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Chlorinated Ethene Source Remediation: Lessons Learned

Hans F. Stroo,[†,*] Andrea Leeson,[‡] Jeffrey A. Marqusee,[‡] Paul C. Johnson,[§] C. Herb Ward,[∥] Michael C. Kavanaugh,[⊥] Tom C. Sale,[#] Charles J. Newell,[▽] Kurt D. Pennell,[○] Carmen A. Lebrón,[◆] and Marvin Unger[†]

[†]HydroGeoLogic, Inc., 11107 Sunset Hills Road, Suite 400, Reston, Virginia 20190, United States

[‡]Strategic Environmental Research and Development Program, 901 North Stuart Street, Suite 303, Arlington, Virginia 22203, United States

[§]School of Sustainable Engineering and the Built Environment, Arizona State University, P.O. Box 879309, Tempe, Arizona 85287, United States

[∥]Department of Civil and Environmental Engineering, Rice University, 6100 Main Street, MS 316, Houston, Texas 77005, United States

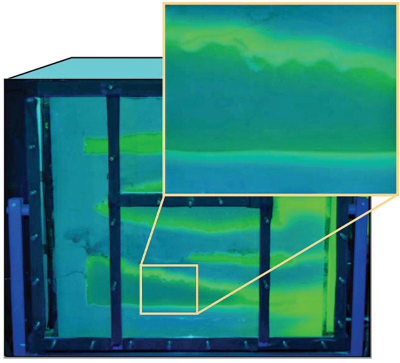
[⊥]Geosyntec Consultants, 1111 Broadway, 6th Floor, Oakland, California 94607, United States

[#]Department of Civil and Environmental Engineering, Colorado State University, 1320 Campus Delivery, Fort Collins, Colorado 80523, United States

[▽]GSI Environmental Inc., 2211 Norfolk Street, Suite 100, Houston, Texas 77098, United States

[○]Department of Civil and Environmental Engineering, Tufts University, 200 College Avenue, 113 Anderson Hall, Medford, Massachusetts 02155, United States

[◆]Naval Facilities Engineering Command Engineering Service Center, 1100 23rd Avenue, ESC-411, Port Hueneme, California 93043, United States



INTRODUCTION

Chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (PCE) are widespread groundwater contaminants often released as dense nonaqueous phase liquids (DNAPLs).[1,2] These contaminants are difficult to remediate, particularly their source zones, and represent a significant environmental liability.[3,4] The seriousness of the problems led the Department of Defense's Strategic Environmental Research and Development Program (SERDP) and the Environmental Security Technology Certification Program (ESTCP) to convene two workshops 10 and 5 years ago to identify and prioritize critical research needs in this area.[5−7] These needs included documenting and quantifying the performance of source zone treatment technologies, improving source delineation and characterization methods, evaluating the benefits of partial mass removal, developing diagnostic and assessment tools, reducing long-term monitoring costs, predicting groundwater plume responses to source treatment, and developing predictive models and technical guidance materials.

The approach to remediating chlorinated solvent sites has shifted over the last 30 years, from initially using pump-and-treat systems to contain and treat plumes and sources, to deploying more cost-effective plume treatment technologies, and more recently to remediating sources.[2] At the same time, there has been a growing understanding of the limits to restoring complex aquifers to concentrations below drinking water standards (e.g., maximum contaminant levels (MCLs)) and a movement toward a risk reduction paradigm. Several technologies were developed or modified to treat sources, including enhanced extraction from the subsurface through surfactant and/or cosolvent flushing,[8] in situ thermal treatment (ISTT),[9] in situ chemical oxidation (ISCO),[10] in situ bioremediation (ISB), and in situ chemical reduction (ISCR).[11] Recently, research has focused on improving existing technologies, understanding their impacts on the subsurface after treatment, and remediating difficult sites (e.g., fractured bedrock)[12] and persistent contamination, notably low-permeability zones within sites.[13]

Beyond identifying high priority research needs, the SERDP and ESTCP workshops called for an enhanced focus on reducing the uncertainties associated with remediation technology application to source zones and the associated management decisions. These technical uncertainties were believed to lead directly to inefficient use of limited resources.[7] There was a consensus that a greater ability to define achievable performance goals and to develop tools and methodologies to assess performance was critical. There was also a broad consensus that the suite of emerging treatment technologies being directed toward source zones, listed above, needed detailed scientific assessments. It was unlikely that a "new" treatment technology

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would emerge that had not already been considered, but the community needed a better understanding of the field-scale performance of the existing technologies and how site conditions can limit their performance. The community also needed better methods to optimize and monitor the performance of source zone treatment, as well as to quantify the benefits of treatment. This review summarizes the progress in these areas over the past decade, and is structured to highlight the important practical lessons learned for improving DNAPL source zone remediation.

■ RECOGNIZING LIMITATIONS TO TREATMENT

The most important idea to arise from the past decade of research, and the most contentious, has been the recognition that the scientific community may not currently have the ability to develop technologies to restore all contaminated groundwater sites. This remains a source of contention and frustration on all sides: the scientific community, site owners, impacted communities and regulatory agencies. All sides would prefer to implement technologies that will fully restore sites but there is growing recognition that this is not always possible, at least not at a reasonable cost. The following sections summarize lessons learned that expand upon these issues.

Complete Restoration Is Rare, And Credible Metrics for Partial Source Treatment Are Needed. Although complete restoration of some DNAPL source zones and even closure of some chlorinated solvent contaminated sites is possible, it is more common to find that even aggressive treatment leaves some residual contamination.[7,9,14] While field experience has demonstrated that impressive reductions in concentrations and mass are often achieved,[15] the typical criteria required for closure are rarely achieved by any technology.[16]

A review of sources treated by different technologies indicated the median reduction in total chloroethene concentrations in source zone groundwaters (the most common metric) ranged from roughly 60−80% for injection-based technologies (ISB and ISCO), to roughly 95% for ISTT.[17] Residual contamination (residual DNAPL or dissolved contaminants in less transmissive materials) is a particularly challenging issue for injection-based technologies, because flow paths often bypass a significant fraction of the total contamination.[18] Residual contamination is challenging for any technology, since most source zones have groundwater concentrations that are at least 3−4 orders of magnitude above drinking water criteria.

A common strategy is partial source treatment to a level allowing subsequent passive management (e.g., natural attenuation). Measuring the performance of aggressive treatment technologies poses some technical challenges, and useful guidance on monitoring source zone treatments has been developed.[19,20] Regulators as well as practitioners increasingly accept that only partial treatment is inevitable in many cases, and that relying on mass flux data in addition to groundwater concentrations may be helpful when evaluating restoration to achieve a "functional objective" such as natural attenuation.[21] Important tools that can assist in determining when to transition to natural attenuation include the Natural Attenuation Software (NAS) model,[22,23] as well as the model REMChlor, and its modification to allow probabilistic assessments (PREMChlor).[24,25]

DNAPL Source "Architecture" Is an Important Feature Affecting Treatment Performance. Source architecture refers to the spatial distribution of DNAPLs, consisting of both ganglia and pools (quantified as the pool fraction), as well as to the distribution between more and less transmissive zones within the source.[26,27] Source architecture features evolve over time and these transformations will have a significant impact on how sources respond to remedial efforts (Figure 1).

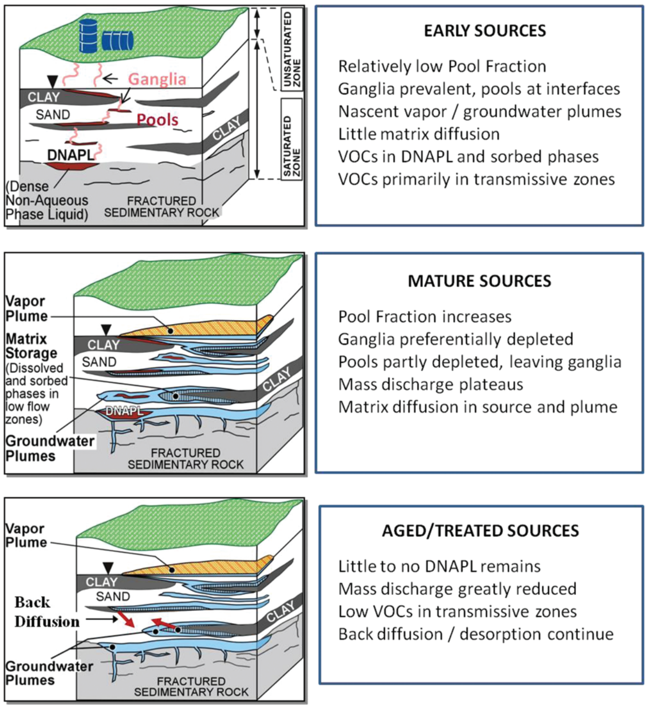

Figure 1. Evolution of a DNAPL source zone and key features of different stages (modified from ref 16).

Consequently, characterizing the architecture is important because it strongly influences the performance of different technologies, and impacts how source treatment will affect the downgradient plume.[18,28] For example, the presence of DNAPL pools largely determines the performance of flushing technologies and ISB.[29] Generally, partial treatment of sources results in ganglia depletion and rapid reductions in concentrations and mass discharge, but concentrations typically reach a lower asymptote and persist because only the more slowly-depleted pools remain. Conversely, treatment of ganglia-dominated sources results in relatively slow reductions in mass discharge until most of the mass is removed, after which concentrations and discharge decline rapidly.[30−32]

Improving source characterization to better describe source architecture has proven difficult. The pool fraction, for example, cannot be determined by conventional characterization methods, and thus this concept has so far had little practical impact on site management. One approach to better architecture definition uses an equilibrium streamtube model that can predict source depletion.[28] The parameters for the model source zone can be determined using partitioning tracers.[33] Another approach being tested is to use push−pull testing with multiple tracers combined with advanced signal processing.[34]

The Distribution of Contaminants between More and Less Transmissive Zones Is Critical. Many sources have aged for decades since the original releases, and during that time contaminants may have migrated and diffused into less permeable zones.[35,36] Back diffusion from these reservoirs can sustain plumes long after the source has been treated, a phenomenon recognized decades ago, though its importance for site management has become more apparent over time.[37] This insight has led to development of a conceptual model that can be useful in describing DNAPL sites because it illustrates potential technology limitations.[16] Known as the 14 compartment model, it describes how the contaminant phase and location (plume versus source) impacts the effectiveness of remedial technologies. Back diffusion can limit performance of any technology based on advective transport (all technologies except excavation and ISTT), as contaminants in less permeable zones may remain untreated. For example, concentrations rebounded after permanganate injection at a fractured bedrock site because the reagent did not reach contaminants in the rock matrix.[38] Current research is focused on developing methods to assess when storage in less permeable regions is significant, and how to manage these sources.

Plume Features Must Be Considered When Making Source Treatment Decisions. At many sites, the response of the downgradient plume to source treatment depends on the plume features, particularly the contaminant mass within the plume and its natural attenuation rate.[39] The mass stored in lower permeability regions downgradient of the source can sustain a plume long after source removal or containment.[16] This plume mass affects the magnitude of any back diffusion, and natural attenuation within the plume is critical if there is remaining contamination. With appreciable natural attenuation, any residual contaminants may be effectively contained or destroyed, greatly decreasing the plume longevity and overall lifecycle costs.[40] Natural attenuation rates can be estimated using software tools, notably the NAS package.[41,42]

IMPROVING CHARACTERIZATION

DNAPL site characterization has always been constrained by the difficulties inherent in working in the subsurface, the temporal and spatial variations in hydrogeological conditions, and the complex distribution of contaminants between phases.[3,16] Improving source characterization—before, during and after treatment—has been a long-standing need.[7] There is a growing realization among regulators and practitioners that the typical level of characterization is often inadequate for delineating and treating DNAPL source zones.[21] For example, several otherwise well-designed treatment systems have had limited success due to poor DNAPL delineation.[43] Recently, mass discharge and mass flux methods have been promoted as useful metrics for source zone remediation, as opposed to relying solely on concentrations or total mass.[44,45] Despite recent improvements in our characterization tools,[46] significant constraints remain and are further discussed in the following sections.

Source Remediation Is Only As Effective As the Source Delineation. DNAPLs are notoriously difficult to locate, and yet the performance of most treatment technologies depends on reasonably precise delivery of remedial agents to the contaminants. Even in situ thermal treatment often leaves residual contamination, because the extent of the source was not identified during site characterization.[43] Several techniques to improve source delineation have been developed and tested, including rock crushing and analysis using intact bedrock cores, membrane interface probes, and chemical sensors combined with direct-push equipment.[46] One notable advance has been development of an optimized source zone search strategy,[47] designed to identify where to initially sample the subsurface to determine the DNAPL source characteristics and optimize the investigative strategy.

Sampling Transects at Relatively High Resolution Can Improve Characterization. Several projects have used transects of multilevel monitoring wells, sampled before and after remediation, to measure the source treatment impacts on contaminant mass discharge and concentrations. Typically, most discharge occurs over a small fraction of the total cross-sectional area of the plume, even in unconsolidated materials.[44,48,49] These detailed observations suggest that remediation can be targeted more effectively if "high resolution" sampling is conducted along one or more transects to define the high-concentration and/or high-flux portions of the plume.[50,51] Transects located immediately downgradient from a source can reveal locations within the source contributing the most to overall discharge. In some cases, this approach also has identified sources not found by using soil borings, drive-point samples, and conventional monitoring wells.[9]

Measuring Mass Flux and Discharge Can Improve Characterization and Monitoring. Mass flux and discharge measurements have proven useful for prioritizing sites, targeting remediation efforts, assessing remediation performance, and determining when to transition from aggressive treatment technologies to more passive, long-term remediation strategies.[51,52] Passive flux meters for unconsolidated and fractured rock systems[53] have allowed better measurements of mass flux and discharge, and guidance on their use[54] and on mass flux data analysis[55] has improved field measurements. Studies of the strengths and limitations of different flux measurement methods have led to guidance on methods and data interpretation,[52] and on estimating and managing the uncertainty involved.[56]

Mass discharge reductions of roughly 1 to 2 orders of magnitude are common after source remediation.[8,49,52] Discharge and flux measurements provide credible assessments of performance and source status, and thereby lead to better-informed decisions than relying on concentration data alone, especially at DNAPL sites.[30] Mass discharge can be linked directly to natural attenuation rates, for example, or to the risks posed to downgradient receptors.[46]

ENHANCING TREATMENT

As noted previously, there has been a broad consensus over the past decade that the treatment technologies currently in use are sufficient for effective DNAPL source zone management. However, to some extent, the performance of these technologies is limited by a lack of mechanistic understanding of the technologies and by an insufficient grasp of their limitations. Results from the field-scale demonstrations performed to date indicate that reductions of 90−99% or more are possible, though reaching MCLs is rare (Figure 2). These results reflect the difficulties in both characterizing and treating source zones, but they also suggest that the major technologies can be further improved. The following sections provide lessons learned on the major remedial technologies, including natural attenuation, in situ bioremediation, thermal treatment, ISCO and ISCR, and the potential for improving these technologies.

The Natural Attenuation Rates of Source Zones Can Be Estimated from Field Measurements. The mass of contaminants in the source, and the mass discharge to the plume (the source strength), will decline over time due to dissolution, degradation, and volatilization. Empirical studies suggest that the rate of chlorinated solvent source attenuation can be meaningful (e.g., half-lives of a few years).[57] This source zone natural attenuation (SZNA) can be critical when making

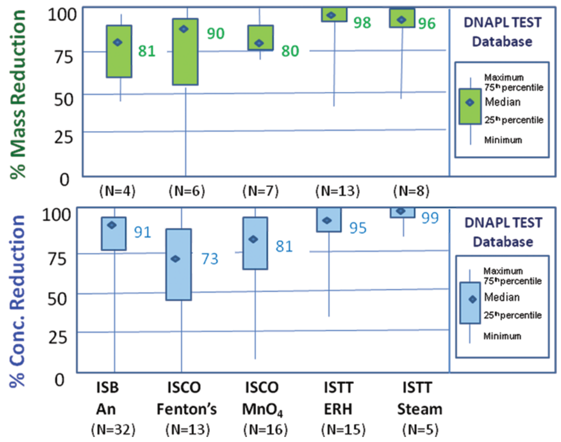

Figure 2. Field-scale performance of the major source zone remediation technologies (Anaerobic ISB, ISCO with Fenton's Reagent or permanganate, and ISTT by electrical resistance heating or steam injection). Median values, percentiles, and ranges are shown for each technology. Results are taken from analyzing all chloroethene-contaminated sites with relevant data in the DNAPL Technology Evaluation Screening Test database.[133] Reductions in total chloroethene source mass and average concentrations (including daughter products) within or immediately downgradient of the source are plotted. *N* = number of case studies used for each technology and metric.

management decisions, particularly at complex sites. Decision makers need to know the rate at which SZNA is occurring, what natural processes are responsible, and if SZNA processes and rates are sustainable.

ISB is Relatively Slow But Can Be Effective and Economical. Initially ISB was considered a plume treatment technology only, but it has proven effective for treating some sources.[58] ISB enhances the destruction and removal of contaminants through the addition of electron donors to stimulate reductive dechlorination.[59−61] Combinations of ISB with other, more aggressive, technologies are particularly attractive, as discussed in later sections.

Despite initial skepticism regarding ISB's ability to treat sources, data mining shows that ISB is as effective as other injection-based technologies, and less expensive.[17,62] ISB is probably not appropriate for sources with significant separate phase accumulations of DNAPL,[62] but it can enhance dissolution rates during treatment and thereby reduce groundwater concentrations after treatment.[63] Dissolution enhancement factors of 2−4 have been observed in unconsolidated materials[64] and in fractured bedrock.[65] ISB can cause reductions of 1 to 2 orders of magnitude in chlorinated ethene concentrations within and downgradient from the source, for extended periods of time.[17] In one field test, a single edible oil injection produced almost 90% reductions in total molar concentrations, with evidence that treatment was improving after 1 year.[66]

Whether concentrations will rebound eventually is unclear, but sustained treatment for at least 3−5 years seems common. Reasons likely include the slow decay of biomass built up during the active remediation period,[67] diffusion of electron donors into the matrix, and formation of reduced iron minerals capable of later dechlorination.[68,69] One potential improvement is the use of "partitioning electron donors" (such as n-butyl acetate) that can partition into the DNAPL phase and then slowly dissolve at rates similar to the DNAPL constituents, thereby providing long-term rebound control after a single injection.[70]

Bioaugmentation Can Improve Source Zone Remediation by Reducing Lag Times and Costs. Bioaugmentation is particularly attractive for source zone ISB because the overall costs are higher than for plumes (especially if recirculation is used) and concerns over VC accumulation may be greater because the concentrations are higher. Early performance optimization is critical, and bioaugmentation can improve initial performance even when competent *Dehalococcoides* are naturally present and sufficient electron donor is available.[71] Bioaugmentation was controversial before the 2000s, but experience has demonstrated its benefits for source treatment. This experience has led to models useful for designing bioaugmentation systems,[72] a summary of the state of the practice of bioaugmentation,[73] a review of the lessons learned from field experience,[74] and a bioaugmentation monograph.[75]

ISB Secondary Effects Persist For Several Years In Treated Source Zones. ISB can cause undesirable side effects, notably pH decreases, methane generation and increases in dissolved metals (especially Fe and As).[76] These effects can persist for several years within the reaction zone, but generally return to near-baseline conditions within a short distance downgradient from the source.[62] While site-specific concerns over secondary impacts remain, and should be considered in design,[77] ISB has been rapidly adopted and such impacts have rarely limited its use.[62] Guidance is available to help understand potential secondary impacts and design appropriate loading rates to minimize these problems.[78]

ISB May Be Attractive for Treating Residual Contamination and Low-Permeability Zones. As discussed earlier, low permeability zones are a critical complicating factor for chlorinated solvent sites. Treating residual contamination in low-permeability zones within either the source or the plume may be both costly and difficult. Such "polishing" may differ from more typical source zone treatments, since most technologies will treat the most transmissive zones preferentially. Although electron donor distribution is generally limited to more transmissive zones, ISB has promise to treat less accessible regions because some donor materials (vegetable oil, for example) can persist and diffuse into less permeable materials over time. ISB is a promising approach to manage the slow release from less transmissive regions because of the long-lived effects of ISB treatment.[17,67,68] In fact, ISB may be well-suited for treating less permeable regions, given the low influxes of oxygen and other electron acceptors and the potential for electron donors to diffuse into these regions. Finally, coinjection of shear-thinning fluids like xanthan gum could improve delivery by increasing the flow of injected fluids into the less transmissive zones.[79]

Thermal Treatment Can Be Effective, Though It Is Expensive and Still Has Technical Limitations. ISTT has been rapidly developed and adopted as a source remediation technology. Three primary approaches have been commercialized—steam injection, electrical resistance heating (ERH) and thermal conductive heating (TCH). ERH and TCH are particularly attractive for treating sources in less permeable materials or in fractured media, where other technologies face serious delivery challenges. In contrast, steam injection relies on advection for delivery and is more appropriate for higher permeability media; it may be coupled with ERH or TCH to effectively treat heterogeneous sites containing both high- and low-permeability media.

Thermal treatment is capable of removing the vast majority (>99%) of the contaminants from even heavily contaminated sources, but real-world performance is often less impressive, and the costs are higher than for most other in situ technologies.[9,80,81] However, even when the entire source zone is treated, a small fraction of the contaminant mass may remain after treatment, especially at challenging sites (e.g., fractured bedrock). For example, a recent field demonstration of TCH for treating fractured bedrock measured extensive but not complete removal of contaminants (roughly 90%), although earlier laboratory testing indicated that complete removal is possible under ideal conditions.[82]

Key limitations to ISTT's performance include the cooling effect caused by locally rapid groundwater fluxes (so that portions of the treated zone remain too cool for effective treatment), and retention of some fraction of the contaminant mass in lower-permeability materials.[83] Research also has shown that ISTT is primarily due to steam-distillation (coboiling of water and NAPL), so there is little destruction in situ and vapor extraction is required.[8,83,84] Finally, simulations of contaminant removal with different thermal treatment strategies suggest that ISTT may remove more mass if two or more separate rounds of heating are employed, and that the temperature may need to exceed the boiling point of water in low-permeability materials because the boiling point increases as the matrix vapor pressure increases.[85]

Thermal Treatment Can Be Compatible with Other Technologies. Several combinations of ISTT with other technologies have been proposed. For example, ISB after ISTT is feasible, because key microorganisms, including *Dehalococcoides* spp., can quickly recolonize the subsurface.[86,87] There may be a delay, but appropriate microorganisms can be added or become reestablished naturally. In fact, ISTT may increase levels of readily available carbon, stimulating subsequent dechlorination and reducing the competition for electron donors. Low temperature treatment may be combined with ISB, because microorganisms can degrade contaminants at moderate temperatures (<40−45 °C), although little biotic or abiotic destruction of chloroethenes normally occurs at temperatures above 50 °C.[84] Another possibility is to combine ISTT with chemical reduction. Addition of reactive amendments such as zerovalent iron (ZVI) during thermal treatment can increase the rates of contaminant recovery from slowly desorbing soil fractions.[84] Initial results from field testing of low-energy ERH with ISB and ISCR (ZVI injections) suggest both combinations can be economically beneficial.[88]

ISCO Rapidly Destroys Chloroethenes But Has Important Limitations. Prior to 2000, research and practice had shown that ISCO was effective for treating dissolved and sorbed phase organics rapidly. Although the applicability of ISCO for treating DNAPL source zones was not demonstrated, there were claims of effective remediation. Catalyzed hydrogen peroxide (CHP), potassium permanganate, and sodium persulfate are the most commonly used oxidants, although others have also been used.[89−92] ISCO is attractive because it provides rapid in situ destruction, but rebound and incomplete treatment have been consistent problems.[17,89,93]

ISCO has been marginally successful for chloroethene source treatment. Key limitations have been delivery difficulties, frequent concentration rebounds following treatment, and relatively high costs.[43,63,93] Rebound has been observed in several studies, and has been attributed to several factors, including (1) reactants are short-lived and thus do not reach contaminants in low permeability matrices; (2) natural attenuation processes may be disrupted by reducing bacterial populations or oxidizing fermentable carbon; (3) sorbed contaminants may be released following oxidation of natural organic matter.[89] A recent survey of ISCO applications found no DNAPL sites that had reached MCLs or closure, with average reductions in maximum concentrations of 55% and a median cost of $94/cy.[93] Nevertheless, ISCO continues to be used for source treatment, because it offers rapid mass and concentration reductions, and does not require aboveground treatment. A recent *Technology Practices Manual* has been published to provide guidance on ISCO applications,[89] and guidance on injecting amendments, including oxidants, has been developed to evaluate key design variables for site-specific applications.[94]

Improvements in ISCO May Increase Its Effectiveness for Source Zone Treatment. Improvements in ISCO formulations include development of CHP and activated persulfate.[95] Also, techniques have been developed to stabilize hydrogen peroxide through additions of organic acids (e.g., phytate), allowing the oxidant to persist longer and move further downgradient.[96] Activated persulfate has recently become widely used because it can treat a wide range of contaminants, and it is relatively stable and nonreactive with natural organic matter (NOM). However the fundamental limitations of cost, rebound and delivery remain.[89] Fractured matrices can be particularly difficult to treat effectively with ISCO.[97] Another issue with the most-used oxidant, permanganate, has been the formation of manganese dioxide (MnO_2) precipitates, which can impact the flow regime, and form "rinds" around DNAPL accumulations.[98] Research has addressed controlling MnO_2 particle formation (by adding stabilizing agents) and improving delivery to lower-permeability zones (by adding water-soluble polymers).[99]

ISCO Can Be Used with Other Technologies, But Its Secondary Effects Must Be Considered. Most ISCO source zone efforts require multiple treatments,[93] so it is particularly important to understand ISCO's post-treatment impacts. These impacts include oxidizing the NOM and native metals and partially sterilizing the subsurface, but research examining the coupling of ISCO with bioremediation and surfactant flushing indicate such impacts are generally minor. In fact, ISCO may improve later bioremediation by increasing dissolved organic matter content.[100] Testing of sequential treatment using ISCO initially followed by ISB suggests that this combination could be less expensive than ISCO alone.[101] However, permanganate treatment increased the overall electron donor demand, and Mn reducing bacteria used hydrogen to reduce the MnO_2 precipitates formed during ISCO, thereby inhibiting later dechlorination. One notable example of combining ISCO with other technologies is heat-activated persulfate,[102] which can increase chloroethene removal during thermal treatment by increasing the accessibility of the contaminants.[103] All these studies indicate that ISCO is compatible with other technologies, and that its secondary effects can be managed with careful design.

Injection-Based ISCR Has Significant Limitations As a Source Treatment Technology. In situ chemical reduction (ISCR) occurs naturally, as Fe(II) minerals can degrade chlorinated ethenes without harmful intermediates, but this process has not been used for source treatment.[69] Engineered ISCR is a proven plume treatment technology, based on the use of ZVI in permeable barriers,[104,105] but the microscale ZVI used for barriers is difficult to distribute effectively during injections, so it is rarely used to treat sources except in combination with ISB. One approach to using ISCR for source remediation is subsurface mixing, a process using large (up to 12 ft diameter) augurs to mix the source zone and simultaneously inject ZVI and clay.[106]

Another approach is to inject nanoscale ZVI (nZVI) because it is highly reactive (due to its high specific surface area) and should move further in the subsurface than microscale ZVI.[107] Rapid reductions in chloroethene concentrations have been observed in field-scale tests of nZVI injections.[108] However, the particles tend to agglomerate rapidly after injection, clogging pores and limiting migration. This agglomeration, along with the rapid evolution of hydrogen after injection, can lead to flow bypassing the injected material, so research has focused on improving nZVI delivery. Material costs and environmental concerns regarding nanoparticles may also limit nZVI use.[109]

One approach to improve nZVI delivery is to modify the surface properties of the particles to reduce agglomeration.[110] Surface-modified nZVI migrates further through subsurface materials, based on large-scale column testing,[111] but the amounts required for treating most source zones appear costly compared to other technologies. Also, the mass of nZVI needed may cause pore clogging eventually, thereby precluding the multiple injections needed for effective treatment. Another approach to increase subsurface transport is to inject oil-in-water/nZVI emulsions.[112] The nZVI can retain reactivity within such emulsions,[113] but again the costs may be high. For both approaches, it appears that nZVI treatment is more appropriate for source containment (i.e., injection immediately downgradient) than for direct DNAPL treatment.[114]

ISCR May Be Combined with Other Technologies to Provide Effective Source Treatment. ISCR has been proposed for combination with ISTT[115] and ISB.[116,117] Combinations of ZVI with electron donors such as lactate or emulsified oil are commercially available (the latter is known as emulsified ZVI, or EZVI). Such products offer the potential for rapid chemical degradation of the most accessible contaminants (and other electron acceptors) combined with longer-lasting bioremediation. A field demonstration of EZVI showed it can be effective, given adequate delivery.[118] The effects of nZVI on biogeochemistry and indigenous microbial populations appear minimal, and in fact nZVI additions may result in sustained reductions in the oxidation−reduction potential that can enhance subsequent anaerobic biodegradation.[119]

Surfactants and Cosolvents Have Not Been Adopted As Stand-Alone Technologies. Surfactant and cosolvent flushing can be highly effective under controlled laboratory conditions, but field-scale applications have yielded mixed results.[120−122] Well-controlled field-scale tests of surfactant flushing indicate that DNAPL recoveries in the range of 60−70% can be expected,[46,123,124] and that mass recoveries of greater than 90% are achievable.[125−127] However, costs of active ingredients can be substantial, and as with all flushing-based technologies, flow bypassing can limit mass recovery at heterogeneous sites. One potential solution for minimizing flow bypassing is the use of foams such as those used in enhanced oil recovery.[128] Furthermore, above-ground treatment, recycling and/or disposal of the extracted effluent waste stream can be problematic and expensive. For these reasons, recent activities have focused on coupling surfactants and/or cosolvents with other technologies (e.g., ISCO), rather than a primary, stand-alone source treatment technology. Coupling surfactants with ISB as a polishing step holds promise,[129,130] and coupling surfactants with ISCO to improve oxidant delivery has been demonstrated and used commercially.[131,132]

SUMMARY

The past decade has seen rapid progress in source zone remediation, and an increasing understanding of the capabilities and limitations of potential technologies. Research has produced a large database from well-monitored demonstrations, more effective models to improve decision-making, and a better understanding of the physical, chemical, and biological constraints to achieving complete restoration. This experience has led to technology selection guidance to help managers develop reasonable expectations for treatment.[133] It also has led to several publications from researchers funded through SERDP and ESTCP on source zone treatment (including technology-specific cost and performance reports), available at http://www.serdp-estcp.org/Featured-Initiatives/Cleanup-Initiatives/DNAPL-Source-Zones.

Experience also has shown that different technologies are needed for different times and locations, and that deliberately combining technologies may improve overall remedy performance. Guidance on adaptive management and integrated strategies for DNAPL sites has been developed to help practitioners select the best combinations and develop realistic objectives.[52,134] Such guidance should improve source treatment and save money, through more cost-efficient characterization and monitoring, more efficient and appropriate uses of remedial technologies, and greater consensus on source treatment decisions.

Challenges remain, however, particularly at complex sites that are difficult to characterize and where prolonged treatment and/or multiple technologies have failed to achieve remedial goals. Many DNAPL sites still cannot be restored to regulatory criteria within a few years or within a "reasonable time frame" (often considered roughly 30 years), and therefore will require long-term management.

AUTHOR INFORMATION

Corresponding Author

*Phone: 541-482-1404; fax: 703-471-4180; e-mail: hstroo@hgl.com.

Notes

The authors declare no competing financial interest.

Biography

Hans Stroo is a principal technical advisor with HydroGeoLogic, Inc. and technical advisor to SERDP and ESTCP. Andrea Leeson is a program manager and Jeffrey Marqusee is executive director for SERDP and ESTCP. Paul Johnson is a professor at Arizona State University and dean of the Ira A. Fulton Schools of Engineering. C. Herb Ward is the Foyt Family Chair of Engineering at Rice University. Michael Kavanaugh is a principal scientist at Geosyntec. Tom Sale is an associate professor at Colorado State University. Charles Newell is a vice president and environmental engineer at GSI, Inc. Kurt Pennell is chair of the Department of Civil and Environmental Engineering at Tufts University. Carmen Lebrón is an environmental engineer with the U.S. Naval Engineering Services Center. Marvin Unger is a principal scientist with HydroGeoLogic, Inc. and technical advisor to SERDP and ESTCP.

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