

Technology Assessment for Remediation at Solvent Contaminated Drycleaner Sites

Project Management/Technical Issues Subgroup – State Coalition for Remediation of Drycleaners

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INTRODUCTION

Soil and groundwater contamination is an ongoing problem in the United States, especially in areas that rely on groundwater for their drinking water source. Drycleaners are sources of contamination that are typically associated with urban areas, but the impact of contamination from a small town drycleaner can have a devastating effect on a community's ability to provide a safe drinking water supply to its residents.

The Environmental Protection Agency's Technology Innovation Office (EPA TIO) brought together states with drycleaning solvent cleanup programs to share information regarding administration and implementation of their programs. The resulting organization is the State Coalition for Remediation of Drycleaners (SCRD), which is composed of thirteen member states and several associate member states that are considering cleanup programs or are very active in drycleaner remediation through another state program. The member states include: Alabama, Connecticut, Florida, Illinois, Kansas, Minnesota, Missouri, North Carolina, Oregon, South Carolina, Tennessee, Texas and Wisconsin. Associate states include: California, New York, and Virginia.

This remediation paper will discuss the general drycleaning process, how contaminants can get into the soil and groundwater, assessment methods including the impacts of chlorinated drycleaning solvents in the soil and groundwater, and remediation methods commonly used to clean up the lingering contamination. The remediation methods will be based on a snapshot of the remediation technologies that have been used at drycleaning sites under the oversight of SCRDR member states as of March 2005. This paper is intended to provide background information on the technologies that have been used at chlorinated solvent sites to aid those conducting remediation at similarly contaminated drycleaning sites. The paper will not address remediation of petroleum-based drycleaning solvents, as those are amenable to the wider range of remediation technologies commonly used at petroleum sites, such as gasoline stations. Because remediation technologies are constantly evolving, the reader is urged to research and review the latest pros and cons of any new technology prior to selecting a remedy for a site.

OVERVIEW

Why dry cleaners?

Soil and groundwater contamination by drycleaning solvents is widespread in both urban areas and small town America. A recent study conducted by the State Coalition for Remediation of Drycleaners (Schmidt, 2001) estimates that 75% of the drycleaning facilities in the United States are contaminated. The contamination often came from industry accepted practices rather than the typical spill or release common with other types of contaminated sites. One of the most common site-specific sources of contamination was the discharge of separator water into the sanitary sewer system and the subsequent leakage of the dissolved phase or solvent through leaky sewer lines. The drycleaning industry and state environmental programs have since learned that enacting pollution prevention programs can greatly reduce the potential contamination, even though the type of solvents are commonly the same as those used in the 1960s.

In 1994 legislation was introduced in several states to create drycleaning solvent cleanup programs to address the contamination. Often the legislation was introduced by the drycleaning industry and supported by the state's environmental agency. Many state drycleaner programs included pollution prevention as a regulatory requirement.

Drycleaning Solvents, Wastes and Waste Management Practices

The solvents historically used for drycleaning are often divided into two general classes, petroleum solvents and chlorinated solvents. Other types of solvents, such as carbon dioxide and Green Earth (silicon-based solvent) are also available. Petroleum solvents that have been used in drycleaning operations include naphtha, benzene, white gasoline, Stoddard solvent, 140 flash solvents, and the newer high flash point synthetic petroleum solvents. Chlorinated drycleaning solvents include carbon tetrachloride; 1,1,1-trichloroethane; 1,2-trichloro-1,2,2-trifluoroethane; trichloroethylene (TCE) and perchloroethylene (aka: tetrachloroethylene, perc, PCE). In the early 1960s, PCE displaced petroleum solvents and other chlorinated solvents as the most widely used solvent in drycleaning operations in the United States. PCE currently accounts for approximately 80% of the solvents used in drycleaning operations (HSIA, 1999). PCE's cleaning abilities have led to its long-lasting use.

Chlorinated solvents used in drycleaning operations are considered hazardous chemicals that are historically known as recalcitrant compounds that are exceedingly difficult to remediate unless the conditions are ideal for remediation. Under certain conditions, chlorinated compounds will degrade, but the degradation products may be more toxic than the parent solvent, as in the case of PCE degrading to TCE or vinyl chloride. Chlorinated solvents are “dense non-aqueous phase liquids” (DNAPLs), which are heavier than water.

Many of the waste streams generated by drycleaning operations are now classified as hazardous wastes and therefore subject to waste disposal regulations. Prior to the promulgation of the Resource Conservation Recovery Act (RCRA) in 1980, there effectively were no regulations governing these wastes. Often the state drycleaning programs regulations are more stringent than the current RCRA regulations. Wastes from drycleaning operations include, but are not limited to distillation residues (still bottoms), spent filters, separator water, vacuum water (press return water), lint, and pre-cleaning/spotting wastes. Wastewater from conventional laundry operations may contain solvents if clothing is pre-cleaned or spot cleaned prior to laundering. Even water from mopping floors inside drycleaning plants may collect significant amounts of solvents.

Historical drycleaning waste management practices have included discharging drycleaning wastes to sanitary sewers, septic tanks, storm sewers, floor drains, blind drains, lint traps, surge tanks, and dumpsters, as well as directly to the ground. These practices have resulted in widespread contamination of soil and groundwater in urban areas and impacts to drinking water aquifers. In addition to contamination associated with waste disposal, solvents have been released to the environment during solvent delivery, transfer and storage (hose coupling failures on tank trucks, leaking storage tanks, overfilling of tanks and machines, etc.), and drycleaning equipment operation and maintenance (boil-over of distillation units, leaking drycleaning machine valves, gaskets and fittings, spillage during filter changes, pump maintenance, distillation unit cleanouts, etc.).

Conducting Contamination Assessments at Drycleaning Sites

A thorough site assessment builds the foundation for a successful remedial action. This is particularly true with sites that are contaminated by chlorinated solvents. A small amount of

residual DNAPL solvent missed during the assessment can continue to feed a dissolved plume for years to come. This can have the effect of masking whether the selected remedy is in fact effective for a site. For a complete discussion of the complexities of environmental investigations of drycleaning sites see the SCRD companion paper, **Conducting Contamination Assessment Work at Drycleaning Sites** available at <http://www.drycleancoalition.org>.

In general, chlorinated solvent plumes are deeper and cover larger areas than many other types of contaminant plumes due to the recalcitrant nature of the contaminant. Therefore, the costs to conduct a thorough contamination assessment are generally higher at chlorinated solvent sites than at other contaminated sites. The drycleaning contaminant plumes almost invariably extend off the property where the drycleaning business is/was located and offsite access for assessment is often problematic.

It is not uncommon for other drycleaning facilities to be located in close proximity to the drycleaning site being investigated. Co-mingling of solvent plumes can occur and it may be difficult, if not impossible, to determine which drycleaning operation is associated with a particular portion of the plume. Although drycleaners are generally thought to be responsible for chlorinated plumes, other nearby businesses may have also used chlorinated solvents. Uniform rental/linen supply businesses, auto-repair facilities, paint dealers, furniture strippers, power stations, boat dealerships and elevator service companies have historically used some of the same solvents common in drycleaning operations. The printing and publishing industries, for example, have used PCE, TCE, 1,1,1 trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane and mineral spirits, all of which have also been used as drycleaning solvents.

The necessity of installing a remedial system can generally be determined early in the site assessment process. Given this fact, the type of data necessary to choose and design a remedial system should be collected during the site assessment, whenever possible.

Difficulties Associated with Drycleaner Remediation

Drycleaning facilities are commonly located in commercial areas and surrounded by other buildings and infrastructures. Utility lines and foundations can act as preferred pathways for movement of dissolved phase contamination or DNAPL. Remediation systems that can be

implemented at a remote site may not be feasible or publicly acceptable for drycleaning sites located in a thriving commercial setting.

Common locations for drycleaning businesses are in shopping centers or strip malls in a mixed retail commercial/residential setting. These strip malls and shopping centers contain active businesses, some of which are open seven days a week. Scheduling the installation of a remedial system or performing system maintenance must be carefully planned and conducted to minimize any disruptions to ongoing business. In some cases, some of the work must be conducted during non-business hours (nights and weekends). This results in increased costs and raises safety issues.

If the drycleaning business is no longer active, the new site business owner may have little interest in cooperating with the remedial contractor. Establishing and maintaining a good working relationship with business owners and the real property owner is a necessity. Active drycleaning businesses can be continuing sources of contamination so regulatory compliance is critical in order to achieve site cleanup.

Choice of a remedial technology may be limited by the available space for the system, the configuration of utilities, the proximity to residential areas and municipal and county building codes. Drycleaning businesses located in freestanding buildings on small tracts may have limited customer parking space so the business owners/operators are generally not inclined to allow installation of a large remedial system or an infiltration gallery in a parking lot. Noise restrictions in municipal codes may require soundproofing or silencing remedial equipment. Additional soundproofing may be demanded by nearby residents in some areas. In situ remedial treatment reactions that generate heat or gases may not be appropriate remedies at these sites.

Obtaining construction and operation permits from municipal and county authorities may result in long delays in remedial system installation. Local governments may have overly prescriptive requirements about the types of structures that are allowed on a property and may require enclosing remedial systems in structures that may substantially raise the installation costs. A good relationship with the local regulators and knowledge of the local permitting requirements can be invaluable for facilitating installation of the selected remedy.

It is rare to find suitable “as-built” construction drawings available for a facility. Even when they exist, all utilities should be marked and any excavation should proceed with the utmost caution. Unexpected events such as encountering abandoned utility lines often occur during installation of remedial systems in urban environments or when working in and around older buildings. Having the suitable equipment on-hand and contingency plans developed for likely scenarios can drive up the remedial costs.

Many shopping centers and strip malls are constructed on fill material that may be different from native soils. Remedial systems may fail unless a sufficient number of lithology borings have been done that fully characterizes the site. The fill material can also serve as a preferred pathway for the contamination, including a source for ponding solvent or dissolved phase liquid in the slab sub grade. Remediation of permeable sub-slab sediments using vapor extraction can help remove large amounts of contamination, as well as control vapor intrusion from the contamination.

Selection of Remediation Technologies and “Treatment Train Remediation”

Consultants and responsible parties often agonize over which technology will be the most cost effective, yet still meet the cleanup goals. Cost is a key factor in the selection of a remediation system because securing and budgeting funding is a serious problem that requires innovative uses of technologies to address and resolve the contamination issue. Often a single remediation technology is unable to adequately remediate a site’s contaminated soil and/or groundwater to below acceptable levels. Some technologies are not able to completely remove DNAPL or highly concentrated groundwater contamination. Other systems can remove large amounts of contaminant mass, but can’t reduce the concentrations below the regulated “action levels”. Sites may have multiple contaminants that cannot be remediated by a single technology. The ultimate remedy for many sites will be a combination of more than one technology in an approach known as a “treatment train”.

The treatment train approach uses multiple technologies to clean up contaminants over a period of time. For example, the initial phase of the treatment train may inhibit downgradient contaminant migration using permeable reactive barriers or pump & treat. This initial phase may be necessary to protect a sensitive receptor, such as a drinking water well or industrial well for

food processing or subject to human contact. The next phase may be responsible for removing large amounts of mass at a source area or “hot spot”. Another phase may then attack the remaining source area contamination. Source area remediation is vital to help reduce the length of time for complete remediation. A final remedial phase may implement monitored natural attenuation or institutional controls after the contaminant plume has stabilized or contaminant concentrations have been reduced.

Improper use of the treatment train approach can also cause problems if an earlier phase of remediation leaves the site unsuitable for a follow-up phase. For example, some chemical oxidative methods may leave a site temporarily unsuitable for bioremediation. Time usually heals most wounds at remediation sites, but consideration prior to implementation can help guide the way through the treatment train approach and alleviate problems in the long run.

The remedial technologies discussed in this paper have been loosely grouped into three major categories of physical, biological, or chemical based on their primary mode of action. The reader should remain cognizant that some remedial technologies do not fit snugly into these categorizations, but instead have multiple modes of actions. For instance, some physical removal methods enhance biological processes that already are underway on a site and some of the biological methods have significant chemical interactions.

The methods that are discussed in this paper reflect the “Lessons Learned” from drycleaner sites remediated by SCRD project managers. No endorsement of any particular technology is implied, nor should it be assumed. Our discussions do not include the level of detail necessary for design and implementation, but rather present an overview of the technology as used at drycleaning sites across the country. Many of the lessons learned are documented in site profiles can be found on the SCRD web site at www/drycleancoalition.org under the “Site Profiles” section.

Site Closure

The ultimate goal of any remediation is to close out the site because the levels of contamination have been reduced to acceptable levels. In some states, this can only be achieved by complete removal of all contamination from the environment or reductions of concentrations in soil and/ or water below state promulgated criteria. In other states, drycleaning sites can be granted a “No Further Action” status with levels of contamination left in place if it can be shown that the risk to human health and the environment is acceptable. In these states, this can be accomplished through “Monitored Natural Attenuation”, use of “Institutional Controls” or a combination of the two.

Monitored Natural Attenuation

Natural attenuation occurs through various physical, chemical, or biological processes that reduce the amount, toxicity or mobility of contaminants without any human intervention. Monitored natural attenuation (MNA) is a procedural regimen that documents whether these processes are adequate to control the contamination to protect public health and the environment. MNA policies in each state vary with regards to the assessment, monitoring, and plume characteristics. In order to qualify for MNA in some states, a site may require a more rigorous site investigation than sites that receive active remediation. Prior to enrolling a site in MNA, long-term monitoring must usually be performed to document that attenuation mechanisms are underway at the site so the plume is stable or reducing in size so the contamination is unlikely to spread to receptor locations. Therefore, it is necessary to develop a strong understanding of the site-specific hydrogeology, use of the regional aquifers, and lithology (including the distribution and competency of confining units).

Typically, sites enrolled in MNA programs are required to continue monitoring on specific time schedules to track changes in the contaminant concentrations. Analytical parameters routinely include testing of the geochemical processes that are indicative of biotic and abiotic destructive processes. These geochemical parameters commonly include measurement of Redox potentials, dissolved oxygen, alkalinity, ferrous iron, sulfate, nitrate,

methane, and organic carbons. Other analytical parameters that are useful, but less frequently analyzed, include measurement of ethane, ethene, carbon dioxide, and free chlorides.

Chlorinated hydrocarbons can degrade naturally under a variety of environmental conditions. The most important process affecting PCE is reductive dechlorination (where the chlorinated compound serves as an electron acceptor); however, some of its daughter products are subject to oxidation (where the chlorinated compound serves as an electron donor). The environmental conditions that support natural attenuation processes for chlorinated compounds (particularly reductive dechlorination) include:

- Microorganisms capable of degrading the contaminants

- Oxidation-reduction (Redox) capacity of the groundwater

- Sufficient electron donors (e.g., a carbon source)

- Absence of competing electron acceptors

If the geochemical and Redox environment indicates that reductive dechlorination is unlikely (i.e., aerobic conditions, abundance of electron acceptors, ferrous iron and/or methane are absent, etc.), oxidative degradation of lower chlorinated compounds can still occur. Vinyl chloride and cis 1,2-DCE can be degraded through oxidative or abiotic processes. Geochemical footprints for oxidation of chlorinated hydrocarbons include loss of electron acceptors (such as nitrate) and elevated alkalinity and chloride anions.

The existence of degradation patterns (geochemical footprints) indicates that certain microbial processes are likely occurring in the groundwater; however, this does not necessarily mean that natural attenuation processes control the contaminant plume. Incomplete degradation can lead to accumulation of daughter products that may be more toxic than the parent compound. Even if degradation products are present, it is still possible for the contaminants to move with the groundwater flow beyond zones of high carbon content. This is why proper monitoring over time along with a thorough understanding of a site's hydrogeology is critical to remediating chlorinated hydrocarbon contamination.

Most sites contaminated with chlorinated hydrocarbons will require active remediation for source reduction and perhaps for plume control. MNA is more likely to be successful when

used as part of a comprehensive site cleanup, rather than as a sole remedy, at most chlorinated hydrocarbon sites.

Institutional Controls

An institutional control is an administrative mechanism that allows contaminants to remain on a site in excess of applicable cleanup criteria. Institutional controls come in many forms; all place legal restrictions on subsequent use of properties that have not been completely cleaned of contamination. Institutional controls are designed to prevent exposure to the contamination that remains by restricting certain uses of the affected property.

Some states allow a site to be cleaned up to less stringent standards based on the potential use of the affected natural resources and either the current or future use of the property. While the levels of contamination are determined to be safe for the intended use, the concentrations left on the site will exceed the state's cleanup criteria for unrestricted residential use of the property. Therefore, institutional controls become a key element in ensuring that the land use does not significantly change from the scenario used in making the cleanup decisions. An institutional control, such as a deed restriction specifying the allowable uses of the property, may be recorded in the property title records and may be legally binding on subsequent property owners.

In the broadest sense, institutional controls also include local/county zoning ordinances, restrictive covenants, easements, and etc., since these often restrict potential exposure pathways or uses of the property. Other institutional controls may include legally enforceable contracts to ensure that the owners or developers of the property maintain engineering controls, such as a cap placed over the residual contamination, to prevent future exposures to the contaminants. Unlike MNA, institutional controls usually do not have requirements for continued monitoring to verify the contamination levels remain at or below the levels that were determined to be safe for that use of the property.

Oversight of institutional controls can be problematic for drycleaning sites because they tend to be located in areas that have commercial and residential redevelopment potential. New owners of properties often do not feel bound by contracts of previous owners and may alter the engineering controls that restrict access to the contaminant. Local government bodies may change the zoning ordinances and restrictions on which the state drycleaner program based the

assumptions about exposure to the contamination. Because of these and other perceived problems with reliance on institutional controls as a remedy for the site, some states require that contingency remedial action plans be developed for the site to include additional remediation in the event that the institutional controls cease to effectively control exposures to the contamination.

Some state drycleaning programs do not have the necessary staff, finances, or mechanisms to track their sites that rely on institutional controls as part of the remedy. In these states, there is less reliance on institutional controls and more emphasis on active remediation of all contaminants to the levels deemed acceptable by the state for unlimited use. Some states have passed legislation to implement Environmental Use Control Programs specifically to track institutional controls. Inter-program cooperation may become necessary to ensure the sites meets both program's regulations.

PHYSICAL REMOVAL METHODS

Physical Removal Overview

This section discusses methods that physically remove the contaminants from soil or groundwater. The objective of physical removal is to rapidly remove as much of the contaminant mass from soil and groundwater to prevent continued release of residual or free-phase NAPL contaminants. The removal will help restrict the spread of the contaminant mass to off-site receptors.

Some the physical methods exploit the propensity of volatile organics to evaporate off of a source. With these methods, carrier gases (usually just atmospheric air) are moved by mechanical means over the contaminant source area through various injection and recovery points. Usually, the removed contaminants are subjected to ex-situ treatment or/and disposal. However, depending on the regulatory jurisdictions, some of the contaminant mass may be allowed to off-gas into the atmosphere where photolytic processes degrade the contaminants. Other methods may allow a dilute contaminant waste stream to discharge to surface water or treatment plants, where natural processes quickly degrade the volatile compounds.

Unlike the chemical or biological methods discussed elsewhere in this paper, there is no net loss of the contaminant mass. Instead, the contaminant mass is removed directly from the source for treatment and/or disposal off-site, or the contaminant is transferred to another media (either air or water) and is removed from the source area. Physical methods may enhance the action of biological or chemical methods either by creating subsurface conditions that foster biologic activity or by reducing the amount of contaminant mass that must be dealt with. Physical methods are cost-efficient if there are free-phase contaminants that may be removed from the site. Physical removal methods tend to be less cost effective for dissolved phase contaminants and are of limited usefulness with dilute plumes. However, if hydraulic control of a contaminant plume is required to protect a receptor, pump and treat systems remain a viable option.

The two most widely used physical removal methods for source area material in the unsaturated zone soil are excavation/removal and soil vapor extraction (SVE). The primary advantage of these methods is that the source materials are removed from the subsurface quickly, which reduces future movement of the contaminant to groundwater. Other physical removal remedial technologies used at dry cleaner facilities include surfactant/cosolvent flushing and air sparging. These technologies rely upon fluid flushing of the source area to remove contaminant mass. The injected fluids serve as a carrier medium to transport the contaminant mass to the surface. The contaminant mass is removed at the surface through collection and treatment of the flushing fluids. Alcohol may provide an additional benefit when residual alcohol remaining after remediation serves as an electron donor to promote natural attenuation within the plume.

Excavation/Removal

SCRD expertise for drycleaner sites where soil excavations/removals have been conducted includes; contaminant source areas beneath building floor slabs in solvent use areas (location of drycleaning machine), solvent storage areas (including both above-ground and underground solvent and fuel storage tanks), solvent transfer areas (such as parking lots and areas near service doors), waste storage areas and historical waste disposal areas such as leaking sanitary sewer lines, septic tanks/drain fields and catchment basins/storm drains.

Optimum conditions for excavation or removal include accessible contaminant source areas, relatively shallow water tables and sufficient space on site to stage both equipment and

soil stockpile/treatment areas. Most drycleaning sites are located in urban areas, strip malls and shopping centers and conditions for excavation are seldom ideal. Contaminant source areas are often located under or immediately adjacent to buildings that are often occupied by active businesses. Many of the utilities that serve these businesses are located below ground and therefore limit excavation activities. Opportunities for more extensive excavations occur when a building/strip mall is demolished or renovations are made while the building/bay is vacant.

A successful contaminant source removal/excavation begins with the collection of a sufficient number of soil/sediment samples to adequately characterize the extent of the contaminant source area, including variations in lithologies. Some buildings are built over construction debris and rubble that may complicate removals or installation of sheet piling. Locating buried utilities at the site prior to excavation is important. Utility companies may need to be present during the excavation to help reroute or shore up utility lines in the excavation. Coordinating the timing of the excavation with business owners and real property owners to minimize disturbances is also necessary. Developing contingency plans prior to excavations for situations such as a perched aquifer, heaving sands, discovery of undocumented tanks, utilities or other structures and greater than expected volumes of contaminated soil is also advised. Utilization of an onsite mobile laboratory during the late stages of an excavation to analyze confirmatory soil samples may be cost effective by preventing additional mobilizations to complete an excavation. Utilizing headspace analysis or 24-hour turnaround (must be able to secure pit in the interim) may suffice for smaller excavations.

A variety of equipment has been used to excavate contaminated soil or remove contaminated media at drycleaning sites. Backhoes and track hoes are the most widely used equipment for soil excavations and storage tank removals. Small trackhoes are used inside buildings to excavate contaminated soils inside a building. Vacuum trucks are used to excavate contaminated soil, remove contaminated sediments from soakage pits and cleanout contaminated sludge and wastewater from septic tanks. Vacuum trucks can be used for shallow excavations under building floor slabs where access is limited. At some drycleaning sites a portion of the floor slab is cut out at contaminant source areas (former locations of drycleaning machines and distillation units) and the vacuum truck is parked near the facility, where the vacuum hose can access the excavation via the service door. Contaminated soil is removed down to the water

table and then the excavation is backfilled with grout or sand and the floor slab restored. A soil vapor extraction system can be installed in the excavation for added remediation. Vacuum knife systems are fairly new to the remediation market, but can be useful for excavation of areas where the target source area is small and well defined. Vacuum knife systems use a high vacuum system to remove native soil through a knife-like attachment to a hose. Another excavation option is to use large diameter drilling methods to remove the soil. Large diameter augers and bucket-auger rigs are used to remove the contaminated soil and then the borehole is backfilled with soil, grout, concrete or sand/gravel if a SVE system is to be used as another remedial option. The large diameter drilling option allows drilling near structures without the shoring when using a stable backfill material.

Generally, the largest costs associated with excavation/removal are disposal/treatment of the contaminated media. This is particularly true when the contaminated media has been characterized as a listed hazardous waste. A good knowledge of the EPA Contained In-Contained Out policy is valuable. In addition, the sewer line exclusion may apply to some sites where the release is from the sanitary sewer lines. Detailed discussions with your state's hazardous waste oversight agency is important to ensure compliance with all hazardous waste laws. At a minimum segregating soil by the level of contamination is recommended. Clean soil above the contamination zone should be screened and placed in a separate pile if it can be reused as backfill. Depending upon the waste determination some soil may be screened and segregated as a possible "special waste". All suspected hazardous waste should also be stockpiled separately. At a minimum all special and potentially hazardous waste will need to be characterized to determine the waste designation. Some excavated waste will automatically be considered hazardous waste based on the source and assumed listed waste categorization.

One option for sites where a large volume of contaminated soil is being removed is to treat the contaminated soil on site. Contaminated soil has been treated on-site using variations of soil venting (*ex-situ* SVE). After treatment, the contaminated soil was returned to the excavation. Thermal treatment (Mobile Injection Treatment Unit) was used to treat approximately 3000 cubic yards of contaminated soil onsite at a drycleaner in Wisconsin. Treatment of contaminated soil onsite also eliminates the potential for liability associated with the disposal of contaminated

media in landfills. Chemical oxidation and bioremediation of excavated soils in *ex situ* treatment piles are also viable remedial options.

Where deeper excavations are conducted or where excavations are located adjacent to building or structures, the building foundation may need to be stabilized by underpinning or the installation of sheet piling. Installation of sheet piling and underpinning building foundations substantially increases the cost of an excavation. Segmented trench boxes have also been used as a shoring system in excavations at drycleaning sites.

In terms of contaminant mass removed per dollar spent, simple excavations can be the most cost-effective remedial technology used in a site cleanup. Removal of a contaminant source area can substantially shorten the remedial period at a contaminated site. If the contaminant source area is not removed and contaminants continue to leach into the groundwater, cleanup target levels may not be achieved for many years. At a typical setting for a drycleaning site, a strip mall or shopping center, approximately ninety percent of the property is covered by buildings, asphalt and concrete. Although capping is used at many sites as an engineering control, it does not preclude the leaching of contaminants into groundwater during seasonal rises of the water table into the contaminated soils. Through this seasonal leaching, the presence of even relatively low contaminant concentrations in soils can result in contaminant concentrations in groundwater in excess of cleanup target levels at sites. Contaminant source removal coupled with MNA has resulted in closure at a number of drycleaning sites. Groundwater monitoring has shown substantial decreases in contaminant concentrations (up to several orders of magnitude) at other drycleaning sites where excavations/removals have been performed. An unexpected consequence of excavations at some sites has been the discovery of undocumented contaminant sources areas such buried vaults, tanks and drums. The SCRDR website details many site profiles for many excavations located in various parts of the country at <http://drycleancoalition.org/>.

Soil Vapor Extraction

Soil Vapor Extraction (SVE) is a frequently used remedial strategy for removal of contamination from the soil when excavation is not feasible due to the presence of physical obstructions (e.g. buildings, utilities, trees, etc), or where the extent of soil contamination is

extensive. In addition, SVE systems are also very effective at minimizing indoor vapor intrusion by keeping the contaminated soil vapors closer to the source area.

SVE works best in vadose zones such as sand, gravel, and higher permeability silty clay where soil vapor can be pulled through a permeable formation toward the remediation well(s). The effectiveness of SVE can be greatly inhibited at sites with low permeability soils, significant heterogeneity, or the presence of utility conduits, which can cause short circuits in the negative pressure gradients from the contaminated material to the vapor recovery well(s).

SVE systems have a mechanical blower that applies a vacuum to a remediation well(s) screened in the vadose zone. The vacuum pulls air from and through the voids in soil into the screened interval, then through the well for treatment and/or discharge into the atmosphere. SVE systems are often used in conjunction with groundwater sparging technology to collect the air being used to strip contaminants from the saturated zone.

SVE wells may be vertical or horizontal depending upon the depth to groundwater and the site layout. Vertical wells are more common when the water table is more than five feet below land surface (BLS). Horizontal wells can be used where the groundwater table is shallow or underneath buildings where a vacuum is placed on the floor sub grade. Depending on the installation method, a fair amount of material removed during the well installation may need to be handled as waste. Wells are often strategically located to create treatment zones and need to be properly designed to ensure that the vacuum on the well does not “pull” the groundwater into the screened interval rendering the screen useless. Engineers design the systems to run continuously or on intervals to target certain areas or treatment depths.

Because the systems will be operating in dynamic environments, there are many considerations that should be addressed. Space restrictions inside and out, above and below ground utilities, operational equipment, nearby buildings, right of ways, and volume of traffic will drive the method of installation and location of the system. There may also be government restrictions, ordinances, such as noise or aesthetics, or permitting requirements that will affect the design of the system.

The flexibility of SVE systems means there are often ways to overcome potential problems. Systems may be trailer mounted, skid mounted or permanently attached to a concrete

slab. They may be located at the facility, or installed remotely. Wells may be installed through the floor of facility and piped to the blower system. A pilot test may show that SVE will work in clay with some design adjustments. Wells already installed may be switched from vapor recovery to air inlet to reduce costs or space problems. Air inlet wells can help reduce “dead spaces” and increase the pressure gradient to increase contaminant removal. SVE systems may be paired with groundwater extraction, air sparge or other remedies for increased success. In some cases the equipment may be reused in whole or in part. Once in place, the systems may run continuously or pulsed (turned off and on at timed intervals) for greater efficiency.

SVE systems are typically reliable, readily available and are usable either as part of a treatment train or as a stand-alone remedy. As with any technology, individual site characteristics will dictate the cost of the system. Costs are dependant on the size, the number and the placement of wells installed, the size of the blower, the type of structure housing the system, the effluent treatment system, and operation and maintenance (O&M) costs (operation duration, sampling requirements, utility charges, disposal requirements). While the use of telemetry can help with the efficiency of the system, O&M costs will increase incrementally with the frequency of mobilizations for sample collection, routine maintenance and corrective actions. Utility costs are proportional to the length of time the system operates. Design timeframes range from as little as six months to several years.

A review of the “Lessons Learned” section from site profiles on the SCRCD website where SVE systems were used yielded the following information. Pilot tests, while they offer the most information, are still limited by where the extraction wells are installed. A system may not function as designed due to heterogeneity, freezing weather or smearing of the borehole during well installation. Heavy rains or storm water runoff can raise the water table and help short-circuit the system if the surface above the wells is not capped or the regional water table exhibits dramatic increases from surface infiltration. This is particularly true for horizontal wells or wells screened close to or in the water table. The vacuum applied to the well will also raise the water table depending upon the negative pressure (vacuum) applied to the well. The system should be properly sized for the zone of treatment and care should be taken so that blockages do not disturb airflow. A knockout tank or drip legs (similar to an in-line sump well) in the line can help keep

water from being pulled into the SVE blower and flow/vacuum gauges. Routine cleanout of the tank and drip legs is required during the routine O&M event.

Air Sparging

In-situ air sparging (AS) involves injection of air into the saturated zone to strip the contaminants from the dissolved phase, which is transferred to a vapor phase. An air sparge network consists of sparge points designed to deliver air to a specific zone of contaminated groundwater. Air compressors deliver contaminant-free air under pressure to the target zones. The vapor migrates upward from the saturated zone to the unsaturated zone. The vapor phase is vented through the unsaturated zone to the atmosphere and typically uses a SVE in the unsaturated zone to more effectively control, treat and remove the vapor plume from the unsaturated zone (see SVE section above for additional information). These combination systems are commonly referred to AS/SVE. An aboveground process control system is used to monitor and optimize air delivery. The air can be delivered at a constant flow or may be pulsed to maximize contaminant removal by not allowing constant static subsurface conditions. Systems can also be timed to alternate zones of treatment to eliminate stagnation zones between the sparge points. Although final system design and operation depends on site-specific parameters, the typical components of an air sparge system include sparge points, manifold piping, compressed air equipment, and monitoring controls. Factors that should be considered when designing an air sparge system include radius of influence, airflow rate, and air pressure as discussed below:

The radius of influence, which is defined as the greatest distance from a sparge well that sufficient sparge pressure and airflow can be induced to enhance the mass transfer of contaminants from the dissolved phase to the vapor phase. This factor depends on the hydraulic conductivity of the aquifer materials. It determines the number and spacing of the sparge points.

The airflow rate required to enhance mass transfer of contaminants is a site-specific parameter. Typical flow rates range from 3 to 25 cubic feet per minute per injection well. Pulsing the air flow (i.e., turning the system on and off at specified intervals) may provide better distribution and mixing of air in the contaminated zone, thereby allowing for greater contact with the dissolved phase contaminants.

If the air pressure is too high, it can induce fractures in the soils creating permanent air channels that can significantly reduce AS effectiveness. A typical system will be operated at approximately 10 to 15 psig.

Drycleaning solvents can be present in dissolved phase, free phase DNAPL, and/or residual DNAPL absorbed to soil particles. The effectiveness of AS depends on soil permeability, the contaminants of concern and how readily they partition between dissolved phase and the vapor phase. The ease of partitioning is determined by Henry's Law Constant. In general, contaminants with Henry's Law Constants greater than 100 atmospheres can easily be volatilized. Chlorinated solvents associated with drycleaning solvents are considered good candidates for AS. PCE has a Henry's Law Constant of 1460 Pa-m³/mol.

Soil permeability greatly affects the effectiveness of air delivery to the treatment zone as well as the effectiveness of air recovery from the unsaturated zone. Relatively coarse-grained homogenous soils such as sands and gravels are more effectively treated than fine-grained, low permeability soils. Stratified or highly heterogeneous soils can create the greatest difficulties for this remedy. If site soils are characterized as highly heterogeneous both the injected air and the vented air may migrate along the paths of least resistance (i.e., along the most permeable zones) and may severely limit AS effectiveness and vapor collection. Fugitive vapors not collected by a SVE system could cause problems if the vapors migrate off site.

Other factors that may be needed for design include:

- Initial contaminant vapor concentrations,
- Required final dissolved contaminant concentrations,
- Required remedial cleanup time,
- Saturated zone volume to be treated,
- Pore volume calculations
- Discharge limitations and monitoring requirements,
- Site construction limitations.

Implementation of a safe and effective air sparge system requires a detailed site investigation, complete with a conceptual model of the site. Following the investigation, a pilot-scale study is required to determine the operating parameters that will be used in the design of the full-scale remediation system. Pilot tests should not be conducted if DNAPL is known to exist at the site as uncontrolled vapors can migrate into confined spaces, sewers, or buildings.

System operation and monitoring should be part of remediation system design. Both are necessary to ensure optimal system performance and to track the rate of contaminant mass removal. Long-term monitoring should consist of contaminant level measurements and vapor concentration readings. Measurements should take place at monthly intervals for the duration of the system operational period.

Monitoring the performance of the AS in reducing contaminant concentrations in the saturated zone is necessary to determine if remedial progress is proceeding at a reasonable pace. A variety of methods can be used. One method includes monitoring contaminant levels in the groundwater and vapors in the monitoring wells and blower exhaust, respectively. The vapor and contaminant concentrations are then each plotted against time.

Remedial progress of AS systems typically exhibits asymptotic behavior with respect to both dissolved-phase and vapor-phase concentration reduction. When asymptotic behavior begins to occur, the operator should evaluate alternatives that increase mass transfer removal such as turning the system off for a period of time and restarting it. If asymptotic behavior is persistent for periods of greater than six months and the concentration rebound is sufficiently small following periods of temporary system shutdown, the appropriate regulatory officials should be consulted and termination of operations may be appropriate.

AS provides an aerobic environment that may short circuit reductive dehalogenation of chlorinated VOCs during implementation. Where AS has reached asymptotic levels that exceed remedial goals, sparge wells can be converted to injection wells for in-situ bioremediation as discussed later.

Multi Phase Extraction

Multi Phase Extraction (MPE) is an in situ remediation technology that is effective at removing volatile organic compounds and total petroleum hydrocarbons from contaminated soil and groundwater. This technology can be a modification of the conventional soil vapor extraction technology or use traditional groundwater pumping combined with SVE technology. MPE is a general term used for technologies that simultaneously extract soil vapor and groundwater.

The EPA distinguished two types of MPE, Two Phase Extraction (TPE) technology and Dual Phase Extraction (DPE) technology.

With TPE, both soil vapor and liquid are removed from the extraction well to the surface through the same conduit. A single vacuum source (vacuum pump or blower) is used to extract both liquid and gaseous phases.

The DPE process conveys soil vapor and liquid from the extraction well to the surface in separate conduits by separate pumps or blowers. The DPE process will use a submersible or pneumatic pump inside the well to extract groundwater. Soil vapor is extracted by utilizing a high vacuum (HVDPE) or a low vacuum (LVDPE) pump.

In both cases lowering the water table allows volatile compounds sorbed on to the previously saturated soil to be stripped by vapor extraction. The exposed soil, also called the capillary fringe, is often highly contaminated. For this reason MPE is most effective at sites where the aquifer can be depressed. Sites with low to moderate permeable soils are preferred for this technology. Low yield aquifers may allow the water table to be drawn down many feet past the capillary fringe. Sites with a high groundwater flow rate are not suitable for MPE.

There are specific advantages and disadvantages with both TPE and DPE technologies. Selection of the appropriate method is largely dependant on the depth of the groundwater and whether existing extraction or monitoring wells can be retrofitted for the technology.

TPE technology employs a high vacuum pump to extract both groundwater and soil vapor through a single suction pipe that is lowered into the extraction well. TPE can be applied at existing extraction or monitoring wells. There are no pumps or mechanical equipment inside

the well. However, TPE is limited to a maximum groundwater flow rate of approximately 5gpm. The maximum groundwater depth that TPE can be used is approximately 50 feet below land surface. Implementation of TPE requires a vapor water separator.

DPE technology is not limited by depth of groundwater or groundwater flow rate. Separate pumps for soil vapor and groundwater minimize vacuum losses inside the well. However, DPE systems will require more maintenance due to the mechanical equipment inside the well. Implementation of DPE requires separate water and vapor phase treatment.

The SCRCD web site lists several projects that used MPE usually as part of a treatment train approach.

Recirculating Well Technology

Recirculating Well Technology (RWT) is a method of treating VOC-contaminated groundwater within a remediation well and/or a recirculating zone and does not require surface discharge. RWT utilizes pumps or air-lift principles to pump water, therefore capturing contaminated groundwater moving through the recirculating zone. The water enters the well through an inlet screen in the lower portion of the well and discharges through an upper outlet screen. Depending on the specific technology, the water is treated within the well by air stripping, chemical oxidation or granular activated carbon and returned to the aquifer via the outlet screen into the vadose or saturated zone. The return “clean” water flows back into the aquifer and the portion within the capture zone is once again drawn into the inlet screen. Some of the return water is not re-captured due to groundwater gradients and variations in the hydrogeology setting, such as silt and clay lenses or other variations in the formation hydraulic conductivity. Negative pressure is placed on the remediation wellhead and/or vadose zone to capture fugitive vapors resulting from the air stripping process.

RWT is most effective when the formation at the outlet screen is sufficient to allow adequate gravity recharge into the vadose zone and/or aquifer. Geologic formations with tighter materials may require installation of an infiltration gallery to assist with recharge. RWT relies on groundwater molecules recirculating through the well multiple times to achieve the desired cleanup efficiency. Certain designs reverse the inlet and outlet screens to take advantage of air

stripping technology as the air bubbles rise outside the well through the saturated zone and a pump in the upper inlet screen recaptures the water.

Design of the remediation well system is dictated by the hydrogeologic conditions in the vadose and saturated zone, aquifer characteristics, volume of contaminated water to be treated, and contaminant concentrations. Pilot studies are typically conducted to evaluate the hydrogeologic condition in the recirculation zone that treats the contaminated groundwater. Inlet screens may be strategically placed in zones of higher contamination to induce flow for expedited cleanup.

Oxygenated water can affect the groundwater's geochemistry; therefore control of pH is important to insure inorganic constituents do not precipitate during the remediation process. Remediation wells may foul or plug without environmental controls. Well spacing and pumping rates are designed to capture the target area. Pulsation and on-off rotation frequency can also be designed to help eliminate dead zones. The use of solenoids can pulse rotate the frequency of operation for each remedial well to reduce dead zones in the treatment area. Proper design prior to installation is the key however evaluation after implementation can ensure effective remediation.

The SCRD web Site Profiles section lists several lessons learned for sites that employed recirculating wells as a remedial technology. Some states do not require a water use permit or UIC permit since contaminated water is neither pumped nor treated above ground. Vertical gradients induced in the recirculation zone appear to enhance physical removal of contaminants from low permeability zones. The presence of organic rich sand and peat possibly enhanced remediation by circulating naturally occurring organic carbon (food source) into treatment zone (site was located in Florida). The fouling of well screens with iron bacteria necessitated the incorporation of additional measures aimed at eliminating biofouling at the discharge zone. Biofouling also resulted in major operational and maintenance problems. In Rhode Island, problems were reported with glacial deposits at the site that contained intermittent boulders and some wells had to be installed with a Barber rig and air hammer bit. Proper well development is vital to ensure all sediment and fine-grained sand is removed and will not inhibit the pumping or plug well screens.

Surfactant/Cosolvent Flushing

Cosolvent/surfactant flushing is a NAPL removal technology. This technology has the potential to remove large quantities of NAPL in a short period of time. It can be used in both the unsaturated and saturated zones. To accomplish remediation, the flushing solution, cosolvent or surfactant, or mixture of the two is injected into the subsurface and then extracted from the aquifer. This process acts to distribute the flushing agent through the aquifer, thus sweeping the aquifer and effectively contacting more of the contaminant mass and eventually removing the NAPL. Normally, the extracted groundwater is treated and the surfactant/cosolvent flushing solution is re-injected.

The surfactant/cosolvent solutions lower the NAPL/water interfacial tension and decrease the capillary forces in the aquifer. This enhances NAPL solubility and mobility. Surfactant groups used include sulfonic acid salts, alcohol sulfates, alkylbenzene sulfonates, phosphoric acid esters, carboxylic acid salts, polyoxyethylenated alkylphenols, alcohol ethoxylates, alkylphenol ethoxylates and alkanolamides. Cosolvents used include the alcohols - ethanol, methanol and isopropanol.

Favorable conditions for use of surfactant/cosolvent flushing include a relatively homogeneous aquifer with moderate to high hydraulic conductivity, low to flat vertical and horizontal hydraulic gradients and an underlying low permeability confining unit. A comprehensive contamination assessment, including intensive sampling of soil and groundwater in the contaminant source area is essential to characterize the contaminant distribution, hydraulic properties of the aquifer and groundwater chemistry. Both laboratory batch and column studies, as well as pilot testing may be necessary to properly design an effective remedial system.

Potential problems associated with utilizing this technology include uncontrolled mobilization of NAPL within the aquifer and aquifer plugging due to sorption of the flushing solution to fine-grained sediments. Extracted groundwater can require extensive treatment prior to disposal or re-injection.

This technology has been used at two contaminated drycleaning sites in the United States. Ethanol was used as a cosolvent at the former Sages Drycleaners in Jacksonville Florida and a cosolvent/surfactant mixture was used at the Building 25, Morale, Welfare and Recreation Dry

Cleaners site at Camp Lejeune Marine Corps Base in North Carolina. Both of these sites are presented in the Site Profiles section at the State Coalition for Remediation of Drycleaners website at <http://drycleancoalition.org/>. Also on the website under the References section is a video entitled *In Situ Alcohol Flushing for the Remediation of NAPL sources*.

BIOLOGICAL REMOVAL METHODS

Biological Removal Overview

Biological treatment of PCE involves the engineering of the subsurface environment to facilitate biological degradation of PCE and degradation products to non-toxic end products (e.g. ethene) using native or engineered organisms. At the time of this publication, the sole bacterium known to significantly expedite the reductive dechlorination of PCE to ethene is *Dehalococcoides ethenogenes*. *Desulfuronomas ethenogenes* is another strain being studied to determine the ability to enhance the dechlorination process.

Microbial populations involved in bioremediation require a source of carbon, an electron donor, an electron acceptor, appropriate nutrients, a suitable temperature range, pH, and other environmental conditions. Biodegradation of PCE occurs under anaerobic conditions under a process termed “reductive dehalogenation” or “dechlorination”. Most source zones exhibit anaerobic conditions (dissolved oxygen levels less than 0.5 parts per million (ppm)), but the anaerobic environment may be limited in extent due to factors, such as natural rainfall recharge. Also, natural occurring conditions often do not have an adequate supply of a carbon source required to foster efficient biological activity. Total organic carbon [TOC] levels in groundwater should be above 20 ppm. The carbon source serves as the electron donor for reductive dehalogenation.

The introduction of a carbon source to facilitate anaerobic reductive dechlorination of chlorinated solvents is termed “biostimulation”, as this technology relies on existing microbial populations in the subsurface to degrade the chlorinated solvents. In certain circumstances, the existing microbial populations in the subsurface may lack specific microbial populations necessary for complete degradation of chlorinated solvents, namely the *Dehalococcoides* bacteria. Under these circumstances microbial amendments containing a consortium of desired bacteria and necessary nutrients can be injected into the subsurface to facilitate or enhance the rate of anaerobic dechlorination. This technology is typically termed “bioaugmentation”.

Applicability

Bioremediation is employed to accelerate the biodegradation of chlorinated solvents and facilitate source reduction and improve the overall effectiveness of natural attenuation as a protective remedy. It is typically employed where protection or restoration of the beneficial use of groundwater for drinking water is not a primary remedial objective, and/or at facilities where chemical (e.g. ISCO) or physical (e.g. pump and treat) are not technically or fiscally feasible. Facilities with strong evidence of natural attenuation (see MNA section) are good candidates for bioremediation. Bioremediation may also be considered for facilities undergoing a groundwater pump and treat remedy by accelerating the rate of remediation with in-situ reductive dehalogenation or as a replacement to pump/treat when contaminant concentrations reach asymptotic levels that exceed remedial goals.

Biological treatment methods may be the preferred technology for treatment of dissolved phase contamination of groundwater where:

Groundwater pump and treat methods are not effective due to the low yield of the impacted aquifer(s);

Ex-situ treatment is not feasible due to space constraints;

Chemical oxidation is prohibitive due to high oxidant demand from soil or co-contamination with stoddard solvent or other chemicals;

Health and safety concerns with risk associated with implementation of in-situ oxidation treatment for operators and facility customers; or

Suitable environment that is anaerobic with adequate carbon content to show dechlorination is plausible.

Biostimulation

Carbon source materials that have been injected at dry cleaner facilities include dextrose, molasses, ethyl lactate, potassium lactate, sodium lactate, hydrogen releasing compound (HRCTM), soy or vegetable oil (typically in an emulsion) or combinations (e.g. lactate and oil emulsions). New products, such as whey and milk, are being researched and the list of biostimulants continues to grow. Fast degrading compounds such as molasses and sodium

lactate have the lowest unit cost, but commonly require continued or routine injection schemes to maintain reducing conditions for periods beyond several months. HRC and vegetable oil products may maintain reducing conditions for significantly longer periods of time, up to several years depending on a variety of factors such as groundwater velocity, water temperature, etc. New products continue to emerge that aim to remain effective for several years. Long-lasting carbon sources are well suited for passive in-situ bioremediation with low groundwater velocity and may not require reapplication to achieve remedial goals.

Bioaugmentation

Some sites may not have the bacterial strain necessary for completing reductive dechlorination. Bioaugmentation is a relatively new technology and the environmental remediation industry has vigorously debated whether sites need biostimulation vs. bioaugmentation. The biostimulation proponents believe that proper injection of stimulants over enough time (many years at some sites) will eventually lead to complete reductive dechlorination. Proponents of bioaugmentation believe that enhancing the bioremediation process with a bacterial consortium will save time and money in the long run and that some sites may never achieve complete reductive dechlorination without the boost from their products. Sites that desire quicker cleanups and/or seem to stall at cis-1,2-DCE or vinyl chloride tend to benefit from bioaugmentation efforts. Quicker cleanups may be desired if a property transaction is desired, redevelopment is pending, or vapor intrusion is a concern.

Case studies have indicated that bioaugmentation products can quickly remediate sites source areas to below cleanup levels in a short period of time. Several products currently offer a consortium of bacteria and nutrients to “kick-start” bioremediation at drycleaning sites. Most companies warn that proper design of the injections and handling of their product is key toward success with bioaugmentation. Most products have a recommended “shelf life” for optimal implementation so product should not be stored for several years and then assumed to still be effective.

Planning

The carbon source for bioremediation can be any material that acts as an electron donor, such as corn syrup, molasses, food-grade lactate, HRCTM, emulsified soy oil, sugar, etc. The first

step is to establish remedial goals based on the beneficial groundwater use for the impacted aquifer(s). These goals will determine the remedial approach for the bioremediation component of the remedy (e.g. hydraulic control a necessary element of the remedy to protect off-site drinking water supply wells). In these circumstances, bioremediation can be incorporated as a remedial element through a re-circulating system. Low cost carbon sources such as molasses or lactate are typically used for these applications.

Long-term electron donors such as HRCTM, vegetable oil or emulsified soybean oil are common in circumstances with significant residual sources and where beneficial groundwater uses do not prohibit the use of passive remediation approaches. Product vendors have developed spreadsheet programs to estimate the amount of product needed to treat the mass of PCE in soil and groundwater. Vendors will also commonly provide technical assistance in the conceptual design of the injection program. Short-term electron donors and augmentation products are used when a more rapid bioremediation approach is desired or the bacterial population in an area is insignificant.

Injection of electron donor triggers Underground Injection Control (UIC) regulations for Class V injection wells. State or Federal UIC Programs should be consulted during the planning phase to ensure the design and monitoring requirements are considered in the remediation plan. Other types of permits or permission may involve dirt cut permits for city property drilling and trenching, approval for pumping make-up water and reinjection after mixing with the stimulation or augmentation products, and water rights if re-circulation systems are used. Some states may not require water rights approval if the pumping system is a closed loop and reinjected on site.

Injection Equipment and Methods

Equipment used for injection of electron donor and augmentation material varies depending on the application. The carbon source can be placed at the base of an excavation following soil source removal, injected using push-pull methods using direct push probe methods, injected into monitoring wells or other vertical or horizontal piping installed for SVE or AS remediation, etc. Additional equipment that may be needed for an injection event include a mixing tank, hoses, and flow and dose meters.

Use of bioremediation as a treatment train approach may involve removal of mass via excavation and then mixing a stimulant or augmentation product in the pit basin to help complete

the groundwater remediation. The type of excavation could be standard pit excavation or large diameter auger soil removal.

Injection of long-term electron donor using push-pull methods involves pumping of prescribed volume/mass of donor over a specified interval (i.e. 10 pounds/foot of saturated zone). Viscous material such as HRC is injected using a grout pump, and may need to be heated. Less viscous donors (e.g. vegetable oil) do not need to be heated. Injection into horizontal or vertical wells can be done by either gravity feed or pressure injected. Some designs call for pumping make-up water from on-site, mixing the stimulation or augmentation products and then reinjecting the mixture.

Recirculation systems can be used to accelerate the movement of injected materials throughout the aquifer and to provide hydraulic control of the plume. Extraction occurs at the downgradient end of the treatment zone and is piped back to the source area. The stimulation or augmentation product is added to the extracted water and reinjected into the subsurface, or the water can be injected directly into the subsurface in the source area without adding more product. In either case, recirculation helps to provide more complete distribution of the carbon source throughout the plume and thus accelerates the cleanup. Reinjection is commonly through vertical wells, horizontal wells, or infiltration galleries (trench system). Closed loop systems may allow bypassing the requirement for obtaining water rights in areas with limited groundwater supplies.

PRB Biowalls

Permeable Reactive Barriers (PRBs) installed with carbon source material perpendicular to groundwater flow is an alternative remedial approach to impede contaminant migration in groundwater. Barriers may consist of a funnel-and-gate system designed to direct water through a treatment zone, continuous treatment walls, or wells spaced to maximize contact with the PRB material or diffuse materials into the subsurface. Reactive media under this remedial approach would include a long-lasting electron donor. Bark mulch has been demonstrated to be effective in biowalls used to control plume migration off-site at industrial facilities, but has not been employed as a component of a dry cleaner remedy based on case studies in the SCRD website.

Funnel-and-gate systems are beneficial when water can efficiently be directed to a smaller treatment zone. The reactive material is placed in a centralized location (gate) that

provides adequate retention time within the treatment zone. The “funnel” walls consist of interlocking metal sheet pilings or impermeable slurry walls that direct groundwater to the “gate” opening. Walls are installed to prevent contaminated groundwater from going through, above or around the walls. Groundwater velocity increases as the directed water approaches the gate. Replacement of the reactive material is easier with the funnel-and-gate system since the material is concentrated in the gate area.

Continuous treatment walls commonly use continuous one-pass trenchers that dig and simultaneously replace excavated soil with reactive media in the trench. Trenchers can extend to approximately 35 feet below the ground surface (bgs). Designs must ensure the groundwater continues to flow through the walls.

Permeable reactive walls are filled with reactive media and simulate a “wall” through the installation of several rows of wells to effectively form a treatment zone through which contaminated water must pass. Probes or jetting can be used to inject an oxidant, biostimulant, bioaugmentation material, or nano-scale zero-valent metal. Jetting is a method of injecting the materials directly into the formation and does not require the installation of wells or advancement of direct-push probes. Some of the injectants diffuse into the formation helping to create the PRB treatment zone.

PRBs are passive systems that generally have lower monthly O&M costs. The installation cost is usually fairly high and the duration of remedial effectiveness is unknown. Installation can be inhibited by underground utilities and unfavorable geologic conditions. O&M for biowalls may include replacement of carbon source material such as compost following depletion of available carbon. Materials such as HRC may require multiple injections depending on the reduction of the contaminant mass upgradient of the PRB system.

Anaerobic Bioventing

Anaerobic bioventing is an in-situ remedial method that stimulates anaerobic biodegradation of chlorinated solvents in the vadose zone. PCE will not naturally biodegrade in an aerobic environment. Venting of the vadose zone with gasses to displace oxygen produces the anaerobic subsurface environment favorable for reductive dechlorination of VOCs.

Remedial designs typically utilize nitrogen gas to lower the oxygen content in the subsurface. Hydrogen gas is also injected to promote anaerobic conditions. These conditions help stimulate the natural microorganisms to biodegrade the chlorinated compounds. Sparging propane is an alternative approach to introduce a carbon source to produce anaerobic conditions for reductive dechlorination of PCE in both the saturated and vadose zones.

Design of the remediation system is dictated by the geologic characteristics of the vadose zone, volume of contaminated soil to be treated, and contaminant concentrations. Delivery of the gases to the subsurface may be restricted by clayey soils and/or an inadequate number or spacing of injection points. On-site use of the gases requires large compressed gas storage tanks in secure areas that may require multiple permits.

Groundwater Monitoring

A groundwater monitoring network should be installed within the treatment zone and downgradient to determine changes in concentrations of the target constituents and inorganic parameters due to the altered geochemical conditions. Suggested monitoring includes the following, which can be modified based on site-specific conditions:

Target Constituents and Breakdown Products: PCE, TCE, cis1,2-DCE, vinyl chloride, and ethene

General Analytical Parameters: alkalinity, chloride, dissolved carbon dioxide, dissolved methane, dissolved oxygen, electrical conductivity, nitrate/nitrite, oxygen-reduction potential, pH, phosphate, sulfate, total dissolved solids (TDS), total organic carbon (TOC)

Dissolved Metals: iron, manganese (trace metals may also be required by various regulatory agencies; e.g. arsenic, copper, chromium)

Summary and Other Considerations

The main advantage of bioremediation is that it typically has substantially lower O&M costs, even when recirculation systems are used to enhance mixing in the groundwater. Emulsified oils and vegetable oils can sequester PCE into the oil reducing the dissolved phase and vapor phase transport from the treatment area.

The primary disadvantage is the uncertainty involved in estimating the mass of product needed for injection and the depletion of the electron donor prior to reaching the prescribed remediation goals. In this case, additional injection events may be necessary, which will increase the cost of the remedy. Bioremediation also requires analysis of additional inorganics to help track the degradation process and maintain an efficient remediation effort.

The primary cost elements for bioremediation include the cost of the electron donor or augmentation product, drilling costs, field personnel and equipment, and monitoring. The cost for electron donor ranges from less than \$1/lb. to \$8/lb. or more. For drycleaning facilities with source/treatment areas of approximately 1000 square feet, the cost for electron donor will be in the range of \$10,000 to \$40,000, and drilling costs in the range of \$10,000 for a grid injection strategy involving 15-20 injection points to a depth of 20 feet bgs. Monitoring costs are in the range of \$250/well per event.

CHEMICAL REMOVAL METHODS

Chemical removal methods attack the contaminants of concern through chemical reactions. Almost all of the chemical removal methods used at drycleaning sites are done *in-situ*, which means the chemicals are injected into the subsurface, or otherwise emplaced to contact and react with the contaminant absorbed onto the sub-surface matrix. The chemicals fall into two broad categories as either oxidants or reductants based on the principle mode of action. With the oxidants, the chlorine atoms are cleaved from the PCE molecule through catalyst-mediated substitution of oxygen onto the molecule. Daughter products are not usually formed in this process. The reductants employ a mechanism similar to biological reductive dechlorination. The chemicals supply an excess of hydrogen atoms to the PCE molecule, which proceeds through the sequential steps of formation and, ultimately destruction, of transitory daughter products.

Chemical methods offer several advantages over conventional treatment technologies such as pump-and-treat because large volumes of waste material are not generated that must be disposed of or treated off-site. Usually, the chemical methods can be effective over a shorter

time frame than biological reductive dechlorination methods, resulting in significant savings in monitoring and operational maintenance. However, under favorable conditions cleanup times for some bioaugmentation methods may rival chemical oxidation cleanup time frames.

The chemical methods have limitations and are neither practical nor implementable at every site. Furthermore, the chemical methods may be incompatible with other treatment technologies because of native geochemical processes that may have been underway on the site prior to remedial intervention. As a result, insufficient chemical treatments may temporarily cause site conditions to worsen.

In Situ Chemical Oxidation (ISCO)

In Situ Chemical Oxidation (ISOC) is a remedial process where strong chemical agents (oxidants) are introduced into the sub-surface zone to react with the contaminants of concern. ISCO methods used to date at SCRD sites include ozone, sodium and/or potassium permanganate, hydroxide peroxide, and Fenton's Reagent.

ISCO methods are viable remedial alternatives for use at drycleaning sites if the bulk of the contaminant mass exists as a high-concentration dissolved plume over a relatively small area. While ISCO methods can be used to treat the entire plume, it is generally not cost effective to treat outside the general source area because of the amount of equipment and engineering intervention that is necessary to place the oxidizing agent into contact with the contamination over a large spatial area.

Most ISCO methods destroy chlorinated contaminants to complete mineralization without producing levels of toxic daughter products. For example, PCE is broken down to inorganic salts of chlorine and free hydrogen, which then forms a weak hydrochloric acid that is easily diluted out without any significant change in the groundwater's pH. Chemical destruction occurs at a rapid pace as soon as the oxidant is brought into contact with the contaminant. ISCO methods tend to be only moderately effective against free-phase NAPL pools and contaminants sorbed onto soil particles. If NAPLs are present, the contaminant must dissolve into the groundwater or partition into the vapor phase before the nearly instantaneous chemical reaction can occur. Thus, the effective rate of NAPL contaminant mass removal is usually limited by the contaminant dissolution rate rather than by the chemical reaction rate. It should be noted that

some oxidants affect the solubility of the NAPL compound, which may slightly accelerate the NAPL dissolution rate. In actual practice, the increased solubility is unlikely to significantly shorten the time of remediation.

With the exception of ozone, the ISCO chemicals are highly amenable to injection with direct-push equipment. Most of the ISCO solutions are less viscous than the injectants used for bioremediation. Therefore, under the same injection pressure, the ISCO oxidants can penetrate further into the subsurface soils, thereby contacting more of the contaminant mass in the subsurface environment. Also, because of the lower injection pressures, smaller injection equipment can be utilized and multiple injections are feasible over a short time period.

The principal limitation of any ISCO method comes in delivering the oxidant into physical contact with the contaminant. Failures of ISCO methods are almost invariably due to physical interferences within the sub-surface matrix that shield the contaminant from the oxidant. Most of the ISCO costs result from the complicated engineering methods that may be required to bring the oxidants into actual contact with the contaminant. By comparison, the cost of the oxidant is generally the least expensive portion of any ISCO method and does not vary significantly between the various methods.

Another drawback of ISCO methods occurs because the oxidants are not chemically specific for chlorinated compounds but instead react non-selectively with a wide range of naturally occurring organic and inorganic compounds. The natural oxidant demand of many soil types may consume more than 99% of the oxidant agent that can be delivered into the subsurface. As a result, an excess amount of oxidant must be supplied to the sub-surface to overcome the native oxidant demand. There are some soils types where exceedingly high natural oxidant demands make ISCO methods impracticable because of the amount of oxidant that may be required. The native oxidant consumption can easily be determined in lab tests with soil collected from the subsurface zone of interest. These should be routinely performed before selection of ISCO methods as the remedy for a site.

Rebound can be particularly problematic with ISCO methods and occasionally results in post injection increases in groundwater contaminant concentrations. This phenomenon is due to under-dosing of the oxidant agent, either through application of inappropriate amounts or over

insufficient time. An over-abundance of the oxidants are often used with soils that are perceived as being especially high in natural organic matter. It is often not appreciated that these highly organic soils may have a large contaminant mass bound up by the organic matrix. Because the oxidant non-selectively “burns out” the organic matrix, the remaining contaminant mass can then easily partition from the soil into the groundwater. If the subsequent oxidant dosing is inadequate for the newly mobile contaminant load, the result will be increased contaminant concentrations in groundwater. The problem is further compounded because the newly mobile contaminant mass may expand further through soils that are now devoid of the natural organic matter that previously retarded the plume migration.

To counteract rebound, some practitioners advocate injecting only low concentrations of the oxidants over longer periods of time to avoid burning out the natural soil organic matter. This is based on theories that PCE and other small, simple molecules will oxidize more easily than complex soil organics. In practice, this is generally not effective because the low concentrations of oxidant are lost to non-selective reactions and the PCE removal rate is directly proportional to the injected concentration of oxidant.

Another concern of ISCO methods is that the strong chemical reagents may have a sterilizing effect on the bacteria present in the subsurface and producing aerobic conditions. This can temporarily disrupt natural reductive dehalogenation processes that may be underway at a site. However, the sterilization effect tends to be short-lived and studies have shown native bacteria quickly re-populate the sub-surface once the oxidant levels fall off.

ISCO Methods Used at SCRD Drycleaning Sites

The following ISCO methods have been used at drycleaning sites in the collective experience of SCRD member states. The SCRD website, www.drycleancoalition.org, includes several site profiles where the ISCO methods used ozone, permanganate, Fenton’s Reagent, and/or hydrogen peroxide with varying levels of success. Sodium persulfate has been used at a few drycleaning sites; however, sufficient data has not been obtained for listing under the SCRD web site.

Other ISOC methods recently described in the literature include combining ozone with hydrogen peroxide and use of other chemical oxidants. As of the date of this publication, these methods have not been used at drycleaning sites under the supervision of SCRD member states.

Ozone

Ozone is the highly reactive, unstable O₃ molecule generated when molecular oxygen (O₂) is exposed to high-energy fields. Ozone gas has at best a half-life of a few hours. As a result ozone cannot be compressed, stored and transported, but must instead be electrically generated on-site from either ambient air or supplied oxygen. The technology requires a relatively high initial capital outlay with a low-to-moderate long-term operational cost. Unlike some other ISCO methods, the technology is never cost effective for large low concentration plumes because distributing ozone into the subsurface requires a network of permanent injection points.

Once ozone is generated, it is injected in a mixture with ambient air into or below the contaminant zone. The ozone rapidly dissolves into the groundwater, which shortens its half-life shortens to just a few minutes. The ozone forms hydroxyl radicals (OH[•]) via catalytic decomposition of water. Hydroxyl radicals may also be formed by ozone reactions with various geologic media and organic materials in the subsurface.

Ozone's primary chemical action is due to the hydroxyl radicals. The hydroxyl radicals are reactive with most hydrocarbon compounds, ultimately producing carbon dioxide and free inorganic salts (i.e., chloride from PCE). The small amount of ozone that is not consumed by formation of the hydroxyl radical is also chemically reactive at the double carbon-carbon bond found in alkenes, including chlorinated alkenes such as PCE. Intermediate transformation compounds are largely non-existent, or are so transitory as to not be of concern, as long as an excess of ozone and/or hydroxyl radicals are available for the reaction.

The radius of influence around ozone injection points varies depending on the soil type, injection pressure, and other operating constraints. In many instances, it is unclear whether the apparent radius of influence is due to the actual chemical oxidation effects of ozone or just the physical effects of air-stripping due to the volume of ambient air that is injected along with the ozone. Because of ozone's limited half-life once it is dissolved in water, reactive ozone is

unlikely to be found at significant concentrations in the water matrix beyond the immediate area of the injection point and ozone is unlikely to penetrate deep into formations where residual NAPLs may be found.

Reactions with native constituents in the groundwater hasten ozone degradation. Additional ozone must be applied to consume the native constituents in order to have an excess for reaction with the contaminant mass. Temporary injection points are not effective as the ozone only depletes the native constituents without attacking the contamination. Installing permanent injection points and the network of piping back to the ozone generator is generally the largest cost factor incurred with ozone injection.

A typical ozone system usually includes a manifold that allows ozone to be distributed to multiple injection points. Up to twelve injection points may be supplied from one generator. The input to the injection points can be simultaneous to all injection wells or staggered in pulses to various wells. Operation of the ozone generator generally does not consume large amounts of power so monthly electric bills are low; however, other costs for periodic maintenance and replacement parts can greatly elevate the long-term O&M costs. Because of the number of components (pumps, manifolds, flow controllers, etc.) and the various permutations of ozone concentrations versus air delivery volumes, considerable expertise is required to bring the system into, and maintain it, in optimal operation. Using ozone-compatible components is vital to long-term operation with minimal down time. The typical ozone system includes many component parts to improve the electrical ozone generation efficiency. These components can be housed in a small utility building or structure on the site. Alternately, a system can be trailer-mounted and moved between sites and connected to permanently installed injection points. Because ozone can be explosive at high concentrations and is a potential toxic inhalation hazard, any equipment housing structure should be properly ventilated and/or monitored.

Permanganate

Permanganate is a common disinfectant widely used in industrial and health care facilities. For environmental injection, it is available as either potassium permanganate in a solid form or liquid sodium permanganate. Regardless of which compound is used, both are diluted with water prior to being injected into the subsurface. Once diluted, the permanganate anion dissociates from the salt and acts as the chemical oxidant.

Sodium permanganate is generally more expensive than potassium permanganate for an equivalent amount of oxidant; however, it can be more cost effective because greater concentrations can be injected because of its higher solubility in water. Sodium permanganate solutions may have a slight advantage over potassium permanganate for use in clay soils. This is because the sodium cation acts as a deflocculant that creates micro-channels in certain clay types that allow the oxidant to spread more easily. Conversely, this can cause problems with clays that are especially prone to swelling.

One of the advantages of permanganate over other ISCO methods is that permanganate does not self-decay. Therefore, permanganate will persist in the subsurface for a much longer time than other ISCO injectable agents. Because the permanganate is persistent until it is chemically consumed in the subsurface, it is able to migrate further from the point of injection. Consequently, permanganate is especially appealing for treating residual contaminants trapped in soil, which may be oxidized when the oxidant finally reaches the residual untreated zone. These same properties make permanganate a hazard if injecting directly upgradient of sensitive receptors, such as water wells, surface water, etc.

Manganese dioxide precipitation can be a problem in some aquifers. While manganese dioxide is a naturally occurring harmless mineral, the accumulation can cause plugging of the aquifer. This may result in the flow bypassing the area of contamination and subsequent failure of the remedial project. Lab-scale experiments also suggest that interaction between the oxidant and the soil may result in altered soil structure and loss of effectiveness of subsequent oxidant delivery. Measurements of background manganese concentrations may be of value to establish existing conditions prior to remediation. At sites that are adjacent to drinking water supplies, the effect of permanganate application to the unsaturated and saturated zones should be carefully evaluated, including consideration of the effect of manganese dioxide precipitation on the aquifer.

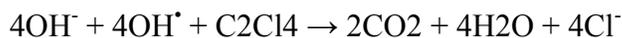
Another problem with permanganate arises because commercially available permanganates have heavy-metal impurities, including chromium. If a site is adjacent to a drinking water supply, the potential for groundwater contamination due to metals from permanganates should be evaluated and may be of sufficient concern to warrant selection of an alternate remedy.

One of the disadvantages of permanganate over hydrogen peroxide is that the solubility of potassium permanganate is temperature dependant. This is important because the kinetics of the chemical oxidation reaction is generally concentration dependant. Therefore, if one can only introduce low dissolved phase concentrations of the oxidant, the speed of the reaction (i.e. the kinetics) will be relatively slow.

Unlike some other ISCO methods, permanganate does not produce any toxic gas. However, appropriate handling gear and storage equipment is very important. Direct contact with any chemical oxidant should be avoided. There are minor differences in handling the permanganate chemicals, with the Sodium Permanganate being more problematic from a worker-exposure standpoint. Permanganate compounds are potentially explosive when mixed with combustible chemicals and may release oxygen gas during decomposition, which may further fuel a fire or explosion. Permanganate will start a fire if spilled on wood or paper.

Hydrogen Peroxide/Fenton's Reagent

Hydrogen peroxide is a powerful oxidant that is useful at drycleaning sites under carefully controlled conditions. Although straight hydrogen peroxide has been used to remediate contaminants, the most common application uses Fenton's Reagent, which is hydrogen peroxide combined with a ferrous iron (Fe^{++}) catalyst in a low pH solution to generate hydroxyl radicals (OH^{\cdot}). The hydroxyl radicals are stronger oxidants than hydrogen peroxide. Oxidation of PCE by Fenton's Reagent occurs in the following manner:



Fenton's Reagent will effectively destroy drycleaning contaminants upon contact. A benefit of Fenton's Reagent is that it can create aerobic conditions in the treatment zone. While aerobic conditions are detrimental to PCE degradation, some PCE daughter products, notably dichloroethylene and vinyl chloride, biodegrade more rapidly in aerobic conditions. Another benefit of Fenton's Reagent is that there can be an increased rate of contaminant volatilization resulting from the heat generated during the subsurface oxidation reaction.

The oxidation reaction is strongly exothermic, therefore the heat of the reaction may cause problems during site remediation. Use of high-concentration hydrogen peroxide solutions can generate considerable heat that can damage buried utilities commonly encountered near

drycleaning businesses. Worse yet, the rapid decomposition reaction can create explosive conditions if used in the presence of flammable or combustible compounds due to the resulting mixture of heat, oxygen, and flammable compound. The ENVIRONMENTAL PROTECTION AGENCY (EPA) indicated a hydrogen peroxide reaction was the source of a sewer and home explosion at a Wisconsin remediation site that resulted in one fatality and three injuries. A similar project conducted at an underground petroleum storage tank project in Cherry Point, North Carolina resulted in an asphalt parking lot buckling and a subsequent fire and explosion. As a result of these and similar incidents, the EPA urges caution in any use of hydrogen peroxide for in situ chemical oxidation of flammable compounds, such as gasoline. This may restrict peroxide use at many drycleaning sites, as it is common to find co-mingled PCE and petroleum plumes due to unrelated drycleaning and service station sources.

Hydrogen peroxide also presents additional hazards for worker during shipment and handling of the chemical. Hydrogen peroxide can rapidly self-decompose in contact with certain metals or combustible compounds at elevated temperatures, releasing considerable amounts of heat and oxygen gas. Hydrogen peroxide solutions ranging from 5% to 50% have been used for remediation activities; however, lower concentrations (i.e., less than 11%) are more controllable because the kinetics of the chemical reaction are concentration dependent.

Hydrogen peroxide rapidly degrades in the aquifer and the hydroxyl radicals are quickly consumed by natural organics. For this reason, this technology requires closer spaced injection points and higher volumes of injectants than many other reagents, and it is common to repeat the injections on a periodic basis. Injecting higher volumes of reagent increases the probability of displacement of contaminants in the aquifer. If permanent wells are used for injection, more wells with shorter screened intervals are preferable to wells with long screened intervals. Direct push injection, when feasible, allows for greater flexibility for injection point placement. Not only is reagent placement more precise, since multiple injection events will normally be required to remediate a site, but the use of direct push allows for a more economical placement of injection points.

Persulfate

As of the date of this publication, sodium persulfate has not been listed as a remedial alternative for any site profile listed on the SCRDP website. While it has been used at a few

drycleaning sites in the USA, sufficient data has not yet been accumulated to justify inclusion as a profile.

Sodium persulfate is a relatively stable, crystalline material that must be activated to form a reactive persulfate radical, which becomes a strong oxidant. Activation is accomplished by either heating or catalysis with proprietary transition metals. Activation by heating requires that heat must be applied to the soil or groundwater after a dilute concentration of sodium persulfate (usually ~10%) has been applied. Use of catalytic metals may involve a two-stage application process where the catalysts are applied after the sodium persulfate solutions; however, some proprietary methods have been developed that inject an activated persulfate/catalyst mixture. Methods have also been developed that combine persulfate along with hydrogen peroxide or permanganate.

Unlike hydrogen peroxide, sodium persulfate is persistent and does not result in significant heat or gas generation. Standard injection methods such as direct push probes can be used. The use of a high pressure, low volume injection lance system has also been used to facilitate mixing.

Similar issues associated with other ISCO methods exist such as storage of the oxidant, proper delivery of the product into the subsurface with good mixing, etc. Persulfate will erode metal conduits, pipes, etc. One potential problem with the use of persulfate arises because it forms a by-product, sodium sulfate, which may accumulate in the aquifer. While sodium sulfate has a low toxicity, the EPA has set a secondary drinking for it because it imparts a salty taste to drinking water. Use of sodium persulfate should be carefully evaluated for the potential impact on drinking water supplies.

Chemical Reductive Methods

Chemical reductive methods work by furnishing an excess of hydrogen atoms that promote sequential dechlorination of PCE. The reducing compounds have a direct impact via chemical reduction on the PCE molecule, but also foster sub-surface conditions that promote the growth of anaerobic bacteria that mediate biological reductive dechlorination. Almost all of the chemical reductants currently described in the remediation literature use Zero-Valence Iron (Fe^0) and vary only in the methods employed to bring the ZVI into contact with the contaminants.

The basic chemical mechanism underlying of ZVI is driven by water causing corrosion of the Zero Valence Iron (Fe^0) to Ferrous Iron (Fe^{++}). In the process, hydrogen gas (H_2), and a hydroxyl ion (OH^-) are released. The hydrogen gas combines with the halogenated organic compounds in the presence of the iron, which acts as a catalyst on the reaction. The end products of the reaction are ferrous iron, chloride ions, and the dehalogenated compound.

As of this publication date, only one of the site profiles on the SCRCD website documents the use of a chemical reductive methods. A permeable reactive barrier wall utilizing granular zero-valent iron and iron sponge was installed at a drycleaning site in Germany. It is uncertain whether any of these methods have been implemented at other drycleaning sites in the United States. A ZVI Permeable Reactive Barrier wall has reportedly been installed near a New York State drycleaner site; however, it is unclear whether the drycleaning site was the sole source of the contamination. The other ZVI technologies are briefly discussed below because pilot test data suggests these may become viable alternative remedies at drycleaning sites.

ZVI Permeable Reactive Barriers

Permeable Reactive Barriers (PRB's) have been a remedial technology for chlorinated plumes for approximately fifteen years. PRB's are filled with reactive iron filing media and simulate a "wall" to effectively form a treatment zone through which contaminated water must pass. To date, PRB's have been used on large sites where there is sufficient amount of property to allow installation of the systems.

PRBs are passive systems that generally have lower monthly O&M costs. The installation cost is usually fairly high and the duration of remedial effectiveness is unknown. Installation can be inhibited by underground utilities and unfavorable geologic conditions. Fouling and plugging of the reactive material can greatly reduce system effectiveness.

Traditionally, PRB's have been installed by excavating a deep trench perpendicular to the groundwater flow and filling the trench with iron filings. Chemical reduction as the groundwater flow carries the dissolved phase chlorinated plume through the reactive media. Continuous treatments walls commonly use continuous one-pass trenchers that dig and simultaneously replace excavated soil with reactive media in the trench. The trenchers can extend to approximately 35 feet below the ground surface and are huge pieces of machinery. Because of

disruption of underground utilities and the sheer size of the excavation equipment, PRB's have not been considered as viable remedy alternatives for drycleaning sites. Recent advancements in PRB placement technologies now allow injection of continuous barrier walls without trenching or with only minor disruption at the surface. It remains to be seen whether any of these methods can be cost effective for a drycleaning site.

A slightly less expensive option to a continuous PRB barrier wall of reactive iron filings is to construct the PRB as a funnel-and-gate system designed to direct water through a treatment zone. Funnel-and-gate systems are beneficial when water can efficiently be directed to a smaller treatment zone. The reactive material is placed in a centralized location (gate) that provides adequate retention time within the treatment zone. The "funnel" walls consist of interlocking metal sheet pilings or impermeable slurry walls that direct groundwater to the "gate" opening. Walls are installed to prevent contaminated groundwater from going through, above or around the walls. Groundwater velocity increases as the directed water approaches the gate. Replacement of the reactive material is easier with the funnel-and-gate system since the material is concentrated in the gate area. Even with the cost savings from only having to fill the gate portion of the wall with reactive media, the capital cost of installation is still considerably higher than other remedies for small sites. For instance, the proposed cost of a ZVI funnel and gate system at a drycleaning site in South Carolina was approximately four times higher than the next cheapest remedy under consideration.

Injectable ZVI: Powders, Nanoscale, and Emulsions

Recent advances in ZVI technologies have been directed towards delivery techniques that place the reactive iron in contact with the contaminant without the extensive trenching methods and disruptions that occur with installation of PRB's. Previous attempts with injecting colloidal powdered iron (roughly one micron diameter) have been problematic, as clogging of aquifers have resulted. New manufacturing technologies have led to commercial availability of increasingly smaller iron particles. Nanoscale iron particles on the order of 100-200 nanometers (i.e., 0.1- 0.2 microns) have proven adaptable to injection directly into dissolved phase plumes without aquifer plugging. Because of the smaller particle size, there is a dramatic increase in the reactivity of the iron due to the much larger surface area per unit weight of material. This results in a shortened half-life of the ZVI once it is injected into the ground. Because of the shorter half-

life, multiple injections have been required at the chlorinated plumes (non-drycleaning sites) that have used these remedies. Even smaller, 10 nanometer, particles have also been developed that combine reactive iron with Palladium and other proprietary metals that accelerate the reaction rate. Pilot test data suggests the bimetallic particles may require fewer injections to achieve complete contaminant destruction. Unfortunately, the bimetallic particles are only commercially available in limited quantities and are inherently costly.

To extend the reactive life of the ZVI particle, some methods have been developed that encapsulate the iron in either a protein coat or an emulsified soy-oil coating. The coatings protect the reactive particles for a period of time until the coating degrades. This allows the emulsified ZVI particle to remain in the sub-surface longer, potentially spreading further from the injection point before the reaction occurs. The protein or oil coating may also enhance natural reductive chlorination by stimulating the bacteria as the coating breaks down. Pilot test data also suggests that these encapsulated ZVI particles may be used for direct injection into DNAPLs, unlike other methods that are only effective against dissolved phase contamination. This is thought to be due to the protein or oil coating acting as a solvent that desorbs the NAPL into an aqueous matrix immediately adjacent to the reactive iron particle.

As of the date of this publication, Nanoscale ZVI or emulsified ZVI have not been injected in any drycleaning site under the control of SCRDR member states. The expense of a pilot test with Nanoscale ZVI proposed for a drycleaning site in the Florida Drycleaning Solvent Cleanup Program appears to be competitive with other remedial technologies.

SUMMARY

Remediation of drycleaning sites continues to be of great interest to states with remediation programs, as well as interested parties in the remaining states. SCRDR hopes this paper helps to provide a general guideline for determining what technologies are feasible at drycleaning sites. The logistics for completing a design can be challenging and when the financial burden is considered, contamination at drycleaning sites can challenge even the most experienced engineers and geologists. For additional information regarding drycleaning sites, processes, site profiles, etc. visit the SCRDR web site at www.drycleancoalition.org. Special thanks to all the state contributors for this paper and EPA TIO for their continued support of

SCRD. An electronic version of the paper may also be found on the SCR D web site at www.drycleancoalition.org under the Publications section.

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