanthan gum. Due to their solubility, they are ideally suited for subsurface remediation applications where injections of water-based amendment solutions are frequently used. For the enhanced amendment delivery process, the shear-thinning behavior causes a more significant viscosity reduction to the fluid flowing through the lower-k zones relative to the viscosity reduction of the fluid flowing in higher permeable zones. Therefore, the preferential flow through the more permeable zones is significantly reduced while the flow into the lower-k zone is increased. In addition, mobility reduction behind the viscous injection fluid front in a higher-k layer creates a transverse pressure gradient that drives cross-flow of viscous fluids into adjacent less permeable layers. These mechanisms result in an improvement in the sweep efficiency within a heterogeneous system and lessen by-passing of low-k zones.(04)

The proposed use of shear-thinning fluids as a delivery technique in bioremediation applications represents a further advancement in promoting efficient treatment of low-k zones. The delivery technique addresses limitations due to diffusion process in low-k zones and advective processes within high-permeability, or high-k, zones. The technology is expected to deliver bioremediation amendments to low-k zones for which treatment is typically limited by matrix diffusion effects when standard amendment delivery processes are used. In addition, the enhanced amendment delivery can reduce overall treatment cost by decreasing treatment time, promoting efficient bioremediation through the temporary exclusion of competing electron acceptors, and potentially serving as a long term carbon source.(04)

When using an activation strategy, it is desirable that the activation occur only in the target treatment zone; otherwise, significant oxidant and activator loss can occur elsewhere. For diffusive oxidant delivery to lower permeability layers, one should consider employing sequential rather than co-delivery of oxidant and activator to the higher permeability layer.(12)

An innovative technique—electrokinetically enhanced in situ flushing—has the potential to increase soil–solution–contaminant interaction and PAH removal efficiency for low permeability soils; however, the electrolysis reaction at the anode may adversely affect the remediation of low acid buffering capacity soils, such as kaolin. Therefore, to improve the remediation of low acid buffering soils the pH at the anode is carefully controlled to counteract the electrolysis reaction...Controlling the pH was beneficial for increasing contaminant solubilization and migration from the soil region adjacent to the anode, but the high contaminant concentrations that resulted in the middle or cathode soil regions indicates that subsequent changes in the soil or solution chemistry, or both, caused contaminant deposition and low overall contaminant removal efficiency.(74)

In Situ Chemical Oxidation. Typical petroleum compounds addressed with in situ chemical oxidation (ISCO) include benzene, toluene, ethyl benzene, xylenes (BTEX), methyl tertiary butyl ether, and sometimes polyaromatic hydrocarbons (PAHs). (16)

The development of a complete conceptual model is important to the success of all remedial technologies, although it is most critical with ISCO because this technology relies on a liquid or gas oxidant coming into direct contact with the contaminant in a short period of time on a periodic frequency (16).

- Soil samples must be collected to determine the horizontal and vertical location of remaining source and smear zone contamination, or residual LNAPL, and to determine other oxidant-consuming components.
- The ISCO-specific groundwater parameters of oxidation-reduction potential— alkalinity, ferrous iron, total dissolved solids, and major cations and anions—should be measured in addition to typical water quality parameters such as dissolved oxygen, pH, temperature and specific conductance. (16)

It is recommended that measurable mobile LNAPL, >0.01 feet thick, be absent within the treatment area during two years prior to ISCO application (16).

ISCO technologies that effectively destroy petroleum hydrocarbons include hydrogen peroxide; Fenton's solution, which is hydrogen peroxide with an iron catalyst; proprietary modified Fenton's solutions; sodium persulfate; ozone; or a combination of these oxidants. (16) Aerobic bioremediation can be enhanced by using Fenton oxidation as a soil pretreatment. (93) Persulfate oxidation can also be used for enhanced bioremediation (EBR). (80)

Considerations for use of these hydrogen peroxide-based solutions, that is, hydrogen peroxide and Fenton's reagent, include:

- Hydrogen peroxide and Fenton's reactions increase the dissolved oxygen concentrations of groundwater that will enhance biodegradation.
- The effective porosity may be reduced with the precipitation of Fe^{+3} in soil.
- Low pH can cause metals to be mobilized within the treatment zone.
- Reactions of strong peroxide solutions > 10% are exothermic, although if controlled, this heat can be used to enhance the desorption and dissolution of sorbed LNAPL.
- There is potential gas generation and volatilization of chemicals of concern (COCs).
- Carbonate ions, which are high alkalinity, exert a strong demand on hydroxyl radicals and acids.
- ISCO is a non-selective process, therefore the oxidant will readily oxidize natural organic matter (NOM) existing in soil along with the COCs, thereby consuming the oxidant and reducing the ratio of volume of COCs oxidized per volume of oxidant. (16)

Sodium persulfate is a more powerful oxidant than hydrogen peroxide, although the hydroxyl radicals generated during hydrogen peroxide are kinetically faster in destroying COCs. Because the persulfate anion is kinetically slower in oxidation than the hydroxyl radical, its

reaction with NOM is also much lower. Some design considerations for the use of sodium persulfate include:

- Because the persulfate reaction with COCs is kinetically slower than with hydroxyl radicals, further distribution of the oxidant is possible prior to decomposition.
- Sodium persulfate has the potential to lower the pH in groundwater, although many soils have the capacity to buffer this low pH.
- Persulfate has the ability to degrade soft metals, for example, copper or brass.
- The use of chelated iron may increase the longevity of iron in groundwater.
- Low pH can cause metals to be mobilized within the treatment zone.
- As with all ISCO applications, the presence of NOM reduces the ratio of volume of COCs oxidized per volume of oxidant. (16)

Despite its advantages, ISCO is inefficient in some situations due to geological heterogeneities, insufficient mixing, low oxidant persistence, and formation of troublesome by-products, for example, MnO_2. For example, oxidant delivery limitations have been shown to be responsible for a portion of the contaminant mass to persist following ISCO treatment, and the continuous slow mass transfer from this remaining residual mass leads to contaminant rebound and persistence of dilute plumes downgradient of source zones. In addition, ISCO is generally less cost effective for the treatment of contaminants present at low concentrations. Persulfate-enhanced bioremediation is a less expensive technology for treating lower concentrations of contaminants; however, EBR is often only partially successful in degrading complex organic mixtures. Factors such as the availability of substrates, electron acceptors, and nutrients as well as the site-specific nature of the active microbial communities often limit the effectiveness of EBR. At many sites neither of these two technologies can be applied individually to achieve remediation objectives in a cost- and time-effective fashion. (80)

Unlike permanganate, persulfate oxidizes aromatic hydrocarbons and other fuel-related compounds without activation. Compared to peroxide and ozone, persulfate is more stable and can persist in the subsurface for weeks to months due to its low natural oxidant interaction. These characteristics make persulfate an attractive choice for a chemical oxidant to treat petroleum hydrocarbon or PHC-impacted soils and groundwater. An additional advantage of using persulfate in a persulfate and EBR treatment system is the production of an excess amount of sulfate which results from persulfate decomposition or a reaction with organic compounds and aquifer materials. This excess sulfate can serve as a terminal electron acceptor and enhance subsequent microbial sulfate reduction processes. Therefore, a combined persulfate and EBR remedy is expected to link the aggressive nature of persulfate oxidation to enhanced microbial sulfate reduction. (80)

Another oxidant that can sometimes be used cost-effectively is ozone. Ozone (O_3), is a strong oxidant. It is an allotrope or structurally different, of oxygen and is more soluble than oxygen in water. Ozone is commonly injected into the vadose zone, sparged below the

groundwater table, or injected or re-injected as ozonated water, which is ozone dissolved in water prior to injection.

Ozone implementation design issues include:

- Ozone decomposition provides oxygen to the microbial community, although in high concentrations or long injection times, it can be a sterilizing agent.
- Groundwater with high carbonate concentrations can limit the effectiveness of ozone.
- There is potential gas generation and volatilization of COCs due to oxidation and sparging activities.
- Low pH caused by reactions can cause metals to be mobilized within the treatment zone.
- As with all ISCO applications, the presence of NOM reduces the ratio of volume of COCs oxidized per volume of oxidant. (16)

ISCO injections into soil with higher effective porosity usually yield greater transport rates and more uniform distribution—or radius of influence—of injected oxidants than in soil with low or variable effective porosity. (16)

If the treatment zone is highly permeable, a pressurized or gravity-feed method may be appropriate. Whereas, if the soil in this zone is less permeable, a pressurized delivery method may be necessary. The most effective delivery method will achieve the maximum return on investment while still achieving effective contaminant oxidation. (16)

Multi-Phase Vacuum Extraction. Multiphase vacuum extraction (MVE) is an efficient in situ remediation technology at light non-aqueous phase liquids impacted sites. In the water-saturated zone, the MVE recovery efficiency reaches a limit when the LNAPL saturation becomes close to the residual oil saturation, or S_{OR}, and discontinuous LNAPL droplets are trapped in the soil pores by capillary forces. Dewatering of the source zone coupled with LNAPL volatilization may increase LNAPL recovery, but this process is ineffective in the presence of heavier hydrocarbon products such as diesel. In such cases, the injection of aqueous-based chemical reagents in the saturated part of the source zone is potential MVE follow-up technology. In particular, low concentration, or < 1 percent on a weight basis (wt %) surfactant flushing could offer advantages over high concentration solutions used for micellar solubilization of 3 to 8 wt%, such as: cost savings on surfactants and other washing solution chemicals; elimination of the need for reuse and recycling of surfactants; and simpler above ground process effluent treatment. The technology could therefore be coupled with an existing MVE system and its process effluent treatment system. (73)

Steam Injection. In the unsaturated zone of a low permeability soil, the removal of LNAPL with steam injection is enhanced in areas dominated by high permeability preferential flow paths. The vaporization of semi-volatile and non-volatile compounds at temperatures

lower than 100°C steam distillation coupled with steam stripping are the dominant mechanisms of LNAPL remediation. (85)

Soil Fracturing. Soil fracturing is the process of creating fractures in otherwise competent, typically low permeability, geologic materials by hydraulic or pneumatic means; thus, hydraulic fracturing and pneumatic fracturing are the two primary technologies. These technologies are not themselves remediation technologies, but rather enabling technologies.

Fracturing improves the formation's porosity and thus improves the performance of other in situ technologies. If the permeability of the formation is increased, contaminant transport can be achieved by both diffusion and advection, which leads to a shorter time needed for contaminant removal. (49)

Used as an enabling technology, soil fracturing has been demonstrated for source removal and treatment of dissolved plumes at both DNAPL and BTEX or contamination at low permeability sites (19). Hydraulic fracturing combined with various treatment processes can be designed to treat a wide range of contaminants in both soil and groundwater. Treatment processes that have been demonstrated with hydraulic fracturing include (19):

- Steam or hot air flushing for mass transfer of VOCs, applicable for compounds with vapor pressures > 10 mm Hg, not suitable for recalcitrant non-volatile compounds;
- Zero-valent iron for reductive dechlorination, and may reduce NO_3 and some metals;
- Permanganate for oxidation of alkenes, aromatics, PAHs, phenols, pesticides, organic acids;
- Enhanced soil vapor extraction of VOCs;
- LNAPL recovery;
- Bioaugmentation by placement of porous granular material inoculated with selected microorganisms; and
- Horizontal Lasagna^{TM} (19)

Hydraulic fracturing can improve the performance of remediation methods such as vapor extraction, free-product recovery, soil flushing, steam stripping, bioremediation, bioventing, and air sparging in low permeability materials by enhancing formation permeability through the creation of fractures filled with high permeability materials, such as sand. Hydraulic fracturing can improve the performance of other remediation methods such as oxidation, reductive dechlorination, and bioaugmentation by enhancing delivery of reactive agents to the subsurface. (19)

The advantages of hydraulic fracturing over baseline approaches include:

- Improved accessibility to contaminants and delivery of reagents, such as steam and oxidant, by increasing subsurface permeability, for example, improved mass transfer rates.

- Limited site disruption minimizing adverse effects on surface features, for example, parking areas and buildings, as fewer wells can be installed. (19)

However, in situ technologies tend to reduce site disruption, are generally cheaper, require less handling, and limit potential exposure of workers or nearby residents to the chemical. Alternatives to hydraulic fracturing for low permeability material remediation include other access technologies such as:

- Pneumatic fracturing;
- Trenches;
- Vertical lances;
- Deep soil mixing;
- Vertical wells; and
- Horizontal wells, if some permeability exists. (19)

Location of utility lines or open boreholes may limit applicability. Fractures that encounter backfilled soil will tend to propagate along the wall of the excavation and fracture slurry will vent to the ground surface. (19) Fractures may not be suitable at sites with large, numerous, or delicate surface obstructions or subsurface interferences, such as utility lines. (19)

Fractures created to improve fluid delivery or recovery, for example, hot air injection or SVE applications, are most effective in low permeability material. (19)

Pneumatic fracturing is cheaper and easier than hydraulic; however, the fractures can close, which results in a need for additional fracturing. Hydraulic fracturing is more expensive and complex than pneumatic fracturing; after the process is completed dewatering may be necessary. However, the fractures are filled with sand, and are unlikely to reclose. (49)

Thermal Technologies

Thermal decontamination of soil is widely used in the remediation of hydrocarbon-contaminated soil. It has been proven to be an effective method for the soil remediation. The thermal decontamination of soil can be notably enhanced by increasing the temperature to desorb, mobilize and evaporate pollutants, to start chemical reactions forming nonhazardous products. It is well known that thermal decontamination of soil may offer many advantages, including greatest efficiency above 99 percent in a very short remediation time and a wide range of contaminants. (15)

Temperature and residual humidity profiles show that it is possible to reach the steam distillation point and to generate a vapor stream in a short time by the nonconventional heat transfer phenomenon. In situ traditional heating operations, such as electrical energy or steam injections require a longer process time, or intrusive equipment due to the physical properties

of the soil-water systems, or both. Indeed, conductive and convective heating phenomena are discouraged because of the low thermal coefficient, low electrical conductibility, and the complex operations to prevent short circuit or high-pressure drops of injected vapor fluxes in porous media such as soils. (01)

Unconventional thermal technologies show promise in low permeability soils. Thermal technologies increase in situ removal of volatile compounds by increasing the vapor pressure and evaporation rates. Increasing the temperature decreases interfacial tension between light non-aqueous phase liquids and water, increases water wettability, and increases desorption of contaminants. Once the contaminant is desorbed, pathways are needed for removal. Therefore, a combination of increasing the permeability and thermal techniques is necessary. The more standard techniques of steam, heated air, and hot water require sufficient flow paths for increased volatilization of aromatic hydrocarbons. However, unconventional heating technologies such as electrical resistance (ER) and radio frequency (RF) heating do not. Because ER and RF do not require flow paths, they are more applicable in low permeability soils. However, soil vapor extraction to remove vapors must have sufficient permeability. Extensive field tests and pilot tests need to be done before the combined use of unconventional heating technologies and SVE is applicable in the field (49). As of today, the use of unconventional thermal technologies has not been conclusively demonstrated to be economical at field-scale. (49, 91)

There is no universally appropriate thermal treatment technology. Rather, the appropriate choice depends on the contamination scenario, including the type of hydrocarbons present, and on site-specific considerations such as soil properties, water availability, and the heat sensitivity of contaminated soils. Overall, the convergence of treatment process engineering with soil science, ecosystem ecology, and plant biology research is essential to fill critical knowledge gaps and improve both the removal efficiency and sustainability of thermal technologies. (87)

In situ technologies for source zone depletion are generally limited in their ability to remove contaminant mass from these low permeability zones; however, thermal technologies may overcome this limitation at some sites. Conversely, it is likely that continued release of contaminants from these low permeability zones will be at mass discharge rates substantially lower than those prior to source depletion. Whether this reduction in source zone mass discharge will be sufficient to warrant implementation of a source depletion technology is not currently predictable and remains an important research topic. (84)

Electrical Resistance Heating. Electrical resistance heating (ERH) passes an electrical current through the soil and groundwater that requires treatment. Resistance to this flow of electrical current warms the soil and then boils a portion of the soil moisture into steam. This in situ steam generation occurs in fractured or porous rock and in all soil types, regardless of permeability. Electrical energy evaporates the target contaminant and provides steam as a carrier gas to sweep volatile organic compounds to vapor recovery (VR) wells. After the steam is

condensed and the extracted air is cooled to ambient conditions, the VOC vapors are treated using conventional methods, including granular activated carbon or oxidation. (07)

The ability of ERH to remediate soil and groundwater impacted by chlorinated solvents and petroleum hydrocarbons regardless of lithology is an advantage over conventional in situ technologies that are dependent on advective flow. These conventional technologies include: soil vapor recovery, air sparging, and pump-and-treat, or the delivery of fluids to the subsurface such as chemical oxidization and bioremediation. The technology is very tolerant of subsurface heterogeneities and actually performs as well in low permeability silts and clay as in higher permeability sands and gravels. ERH is often implemented around and under buildings and public access areas without upsetting normal business operations. ERH may also be combined with other treatment technologies to optimize and enhance their performance. (07)

Some advantages of ERH include:

- Areas containing underground utilities have been treated without adverse impacts.
- ERH has been implemented safely under operating facilities and in areas open to the public.
- ERH has been combined with multiphase extraction (MPE) for light nonaqueous phase liquid treatment. (07)

ERH has also been used to enhance fluid-recovery operations by mobilizing heavy hydrocarbons. Heating soil and groundwater makes heavy hydrocarbons less viscous and much easier to pump or vacuum-entrain from the subsurface. (07)

Soil that contains greater than 3 percent water, measured as weight percent, conducts electricity well and, therefore, ERH has no difficulty heating either vadose or saturated zones. The technology performs well in all lithologies—from tight clays to unconsolidated gravels—and is not affected by heterogeneous mixtures of soil types. ERH can heat fractured bedrock but cannot heat competent nonporous rock except through thermal conduction from nearby heated regions. The ability of ERH to preferentially heat silt and clay, and subsequently form steam within these soil types, releases contaminants from the soil matrix and drives them to VR or MPE wells. Through this mechanism, ERH is able to treat portions of the subsurface where advective flow cannot be established. This allows ERH to greatly enhance remediation technologies that are dependent upon advective flow such as soil vapor extraction and MPE. However, when contemplating applying ERH on dissolved-phase plumes, the costs per weight of contaminant treated become less attractive. (07)

Microwave Heating. Microwave heating (MW) is potentially a cost effective and time-efficient technology for remediating soil contaminated with volatile organic compounds and petroleum hydrocarbons. The contaminated soil can be remediated by microwave heating without disturbance or excavation. The remediation is permanent and there is minimal exposure of the public and personnel to the affected contamination site. (15)

The major driving force, which generated a great interest in MW technologies, is its greater ability than conventional thermal remediation to heat the soil rapidly. In fact, heating time is three orders of magnitude lower than with conventional heating. Other advantages that make in situ MW application desirable are (33):

- Homogeneous heating of the contaminated materials.
- Low energy consumption linked to short remediation times.
- High flexibility with possibility of instantaneously controlling the power-temperature response.
- Selective heating in the presence of polar contaminants.

However, despite these advantages, full-scale in situ MW application for decontaminating hydrocarbon-polluted soils is inhibited by a lack of information especially regarding the influence of time and distance of the MW irradiation, the electromagnetic and temperature variation in the soil, and their effects on contaminant removal. (33)

Many laboratory-scale studies strongly suggested that remediation of petroleum hydrocarbon contaminated soil by microwave heating is very effective; however, little definitive field data existed to support the laboratory-scale observations. (15, 33)

Prior to the study published in 2012, the in situ remediation of contaminant soil on-site by microwave energy has never been investigated. In this paper, the suitability of microwave heating for optimizing soil remediation is demonstrated at the field scale. (15)

Other Technologies

Electro-Acoustic Soil Decontamination. The electro-acoustic soil decontamination (ESD) process is based on the application of a direct current electric field and acoustic field in the presence of a conventional hydraulic gradient to contaminated soils to enhance the transport of liquid and metal ions through the soils. Electrodes with one or more anodes and a cathode and an acoustic source were placed in contaminated soils to apply an electric field and an acoustic field to the soil. (64)

Evaluation of the experimental results clearly indicated that application of the field forces reduced the heavy metals zinc and cadmium more than 90 percent in the treated cake. A maximum of 97.4 percent concentration reduction in cadmium was achieved, and 92.3 percent concentration reduction in zinc was obtained. Tests yielded 10-20 percent decane removal. The results on the decane contaminated soil were inconclusive as a result of the large discrepancy in the decane laboratory analysis. (64)

The process is expected to be most effective for clay-type soils having small pores or capillaries, in which hydraulic permeability is very slight. The dominant mechanism of the enhanced flow is electro-osmosis resulting from the electric field. In situ electro-osmosis was

first successfully applied to soils by L. Casagrande in the 1930s in Germany for dewatering and stabilizing soils. (03, 04, 64)

The most likely ESD application for treatment of organics is to enhance the recovery of non-aqueous phase liquids, such as solvents and fuel oils. Another possible application is to enhance recovery of more soluble polar organics. This application would be more like the metals treatment. ESD has the potential to reduce NAPL concentrations at or near saturation levels of approximately 5,000 -50,000 mg/kg to below saturation of approximately 100 - 1,000 mg/kg, but most probably not to low mg/kg or mg/kg levels. This study focuses on the potential for increased NAPL recovery. (64)

Under the federal underground tank regulations in CFR 280.64, the minimum remediation requirements are free product removal to the maximum extent practicable. Achievement of this level of remediation may be difficult using conventional pump-and-treat technology. ESD coupled with a conventional pump-and-treat technology has the potential to reduce relatively rapidly the residual NAPL concentrations to levels below those which would result in the free phase NAPL or free product layer. (64)

Compared to SVE, ESD is unlikely to achieve residual concentrations as low as those possible with soil venting for volatiles. (64)

Some vendors of soil venting services have begun to inject heated air, known as heat enhanced soil ventinq, to accelerate the process and extend treatment to less volatile or semivolatile organics. The cost of energy to heat the soils is moderately high, dependent of course upon the targeted temperature. Comparisons to ESD are similar to those discussed above for soil venting. (64)

Electrokinetics. The electrokinetic (EK) process involves the installation of electrodes into wells and the application of a low electric potential across the anode and the cathode. A low intensity direct current is applied across electrode pairs that have been implanted in the ground on each side of the contaminated soil mass. The electrical current causes different transport mechanisms, such as electromigration or movement of ions to the opposite electrodes; electrophoresis or movement of charged particles, including microorganisms, to the opposite electrodes; and electro-osmosis or movement of water to the cathode caused by superficially charged phenomena. Additionally, different electrochemical reactions occur, such as electrolysis and electrodeposition, so that the remediation process is the result of a complex set of mass transport phenomena and electrochemical reactions. Electro-osmosis can transport a solution through clayey soils much faster than the unaltered hydraulic gradient. Contaminants in the aqueous phase or contaminants desorbed from the soil surface are transported towards respective electrodes depending on their charge. The contaminants may then be extracted to a recovery system or deposited at the electrode. Surfactants and complexing agents can be used to increase solubility and assist in the movement of the contaminant. Also, reagents may be introduced at the electrodes to enhance contaminant removal rates. (14, 25, 28, 38, 49, 62)

Electrokinetics can extract heavy metals, radionuclides, and organic contaminants from saturated or unsaturated soils, sludges, and sediments. (25, 49, 58, 60) It is possible to remove diesel hydrocarbons from a clay soil using an EK-BioPRB or permeable reactive barrier (PRB) technology. According to the well-known effects of the polarity reversal strategy, it has been observed that such polarity reversals allow for maintaining adequate experimental conditions for biological process, and the surfactant addition appears to be necessary to help the diesel transport into the soil. The voltage gradient does not have a strong influence on several experimental conditions, such as soil pH, temperature, and moisture; but it affects the electro-osmotic flow. It has been observed that a higher voltage gradient results in a higher removal efficiency. Compared to other PRB systems, the biological activity has been extended to the entire soil area because of the microbial transport and growth far from the central Bio-PRB position. (62)

After EK remediation, however, the pollutants mainly concentrate in a small area or change to liquid phase in its original form and still need more efforts for complete removal. Through combining EK with other remediation technologies, not only can the reaction time be reduced effectively, but also organic pollutants are decomposed within the soil and thus do not need extra treatment. This review focuses on the enhanced EK technologies with oxidization-reduction, aiming to interpret useful information to the researchers and practitioners in this field and provide promising research directions for future studies. Firstly, implications of many common oxidizing-reducing agents on the performance of EK technologies for soil remediation are analyzed, which include Fenton reagent, permanganate, and persulfate. Various applications of oxidization-reduction technologies in configurations, such as zero-valent iron and Lasagna™, integrated with EK are possible. The potentials and challenges of developing new enhanced or integrated EK technologies are areas for future research, including: photoelectro-Fenton, EK-Fenton with ultrasound, EK-nano-ZVI, bimetallic systems with EK, EK-hypochlorite, EK-percarbonate and EK-ozone, and EK-redox-thermal desorption. (72)

Electrokinetic remediation coupled with technologies such as ISCO has been demonstrated in laboratory studies to greatly accelerate penetration of amendments into low permeability media. EK is the application of a low electric potential or direct current to electrodes inserted into the soil, inducing electro-osmotic flow of the pore fluid and the electromigration of charged ions towards the electrode of opposite charge. Under these circumstances, amendments such as charged oxidants can be injected under a low hydraulic gradient or without injection pressure and be more efficiently transported to the treatment zone and through the low permeability zones, compared to conditions relying solely on transport by hydraulic gradients. To date, demonstrating the feasibility of the coupled EK technologies has mostly been limited to the laboratory scale. Research efforts focused on a limited number of key parameters and properties that control the remediation progress such as the applied voltage, injected concentration, and soil. Furthermore, in experimental studies the implications of heterogeneity on EK transport behavior remained limited to relatively simple block representations of clay lenses. (92)

Of the several electrokinetic remediation techniques, the Lasagna™ process is probably the most well-known and well-publicized; many articles are available for more information, for example 24, 44, 45, 46, 47, 48, 66). It has been found to yield the best removal efficiency of organic contaminants from soils. The general concept of the Lasagna™ process is the transportation of contaminants from contaminated soil section into treatment zones using major electrokinetic transport mechanisms, such as electro-osmosis or electromigration. Once at the treatment zones, the contaminants may be removed from the pore water by sorption, degradation, or immobilization depending on treatment zone design. Detailed studies of all previous works on the Lasagna™ process, which span from bench-scale investigations to full field-scale remediation of contaminated soils, have been reported elsewhere. Lasagna™ process usually uses activated carbon as the sorbent material to improve the removal of contaminants from contaminated soil. (59)

Laboratory and field applications research show EK as capable of separating and recovering oil from water, aqueous sediments, and high clay rock formations, advancing EK to be used as a stand-alone or integrative technique for:

- Remediation of oil contaminated soils and sediments where spills have occurred, such as coastal sediments, coal gasification sites, abandoned oil production, or refinery sites);
- Change in physical properties can be triggered via electrokinetic methods as the classic soil consolidation with the aid of calcium carbonate producing bacteria;
- Product extraction, with special interest for mobilization of crude oil in enhanced oil recovery processes from formations where other extraction methods such as drilling, may not be feasible or environmentally viable. (58)

The efficacy of EK-induced oxidant transport was further examined for a heterogeneous aquifer system with random permeability fields. Oxidant migration under EK was slower in low permeability media due to the increased oxidant consumption of competing reductants. Instead of injecting oxidant only at the cathode, locating injection wells between the electrodes greatly increased the contaminant degradation by decreasing the distance the amendment had to migrate before reaching the contaminant. (92)

However, to date, there has been no comprehensive study that quantifies the effects of a comprehensive range of model parameters on the efficiency of EK-ISCO or other EK-combined technologies. The use of EK-ISCO remediation in the subsurface contains many uncertainties, in a large part due to poor understanding of the natural variations in parameters and geologic heterogeneity. (92)

Although clay and silt tend to sequester large quantities of organic and inorganic contaminants, they are resistant to remediation with traditional technologies because of their low hydraulic conductivities. Recently, attention has focused on developing in situ electrokinetic techniques for the treatment of low permeable soils contaminated with heavy metals, radionuclides, and selected organic pollutants. Although electrokinetics has been used

for decades in the oil recovery industry and to remove water from soils, in situ applications of electrokinetics to remediate contaminated soil is new and fully documented case studies of applying EK in the field are rare. (25)

Factors which limit the performance of in situ bioremediation are often highly site specific and commonly include: 1) mass transfer of electron acceptors and nutrients to microorganisms responsible for biodegradation; 2) limited bioaccessibility of contaminants, for example partitioning to aquifer material for biodegradation; and 3) adaptation of the indigenous microorganisms for biodegradation of a particular contaminant. The aim of coupling EK to bioremediation is to overcome these limitations, increasing the effectiveness of remediation measures. This review covers a number of related topics: 1) EK-bioremediation (EK-BIO) processes at the micro and macroscale, but with greater focus on the interactions between EK-BIO processes and the subsurface environment; 2) mechanisms supporting field application, considering the practical aspects of using EK-BIO in specific cases, such as the direct influence of environmental factors on EK with a critical focus on bioremediation; and 3) up-scaling EK-BIO at the field-scale. An analysis of coupled electokinetic and bioremediation processes and the potential for application of EK-BIO as a sustainable remediation technique is also presented. (38)

Various biological remediation processes were combined with electrokinetics to enhance the transport of microbes or certain nutrients. An electrode polarity reversal system can be used to achieve uniform transportation of nutrients to increase microbial activity. (53)

Due to technical difficulties in delivering nutrients to biologically active zones of soils with low permeability, bioremediation is presently limited to soils with permeabilities greater than 10^{-4} m s^{-1}. However, the electrokinetic process of applying a direct voltage gradient across contaminated soils can facilitate delivery of nutrients and electron acceptors in a low permeability clayey soil, thus suggesting the possibility of in situ bioremediation in low permeability, subsurface soils (57). Electro-bioremediation, which is a hybrid technology of bioremediation and electrokinetics, is a valuable mechanism to transport viable and culturable polycyclic aromatic hydrocarbon degrading bacteria in soil or sediments. (81)

The main advantages of EK include (88):

- Electrokinetics is very targetable to any specific location, because treatment of the soil occurs only between two electrodes.
- Electrokinetics is able to treat contaminated soil without excavation being necessary.
- Electrokinetics is most effective in clay, because it has a negative surface charge, and in soils with low hydraulic conductivity.
- Electrokinetics is potentially effective in both saturated and unsaturated soils.
- Electrokinetics is able to treat both organic and inorganic contaminants, such as heavy metals and nitrates.

- Electrokinetics demonstrated the ability to remove contaminants from heterogeneous natural deposits.
- Good cost effectiveness.

Despite all the advantages, this technique has some limitations, which are(88):

- The solubility of the contaminant is highly dependent on the soil pH conditions.
- The necessity to apply enhancing solution.
- When higher voltage is applied to the soil, the efficiency of the process decreases due to the increased temperature.
- Removal efficiency is significantly reduced if soil contains carbonates and hematite, as well as large rocks or gravel. (88)

Conclusions drawn from the literature on EK include:

- The mechanisms for EK-induced mixing to enhance bioremediation will vary depending on the host geological matrix.
- Novel field-scale applications of EK-BIO exist including the remediation of plume-scale contaminant scenarios and contaminants sequestered within zones of low permeability.
- When EK is applied in the natural environment, complex physicochemical processes generate non-uniform pH, voltage, and moisture gradients that can affect bioremediation performance and need to be considered on a site-specific basis, for example, groundwater flow will influence amendment transport and pH changes at the electrodes.
- Numerous electrode material and configuration options exist to optimize the EK-BIO treatment.
- Simple modelling of a relevant contaminated groundwater conceptual scenario to illustrate the performance of EK-BIO at the field-scale indicates that a considerable reduction in the time for a plume to reach steady-state length can be achieved. Relative to timescales which may typically occur for sites managed using monitored natural attenuation, EK-BIO could reduce overall remediation costs significantly. (38)

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APPENDIX A: Fractured Rock Settings

Background

Fractured-rock aquifers are a challenging geologic environment for characterization and remediation of [contaminated] groundwater… (Tiedeman, *et al.*, 2018)

Preferential flow and transport processes are probably the most frustrating in terms of hampering accurate predictions of contaminant transport in soils and fractured rocks. Contrary to uniform flow, preferential flow results in irregular wetting of the soil profile as a direct consequence of water moving faster in certain parts of the soil profile than in others (Šimůnek and van Genuchten, 2016).

Relatively few fractures can control a majority of the groundwater flow and advective contaminant transport, producing convoluted flow paths and spatially complex distributions of contaminants. (Tiedeman, *et al.*, 2018)

In sedimentary rock with relatively large matrix porosities, this diffusion can cause the majority of contaminant mass to reside in the rock matrix… (Tiedeman, *et al.*, 2018)

…even with increased gradients, diffusion rates are typically slow, and extremely long time periods—from decades to perhaps centuries or millennia—are likely needed to reduce contaminant concentrations of groundwater in fractures to achieve remediation objectives. (Tiedeman, *et al.*, 2018)

Site Characterization

At sites of groundwater contamination, characterizing the spatial distribution of contaminants in the aquifer is a critical element in formulating remedial strategies. In fractured rock aquifers, differentiating between contamination in the groundwater of the fracture porosity and the rock matrix is important in understanding factors affecting the longevity of contamination and the effectiveness of various remediation technologies. At fractured rock sites that have been subject to groundwater contamination for multiple decades, the majority of the contaminant mass is likely to reside in the low permeability rock matrix. Because of limitations in collecting groundwater samples from low permeability geologic materials, collecting and analyzing rock core for contaminants in the rock matrix has become an important component of site characterization in fractured rock. (Shapiro, *et al.*, 2019)

Major challenges exist in delineating bedrock fracture zones because these cause abrupt changes in geological and hydrogeological properties over small distances. Borehole observations cannot sufficiently capture heterogeneity in these systems. Geophysical techniques offer the potential to image properties and processes in between boreholes. (Robinson, *et al.*, 2016).

The results of this investigation illustrate the importance of conducting detailed site characterization in fractured rock, in particular, synthesizing geologic, geophysical, hydraulic, and geochemical information through groundwater flow modeling. The groundwater modeling provided an understanding of the complex groundwater flow regime controlled by bedding plane fractures in the mudstone, which was used to design the injection and distribution of remediation amendments, and interpret the [contaminant] concentrations at monitoring locations and pumping wells. (Shapiro, *et al.*, 2018)

There is a need to characterize the hydraulic properties of fractured rock sites to facilitate remediation of contaminated sites. The dominant flow pathways in fractured rock are usually controlled by joints, weathered bedding planes and formation contacts, fractures, shear zones, faults, and other discontinuities such as vugs. These environments are often poorly understood hydrogeologically due to the complex interrelationships between stress, temperature, fracture roughness, and geometry that affect hydraulic conductivity (Singhal and Gupta 1999), in addition to flow paths that have hydraulic properties varying over orders of magnitude (Shapiro 2010). Characterization of fractured rock aquifers is usually based on interpolation of sparse data points obtained from observations acquired in one or more boreholes. This approach often does not capture the hydraulic complexity of such environments, particularly over the spatial scales that integrate the primary heterogeneity in the hydraulic properties controlling flow and transport. At contaminated fractured rock sites where remediation is attempted through amendment injections (Sorenson 2000; Bradley *et al*. 2012), the spatial extent and migration of amendments is likely to be poorly resolved from a limited number of discrete borehole observations (Benson and Yuhr 1993). Fusing borehole data with geophysical imaging methods (Lines *et al*. 1988; Li and Oldenburg 2000) that can provide information beyond boreholes might result in a more effective characterization of the flow and transport characteristics in fractured rock. (Robinson, *et al.*, 2016)

Synthesis of rock core sampling from closely spaced boreholes with geophysical logging and hydraulic testing improves understanding of the controls on [contaminant] delineation and informs remediation design and monitoring. (Goode, *et al.*, 2014)

The lack of a detailed characterization of the groundwater flow regime at fractured rock sites is sometimes unavoidable because of the expense of installing monitoring boreholes to capture the three-dimensional flow regime and the complex distribution of contaminants. In situations where hydrogeologic information from site characterization can be synthesized using a groundwater flow model, groundwater fluxes can be used to design the injection and distribution of remediation amendments, and identify monitoring locations and expectations at monitoring wells (Tiedeman, *et al.*, 2018). Furthermore, quantifying groundwater fluxes permits the calculation of chemical fluxes under pre- and post remediation conditions to evaluate the contaminant mass mobilized by remediation treatments. (Shapiro, *et al.*, 2018)

…it is important to synthesize site characterization information using a groundwater flow model that includes discrete features representing high and low permeability fractures. This type of model accounts for the highly heterogeneous hydraulic conductivity and

groundwater fluxes in fractured-rock aquifers, and facilitates designing injection strategies that target specific volumes of the aquifer and maximize the distribution of amendments over these volumes. (Tiedeman, *et al.*, 2018)

Groundwater Sampling and Monitoring

Within fractured rock settings, groundwater sampling is used extensively as a characterization tool because of the belief that these formations are too challenging to warrant core collection. This practice is basically a concession that the complexity of fractured rock cannot be characterized, and that the only useful information that can be obtained is through collecting groundwater from hydraulically active fractures. However, this approach generally yields compromised data because it relies on sampling intervals that are not appropriate to the scale of the problem and boreholes that promote cross connection between fractures (Parker, 2007). Just like in unconsolidated formations, these groundwater-based methods ignore mass stored in the soil matrix (in this case, within the rock itself) and provide potentially misleading information on the distribution of contaminants. (Sale, *et al.*, 2013)

As is symptomatic of many contaminated fractured rock sites, [site characterization] is constrained by sparse monitoring locations within the treatment zone. The detailed characterization of the groundwater flow regime is intended to provide reasonable constraints on the distribution of remediation amendments and interpretations of fluxes from a sparse number of monitoring locations that can provide estimates and bounds of the [contaminant] mobilization. (Shapiro, *et al.*, 2018)

Attempting to infer the success of remedial actions in fractured rock aquifers based solely on aqueous concentrations in groundwater samples withdrawn from permeable fractures fails to quantify the [contaminant] mass mobilized by the bioremediation and the magnitude of the [contaminant] fluxes in relation to the contaminant mass in the region of the aquifer targeted by the remediation. (Shapiro, *et al.*, 2018)

The detailed understanding of the groundwater flow regime and groundwater fluxes in the treatment zone allows us to constrain the interpretations of the geochemistry at monitoring locations in formulating a mass balance to quantify the [contaminants] mobilized prior to and after the start of the bioremediation. (Shapiro, *et al.*, 2018)

Evaluating the longevity of groundwater contamination and the efficacy of groundwater remediation strategies in fractured rock also requires information on the diffusive exchange of aqueous phase contaminants between fractures and the intrinsic porosity of the rock, referred to as the rock matrix. (Shapiro, *et al.*, 2019)

…core samples analyzed with sufficient resolution to capture the spatially variable contaminant distribution associated with fracture locations provide a relatively undisturbed evaluation of the contaminant distribution with depth in the aquifer at the time of coring. In contrast, samples collected from mobile groundwater in fractures intersecting boreholes, even

after the installation of multilevel monitoring equipment, may be impacted by the hydraulic disturbances induced by drilling, hydraulic connections between multiple fractures along the length of the borehole, and the installation and operation of monitoring equipment (Shapiro, 2002; Sterling *et al.*, 2005). Additionally, concentrations of [contaminants] in fractures may not be representative of the aqueous concentrations in the pores of the rock matrix (Goode *et al.*, 2014), and are also typically collected at much lower vertical resolution than possible with core analyses. Thus, sampling of aqueous concentrations from permeable fractures will not provide an accurate means of assessing the total contaminant mass retained in the rock matrix. (Shapiro, *et al.*, 2019)

Electrical Resistivity Tomography

Electrical resistivity tomography (ERT) is a candidate technique to image away from boreholes as: 1) electrical current pathways closely mimic hydraulic pathways (a valid approximation when ionic current flow is the dominant mode of conduction); and 2) the imaged volume and spatiotemporal resolution can be adjusted through survey design. ERT permits the imaging of temporal changes in electrical conductivity for a volume of fractured rock mass bounded by boreholes. Compared to point measurements collected at discrete locations within boreholes, ERT can provide information at distances that can more readily capture the heterogeneity that controls flow and transport in fractured rock. Furthermore, whereas drawing fluid samples from boreholes for analysis can disturb the natural flow regime, ERT requires no further alteration to the natural system once electrodes are installed. (Robinson, *et al.*, 2016)

Few ERT studies in fractured rock have been conducted and the hydrogeological information extracted has been limited for a number of reasons, including: 1) the until recent lack of three-dimensional (3D) data acquisition and processing techniques required to accurately image fractured rock; 2) the use of conceptually inappropriate constraints on the model structure resulting in smooth resistivity distributions (deGroot-Hedlin and Constable 1990) unrepresentative of fractured rock systems; and 3) the distances between boreholes that were suboptimal for an ERT study. Surface ERT studies have been used to delineate subsurface electrical conductivity changes in fractured rock to infer flow paths (Nimmer *et al*. 2007; Robert *et al*. 2012) but the resolution is inherently limited when only surface electrodes are utilized. Slater *et al*. (1997) used a natural tracer to image discrete fractures in an early two-dimensional cross borehole ERT study. Day-Lewis *et al*. (2004) showed the value of time-lapse cross borehole radar monitoring of tracer injections to construct and calibrate flow and transport models. Scalable, parallel ERT algorithms are now available that allow 3D inversion of very large datasets with finely discretized unstructured meshes containing millions of elements using distributed memory supercomputers (Johnson *et al*. 2010; see also *https://e4d.pnnl.gov*). Fine discretizations are necessary to correctly model the effects of boreholes (Doetsch *et al*. 2010), being particularly important when conductivity contrast between the electrically conductive borehole and the rock is very large. Scalable algorithms permit fine discretization in regions that exert a strong influence on electrical conductivity, groundwater flow, and solute transport. New algorithms also allow for sharp conductivity boundaries (Günther *et al*. 2006; Johnson *et al*.

2010). Robinson *et al*. (2013a, 2013b) suggest that allowing for sharp contrasts in conductivity at boreholes and fracture zone locations inferred from borehole logs can result in hydrogeologically plausible resistivity models. (Robinson, *et al.*, 2016)

The time-lapse ERT measurements provide valuable information at a meter scale appropriate for capturing migration pathways under a pulsed-tracer injection test. The 3D extent of the tracer migration highlights flow and transport within a heterogeneous fractured rock system. (Robinson, *et al.*, 2016)

ERT resolution is limited by multiple factors, including: 1) the electrical conductivity contrast between the tracer fluid and the pore fluid in the less mobile and mobile domains; 2) the possibility of narrow fracture zones important for tracer transport that are smaller than the image resolution; and 3) the numerical errors in the ERT modeling which exceed the actual data errors indicated by reciprocal measurements in this case. (Robinson, *et al.*, 2016)

Despite these limitations, characterizing fractured rock with ERT clearly enhances understanding of tracer transport pathways relative to point measurements from boreholes alone; such information could help to determine if target regions are reached during remediation treatments based on delivery of amendments to contaminated regions of the subsurface. (Robinson, *et al.*, 2016)

Static ERT imaging has limited resolution to decipher individual fractures; however, these images showed alternating conductive and resistive zones, consistent with alternating laminated and massive mudstone units at the site. Tracer evolution and migration was clearly revealed in time-lapse ERT images and supported by in situ borehole vertical apparent conductivity profiles collected during the pulsed tracer test. While water samples provided important local information at the extraction borehole, ERT delineated tracer migration over spatial scales capturing the primary hydrogeological heterogeneity controlling flow and transport. The fate of these tracer injections at this scale could not have been quantified using borehole logging or borehole sampling methods alone. (Robinson, *et al.*, 2016)

The spatially rich information on tracer evolution into the targeted fracture zone, including evidence of channeling of flow by heterogeneity, could not have been determined from borehole based observations alone. (Robinson, *et al.*, 2016)

The novel electrode array design was essential to this work by integrating packers and a fluid injection port such that tracer fluids were injected and water samples were acquired from targeted fracture zones during ERT imaging. When used in conjunction with local measurements made at boreholes, ERT imaging can provide information at a critical scale needed to track the fate of tracers or amendments beyond injection zones. Our approach demonstrated here could be extended to other field sites for effectively monitoring the fate of amendment injections into fractured rock aquifers beyond borehole walls. (Robinson, *et al.*, 2016)

Remediation

The presence of the VOCs in the bedrock matrix presents many technical and regulatory challenges when it comes to how to remediate the problem and how to define success. The only truly effective remediation technologies for the fractured bedrock aquifer are those that will treat the VOC mass in the rock matrix in addition to treating the VOCs in the groundwater. Failure to treat the VOC mass in the matrix will result in a continuous diffusive transfer of VOCs from the bedrock matrix into the groundwater over an extensive time period. In addition, it should be recognized that, although USEPA Maximum Contaminant Limits (MCLs) or equivalent state standards are always the ultimate objectives, it is unlikely that MCLs will ever be achieved by any remediation technology in matrix-dominated fractured bedrock environments. This leaves mass-based metrics, such as reduction of source mass or reduction in flux, as the only viable measures by which remedial programs in fractured bedrock should be evaluated and by which eventual site closure could be achieved. (Vitolins, *et al*, 2004)

A potentially promising niche for pump and treat is fractured rock settings with low matrix porosity. In this setting contaminants will largely be absent from the matrix blocks or low permeability zones and pumping can induce high rates of flow through interconnected fractures or transmissive zones. (Sale and Newell, 2011)

Although biostimulation and bioaugmentation have been investigated and adapted as groundwater remediation technologies, successful remediation of groundwater contamination continues to be a problem (Bradley and Chapelle 1996; Stroo *et al*. 2012), especially in geologic settings such as fractured rock aquifers where remediation amendments move preferentially through permeable fractures and bypass contaminated groundwater in low permeability aquifer materials. (Shapiro, *et al.*, 2018)

In fractured sedimentary rocks, the matrix porosity can be greater than 10 percent of the rock volume (Dorsch and Katsube 1999; Bloomfield *et al*. 2001), whereas the fracture porosity may only constitute, at most, a few percent of the rock volume (Zuber and Motyka 1994; Moench 1995) resulting in the majority of the [contamination] retained within the rock matrix (Sterling *et al*. 2005; Goode *et al*. 2014). Injecting remediation amendments usually will cause dramatic decreases of [contaminant] concentrations within connected permeable fractures, but will not necessarily achieve thorough biological treatment of both mobile and immobile groundwater (Drew and DeFlaun 2010). (Shapiro, *et al.*, 2018)

In fractured rock, where injected remediation amendments may not contact the groundwater contaminants in the rock matrix or low permeability fractures, treatments are unlikely to yield the desired result of complete in situ degradation of [contaminants]. However, amendment injections may enhance the mobilization of [contaminants] to permeable fractures. Reducing the concentrations of [contaminants] in fractures increases the concentration gradient and the diffusive flux from the rock matrix to fractures and promotes desorption from aquifer materials and NAPL dissolution, if NAPL is present. Thus, increasing the mobilization of [contaminants] into permeable fractures leads to contact with remediation amendments. In

addition, continued operation of hydraulic containment and groundwater flushing by pumping also acts to remove the [contaminants] mobilized into fractures that are not transformed into benign end products. Thus, designing short-term biological treatments in conjunction with ongoing pumping operations may be beneficial in more rapidly achieving long-term remedial objectives. (Shapiro, *et al.*, 2018)

…concentrations of contaminants drawn from permeable fractures during treatments are used as an indicator of the success of the treatment method, and continued chemical monitoring after the treatments have ended serve as a means of evaluating contaminant rebound that would be indicative of untreated contaminants diffusing out of the rock matrix. In many instances, groundwater samples are taken from the same wells where amendments have been injected (DeFlaun *et al*. 2006; Drew *et al*. 2006). Residual remediation amendments in these wells may result in a localized treatment of the groundwater that is not necessarily reflective of the wider contaminant distribution in fractures or the rock matrix. (Shapiro, *et al.*, 2018)

Under conditions prior to the start of the bioremediation characterized by natural attenuation and continued groundwater pumping, it would likely take several hundred years for the [contaminant] mass to diffuse out of the rock matrix. In comparison, [contaminant] mobilization rates indicate that multiple remediation treatments would be required over many decades to reduce [contaminant] mass in the rock matrix to a point where pumping could be discontinued. The results of this investigation indicate the feasibility of proposing multiple remedial treatments, however, a more precise calculation of the time frame to achieve remedial objectives and the cost these alternatives is required. Additional investigations using transport models that explicitly define the retention and release of [contaminants] in the rock matrix and resultant [contaminant] concentrations in adjacent fractures would be needed to evaluate time frames to achieve compliance with groundwater regulations. (Shapiro, *et al.*, 2018)

Remediation also can involve introducing amendments into the aquifer to transform contaminants to nontoxic products. These methods require contact between contaminated groundwater and amendments and thus have been most successful in uniformly permeable geologic settings (NRC 1994; McCarty 2010). In fractured-rock aquifers, where preferential flow paths comprise only a fraction of the total groundwater volume affected by contaminants, these technologies are unlikely to be successful on their own. However, approaches that introduce remediation amendments can be beneficial if the resulting contaminant mass transformations reduce the time frame for applying longer-term remedial actions such as pump-and-treat. (Tiedeman, *et al.*, 2018)

For heterogeneous aquifers, designing bioremediation strategies that achieve adequate spreading requires detailed characterization of hydraulic and transport properties and the spatial distribution of contaminants. Methods for characterization in fractured rocks are widely available, for example NRC 1996; Kueper *et al*. 2003; Interstate Technology and Regulatory Council, ITRC 2011; NAS 2015. However, the qualitative understanding gained from field

characterization alone is insufficient for designing and assessing amendment-based remedial actions. Groundwater fluxes and transport pathways also are needed to guide injection design and to provide information on expected amendment transport during and after injection. In fractured rocks, the extreme heterogeneity of K produces a high degree of spatial variability in fluxes and pathways, which consequently can only be well estimated through groundwater flow and solute transport models developed and calibrated using the field characterization data. (Tiedeman, *et al.*, 2018)

The purpose of this article is to demonstrate the critical role of groundwater flow and solute transport modeling for estimating fluxes and advective transport paths that are key to designing amendment injection and spreading for a bioremediation experiment in highly heterogeneous contaminated fractured sedimentary rocks. This application of modeling is a novel approach to bioremediation design in fractured rocks, in that it explicitly accounts for the spatial variability of hydraulic properties in the vicinity of the treatment area, and the effect of this variability on fluxes and transport paths. Use of the fluxes is then extended beyond the design stage to inform bioremediation monitoring strategies and to set expectations about the extent of the treatment zone. Furthermore, the quantification of groundwater fluxes permits the calculation of chemical fluxes under pre- and post bioremediation conditions, which enables evaluation of the contaminant mass mobilized by the treatments… (Tiedeman, *et al.*, 2018)

This investigation provides guidance for designing bioremediation in source zones of fractured-rock aquifers. Results emphasize that design of effective amendment based groundwater remediation in settings where discrete fractures host the majority of groundwater flow requires detailed knowledge of the distribution of hydraulic conductivity as well as information about groundwater fluxes and advective pathways for solute transport. In fracture dominated flow regimes, methods of injecting and distributing remediation amendments that have been applied in less heterogeneous unconsolidated geologic materials may not be appropriate. Instead, it is necessary to target specific volumes of the aquifer and design hydraulic procedures to maximize the distribution of amendments over these volumes, accounting for the highly heterogeneous hydraulic conductivity distribution. The investigation emphasizes the critical role of groundwater flow and solute transport modeling in designing, monitoring, and setting expectations for amendment-based remediation in fractured rocks. This modeling revealed and quantified solute spreading and dilution that were essential to consider in the remediation design and that were not possible to thoroughly evaluate with field characterization alone. Groundwater fluxes quantified by the model also were essential to evaluating contaminant mass mobilized by the bioaugmentation… (Tiedeman, *et al.*, 2018)

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APPENDIX B: Membrane Interface Probe

High-resolution characterization focuses on increased data density, often by collecting depth-discrete data across transects using different methods in phases. Soil coring and analysis is considered a superior option in low-k zones. This is because coring: 1) quantifies mass in all dissolved and sorbed phases; 2) allows for accurate soil type classification, and 3) permits depth-discrete sampling at tight intervals to understand contaminant and permeability distribution (Adamson, *et al*., 2013).

Soil coring and analysis can be labor- and cost-intensive, but there are several rapid data acquisition tools that can be used to screen locations and depths for more focused (and cost-effective) characterization. One such screening tool is the membrane interface probe (MIP). It is used to collect nearly continuous, depth-discrete data in unconsolidated soils where it can be advanced using direct push equipment (Adamson, *et al*., 2013).

Because the MIP tool is equipped with an electrical conductivity (EC) detector, it can also provide stratigraphic characterization data (typically, presence or absence of clays) that is comparable, yet much less costly, than geophysical methods or logging of soil cores (Adamson, *et al*., 2013).

Comparisons to data collected using soil cores from known depths provides the most appropriate methodology for evaluating MIP results in heterogeneous media (Adamson, *et al*., 2013).

The MIP EC data correlated well with sediment layering observed in cores, demonstrating that the MIP can provide useful information on the hydraulic conductivity variability attributed to the presence or absence of clays (Liu, *et al.* 2012). Elevated EC readings coincided with lower k units, and the EC data could be used to generally identify the upper and lower boundaries. These results are consistent with those obtained by other high-resolution characterization studies that included direct-push electrical conductivity logging (Adamson, *et al*., 2013).

The primary disadvantage of MIP-based lithologic information, or EC data, is that it cannot capture small-scale heterogeneities as readily as some other methods, for example WaterlooAPS or Geoprobe Hydraulic Profiling Tool (HPT). This is because the latter methods directly indicate the hydraulic response of the formation and thus provide information on relative permeability (Liu, *et al.* 2012). The MIP EC sensor provides little information about apparent permeability contrasts in zones where clays (which are naturally electrically conductive) are absent. Note that the latest version of the MIP system incorporates the HPT to improve its overall utility (Adamson, *et al*., 2013).

At a minimum, the MIP helps reveal the presence and relative distribution of contamination within lower-k intervals that are too often ignored in conventional site characterization efforts. The MIP is capable of resolving contamination in low-k zones as well as

it does in high-k zones, and its overall efficacy is not limited to specific soil types. The capability of the MIP to collect a large amount of depth-discrete data is valuable in demonstrating the general horizontal and vertical distribution of contamination at a site in both transmissive and low-k compartments. However, the results of this study emphasize that the MIP data (even if collected using the developed protocol) do not necessarily accurately reflect the actual small-scale, detailed contaminant heterogeneity. MIP data may provide a false sense of confidence that small-scale heterogeneities are well understood, particularly when not compared to soil core data (Adamson, *et al.*, 2013).

The general goal of using MIP during high-resolution site characterization is to reduce the intensity of soil coring which requires expensive lab analyses to accurately delineate contaminant distributions (Adamson, *et al.*, 2013).

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APPENDIX C: Highlights of Article by Horst *et. al* (2019)

The article title is *Groundwater Remediation in Low-Permeability Settings: The Evolving Spectrum of Proven and Potential*. It was published in *Groundwater Monitoring & Remediation*, Volume 39, no. 1, Winter 2019.

The article considers nine technologies "in the context of the applicability to [the] remedy selection framework" as presented in Table 1, which is presented in a slightly modified format below as Table C-1. The authors believe that it is conceivable that some of these options could be sufficient as a stand-alone remedy for a low-permeability site, or that a mix of two or more could be implemented as part of a combined remedy based on the remedial drivers. Except for excavation and high-temperature thermal, the article discusses the remaining seven technologies, presenting some of their advantages and disadvantages. The article did not present the advantages and disadvantages as tabulated bullets; EPA did this to aid readers in evaluating the various technologies.

This Appendix summarizes the article, presenting each of the seven technologies in the same order as the article. One difference is that this summary separates references from the article into the specific technology sections to which they pertain. As with the main body of the literature review and the preceding two appendices, this appendix presents cut-and-pasted passages from the article with only minor editing in limited circumstance to improve readability.

Introduction (p.11)

Low-permeability aquifer settings limit the applicability and effectiveness of many conventional remediation technologies. Remediation approaches that rely on extraction, recirculation or reagent delivery (injection) and distribution can often be expected to fail or notably underperform. On the other hand, plume lengths and contaminant flux are usually limited, and therefore the potential for plume migration and complete pathways for receptor exposure are often very low…[and] these sites are often candidates for long-term monitored natural attenuation or low-threat risk-based closure.

Spectrum of Demonstrated and Promising Technologies (pp.11-12)

As with any site, remedy selection for low-permeability sites must balance potential exposure risk, long-term remedial responsibilities, and site management preferences.

Table C-1
Assessment of Selected Remediation Technologies for Low-Permeability Sites
(adapted from Table 1 of Horst *et.al.,* 2019, p.13)

Treatment Strategy	Technologies	Access/Footprint Requirements	Chemicals of Concern (COC)	Key Limitations
Complete Treatment	Excavation	Significant	Any COC	Depth, costs
	High-Temperature Thermal	Significant	Fuels, VOCs	Soil type, groundwater velocity, depth, costs
	Soil Mixing—Stabilization and Solidification	Significant	Organics, Metals	Depth, costs
Source Reduction	Electrokinetics	Significant	Organics, Metals	Soil type, costs
	Low-Temperature Thermal	Moderate	Organics	Target COCs, depth
	Hydraulic Fracturing	Moderate	Any COC	Reagent distribution, geologic controls
Flux Control	Passive Barrier Systems - Permeable Reactive Barriers - Funnel and Gate - Interceptor Trenches - Media-filled Borings	Moderate	Organics, Metals	Depth, groundwater velocity
	Phytohydraulics/ phytoremediation	Moderate	Organics, Metals	Depth, COCs, access
	HRX Well	Very Limited	Organics, Metals	Elevated groundwater velocity
Shaded cells represent promising technologies. Unshaded cells represent demonstrated technologies.				

Soil Mixing for Stabilization Or Solidification, Or Both (pp.12-13)

- Soil mixing is a well demonstrated technology for remediation of a variety of contaminants at sites with sufficient access at the surface to support mixing operations.
- Soil mixing involves the physical mixing of supplemental amendments with impacted soil to reduce the mobility, toxicity or solubility of the target contaminant.
- Addition of a reactive amendment, that is, oxidants, zero-valent iron [ZVI], acids or bases, is commonly referred to as soil stabilization and has the primary objective of changing the form of contaminants to reduce toxicity.
- Addition of a binding amendment, that is, Portland cement or fly ash, is commonly referred to as soil solidification and has the primary objective of encapsulating contaminants to reduce their mobility by altering the physical nature of the matrix, making it less permeable, versus changing the form of the contaminant.

Advantages	Disadvantages
- Soil mixing can achieve the same level of treatment extent as soil excavation or HT thermal source technologies - Soil mixing can occur in-situ or ex-situ - Soil mixing is typically completed down to depths of approximately 15 ft below grade, but can employ large diameter augers down to potential depths of up to 100 ft below grade	- Low-permeability soils require addition of water for mixing; this can result in soil bulking of 30-100 percent - Addition of water reduces soil compressive strength requiring addition of a binder to increase strength and restore soil integrity. - When applying a reactive amendment, for example oxidants or ZVI, two steps may be required to first achieve treatment and then solidification once the reactive amendment has been exhausted

Electrokinetic-Enhanced Reagent Delivery (p.14)

- Electrokinetic (EK) techniques involve the application of low-level direct current across a target treatment zone through the use of electrodes.
- The applied current results in the creation or enhancement of several transport mechanisms, including diffusion, electromigration or the migration of charged ions, electroosmosis or the movement of pore fluids and associated dissolved constituents, and electrophoresis, or migration of charged particles.
- Key cost drivers for EK-enhanced reagent delivery are treatment zone footprint and thickness, which largely dictates the number of subsurface electrodes and reagent injection wells needed.
- When applying EK, further assessment of site-specific characteristics such as potential ion migration limiting due to the pH buffering capacity of soils is necessary.

Advantages	Disadvantages
• Migration processes are not affected by aquifer hydraulic conductivity; EK migration rates are effectively the same in low-permeability materials as they are in high permeability materials • Can be applied to deliver remediation reagents into low-permeability zones and increase overall reagent distribution uniformity in geologically heterogeneous settings. • Can be used to promote the distribution of organic carbon and microbes for bioremediation • EK operations require very little power; for a PCE site, power requirements usage was equivalent to operating two 100-watt lightbulbs. • May be particularly advantageous for deeper contamination where soil mixing is less practical	• Infrastructure requirements may be expensive (for the PCE site, nine electrode wells and eight reagent supply wells were required for the 40-ft by 40-ft treatment footprint. The reported total full-scale system cost was $688,000).

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Low-Temperature Thermal (p.14)

- Low-temperature thermal applications involve the transfer of thermal energy (heat) to the subsurface to increase the treatment area above ambient temperatures, but generally below 70 °C.
- Elevating temperature within an impacted area will enhance contaminant biological and chemical attenuation processes, or aid in physical removal efforts via extraction applications.
- This technique allows heating to temperatures within the 15 to 40° C optimal range for biodegradation, and for hydrocarbons, leverages the two-fold degradation rate increase for each 10° C increase in temperature.
- Various heating methods may be employed, which can range from conventional heating, to the use of solar radiation, to the capture and reuse of waste heat.

Advantages	Disadvantages
- Heat can be transferred more easily than fluids throughout the same formation - Heat transfer properties of a subsurface soil matrix do not vary considerably, such that an entire targeted treatment zone may be heated to stimulate a desired reaction, such as contaminant partitioning, chemical degradation, biological degradation	May not be possible to raise the temperature of the target area to the desired level in a reasonable timeframe

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Hydraulic Fracturing (pp.14-16)

- A variety of fracturing techniques and tooling have been developed and applied in the remediation industry to support contaminant remediation [hydraulic fracturing is not itself a remediation technology].
- The technology entails the application of pressure to a soil formation at sufficient magnitude to exceed the soil matrix cohesion and propagate planes of failure from points of weakness that establish new zones of secondary porosity to increase the overall formation permeability and support delivery of fluids, propping agents or solids to keep the fracture open, or reagents.
- May be used for either/both long-term permeability enhancement or one-time emplacement of remediation amendments.
- The inability to inject fluids at low permeability sites, a desire to target and reduce source mass, and the low overall cost compared to more comprehensive remedies are all forces that continue to drive fracture-based delivery to the top of feasibility analyses.

Advantages	Disadvantages
• Hydraulic fracturing (the use of a pressurized liquid versus a gas to complete the fracture propagation), primarily because it better allows the emplacement of a sand proppant, that helps to maintain the higher permeability created through induced fracturing. • Induced fractures may extend 50-100 feet or more in some geologic settings • Where source reduction is the objective or where remedial endpoints are amendable to risk-based closure, hydraulic fracturing for amendment emplacement can be a very effective remedial strategy.	• With greater radial distance fractures tend to arc upward toward the surface and may result in short-circuiting • Propagation of hydraulic fractures are often limited and asymmetric and the orientation can be difficult to predict or control • Injection volumes achieved via hydraulic fractures are typically less than 10 percent of the volume that would be applied through an injection well targeting the same radius of influence; therefore 90 percent or more of the aquifer volume may not be reached by injectates. The decreased potential for injection volume results in a decreased treatment capacity.

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Permeable Barrier Systems (p.16)

- Permeable barrier systems represent a class of remediation technology that achieve passive contaminant control and containment by intercepting and treating impacted groundwater as it migrates through a reactive permeable media.
- Systems use permeability contrasts to direct flow into the treatment zone.
- Systems are specifically designed to control the flux of contaminant mass away from a source or site, not accelerate the overall remediation.
- There are many variations of this technology, such as reactive walls, funnel and gate systems, interceptor trenches, and even simply media-filled borings.
- The limited flux of groundwater and contaminants from low permeability sites allows for modification of these treatment remedies to align long-term operational requirements and increase overall remediation efficiency.

Advantages	Disadvantages
- Limited energy cost of operation and long-term benefits of maintaining contaminant control - Can provide long-term flux control	- Because they are passive systems, these systems do not accelerate the overall rate of remediation

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Funnel and Gate with Reactive Treatment (pp.16-17)

- Traditional permeable reactive barriers (PRBs) are typically filled with some combination of reactive amendment, for example ZVI, mulch, and a supportive matrix such as a coarse sand to achieve the desired permeability.
- The reactive media is placed across the full cross-sectional area where contaminant flux is occurring in groundwater, and the cost of reactive amendment is typically one of the primary cost drivers for PRB construction.
- Given that the flux of groundwater and contaminants is much lower at low permeability sites, full emplacement of reactive media across the entire cross-sectional area of a contaminant plume is usually not necessary or cost effective when the distributed flux could be focused into a much smaller area, thus optimizing the use and cost of the remedial amendments.

Advantages	Disadvantages
• Shorter segments of reactive permeable media can be used because physical barriers direct flow into the reactive media (funnel and gate) • System can be designed to be serviceable, for example filled with replaceable media	• Remediation rates are slow due to low groundwater velocities, hence treatment times are long

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Interceptor Trenches or Sparge Trenches (p.17)

- Interceptor trenches are a method of intercepting the flux of contaminated groundwater within a reservoir that can be easily extracted for focused ex-situ treatment.
- Interceptor trenches would be installed in a similar fashion to traditional PRBs but are filled with high-permeability material that serves to focus and collect groundwater flow.

Advantages	Disadvantages
• Can be used to intersect potential heterogeneities and more effectively achieve capture than can be achieved from single well points with limited yield • Can be deployed with low-profile biosparge wells to serve as a long-term biobarrier within which rapid aerobic biodegradation can be achieved	• None cited

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Amendment Filled Borings (p.17)

- These systems are comprised of arrays of non-pumping, vertically oriented wells filled wih high-permeability treatment media, which is amended with oxidants or biological substrates.
- Because of their higher permeability than the surrounding low-permeability soil, groundwater flow would be focused toward the wells where it would contact the treatment media.

Advantages	Disadvantages
• Can potentially be deployed at relatively small sites if the number of wells is sufficient to intersect the contaminant plume	• Effectiveness of the solid phase treatment media has not been widely demonstrated in the field • Difficult to effectively intersect all the flow across a plume, so the potential for contamination bypassing the barrier is high

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Phytohydraulics and Phytoremediation (p.17)

- Phytohydraulics systems consist of fast growing, high transpiration, and resistant vegetation that are designed to: 1) lower the groundwater elevation within the saturated zone; 2) increase moisture content in the vadose zone; 3) reduce lateral groundwater flow; 4) create a robust rhizosphere that enhances biological activity in the vicinity of the water table; and 5) draw dissolved contaminants into the woody mass of the trees where they are sequestered and degraded.
- Plant species are carefully selected to match the local climate, native species requirements and contaminant resilience, as well as a detailed understanding of site hydraulic fluctuations to tailor growth area size and water uptake.

Advantages	Disadvantages
- Employs a natural vegetative system to capture, sequester, and promote the degradation of contaminants in groundwater and soil - Can be highly cost- and technically-effective options compared to trenching or groundwater recovery implementation for maintaining flux control, particularly adjacent to natural habitat or surface waters	- Only effective where depth to contamination (and groundwater) is shallow

No References were provided in this section of the article

Horizontal Reactive Media Treatment Well (pp.17-18)

- The Horizontal Reactive Media Treatment Well (HRX Well[©]) is a new passive flux-control technology that utilizes large-diameter horizontal wells filled with solid-phase reactive media to treat contaminated groundwater in-situ.
- The HRX Well is installed parallel to the direction of groundwater flow and the design leverages natural flow-focusing behavior induced by the engineered contrast in hydraulic conductivity between the high in-well reactive media and the ambient aquifer hydraulic conductivity to passively capture and treat proportionally large volumes of groundwater within the well.
- Clean groundwater then exits the horizontal well along its down-gradient sections.

Advantages	Disadvantages

• May quickly reduce contaminant mass flux and control migration, however, it
  ○ Requires only a limited above-ground footprint and minimal ongoing maintenance
  ○ Can be installed under buildings or other surface infrastructure
  ○ Involves no active groundwater management or above-ground treatment systems,
• Many different types of solid reactive media are already available; therefore, this concept could be used to address a wide range of contaminants[11]
• Reactive media use will be more efficient, and replacement will be simpler and less costly, for an HRX Well than for a conventional PRB.
	• Will not directly treat source mass or contamination located in low-permeability zones
	• Not yet widely tested in the field for a wide variety of contaminants, so performance data is limited

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[11] Table 2 (p.18) in Horst, *et al.* (2019) presents a wide variety of Reactive Media and their Target Groundwater Contaminants; however, hydrocarbons are only listed twice: once as being treatable by Granulated Active Carbon (GAC), and second as being treatable by Sustained Release Oxidants.

Closing Thoughts (p.18-19)

- Complete restoration of most contaminated low-permeability sites to drinking water quality standards may be impractical and very costly due to a variety of physical mechanisms imparted by the aquifer matrix that limit the ability to access contaminants.
- It is critically important to characterize in high resolution the site-specific permeability structure and contaminant mass distribution for more accurate remedy decision making and stakeholder clarity monitoring programs intended to evaluate remediation success and risk reduction need to align with flux-focused remedial goals and monitor moving mass.
- remediation system effectiveness continues to be assessed primarily based on contaminant concentrations measured at conventional monitoring wells. Most site monitoring well networks include wells that were originally installed to delineate the plume and intended to monitor changes in the plume's spatial footprint, rather than measuring changes in mass flux, particularly mass flux emanating from a source zone.
- Monitoring networks should prioritize wells screened in higher hydraulic conductivity materials; wells screened across very low permeability zones should generally not be used for remedial performance monitoring

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