# Cleanup of Soil and Groundwater at the Maryland Square PCE Site

This document describes possible methods for cleanup (remediation) and management of PCE-contaminated groundwater that forms the Maryland Square PCE plume. The plume, as bounded by the 5 parts per billion (ppb) contour, extends approximately 6,000 feet downgradient [View plume map next page]. However, because the shallow groundwater is not used as a drinking water source, the only currently identified exposure is inhalation via the vapor intrusion pathway.

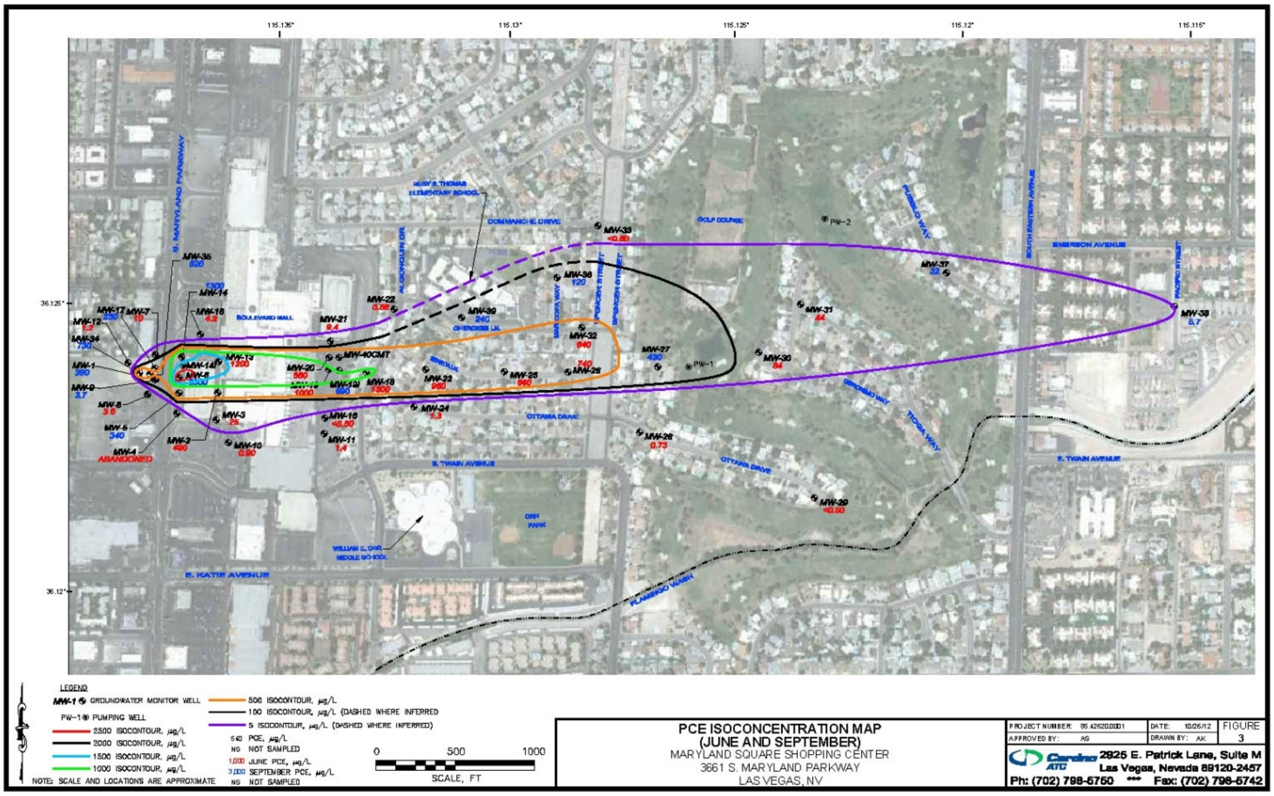
**Remediation of Source Area Soil —** Cleanup of the PCE-contaminated soil at the location of the former dry cleaners was completed in September and October, 2011. PCE-contaminated soil was excavated and sent to offsite facilities for treatment and disposal. An oxidant solution (potassium permanganate, $KMnO_4$) was sprayed onto the floor of the excavation in an attempt to further reduce contaminant concentrations. Complete details of the cleanup are described in the "Corrective Action Report for Source Area Soil"

**Remediation of Groundwater & Goal of Groundwater Remediation —** The long-term cleanup goal at the Maryland Square PCE Site is the cleanup of groundwater to a level that is protective of residential indoor air and of water resources in the Las Vegas area. Although the shallow groundwater is not used as a source of drinking water in Las Vegas, Nevada statutes reference the "maximum contaminant level" (MCL) for drinking water, as established by the U.S. EPA.

The MCL for PCE is 5 ppb, and this represents the long-term cleanup goal for protection of possible future receptors. The more immediate cleanup goal (interim-action level) for PCE in shallow groundwater at the Maryland Square PCE Site has yet to be determined; however, it will be set to be protective of indoor air. The interim-action level for groundwater, once attained, should allow for all home mitigation systems to be turned off.

**Technologies for Groundwater Remediation —** Effective cleanup of PCE-contaminated groundwater is a complex technical problem. The NDEP has conducted literature research on different methods that may be used to clean up PCE-contaminated groundwater. Not all technologies are appropriate for all sites, due to geochemical, hydrological, geological, or engineering issues. The results of the NDEP's research on possible types of remedial technologies for PCE-contaminated groundwater, combined with NDEP's knowledge of the geologic, geochemical and hydrologic conditions at the Maryland Square PCE Site, are summarized in the following paragraphs.

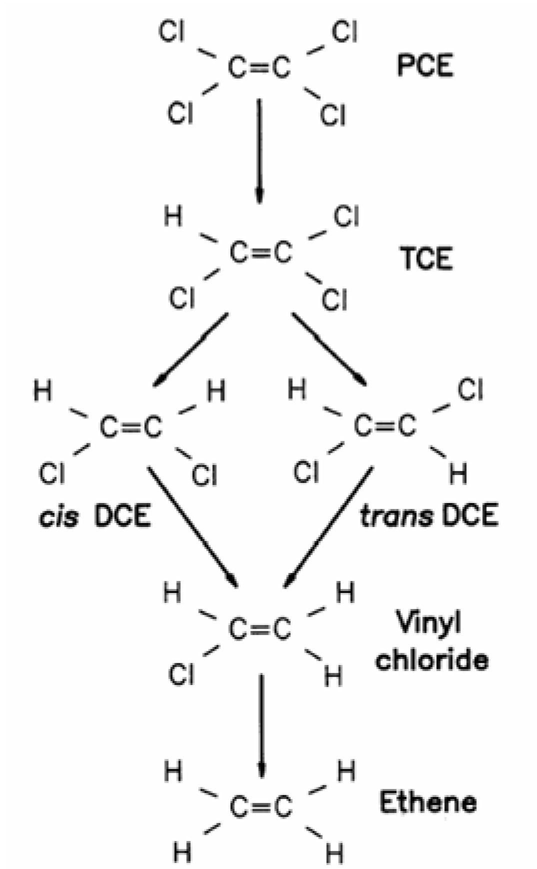
## Plume Map




Monitored natural attenuation (MNA) — MNA is inappropriate for this site because of current exposure risks via the vapor intrusion pathway and because there is no evidence that natural attenuation processes are providing, or will provide, any level of protection within a reasonable time frame.

Reductive Dechlorination Technologies — During reductive dechlorination (also known as "reductive dehalogenation"), each molecule of PCE ($C_2Cl_4$, which contains four chlorine atoms attached to two carbons that share a double bond), is degraded to trichloroethylene (TCE), ($C_2Cl_3H$, which contains three chlorine atoms), then to 1,2-DCE ($C_2Cl_2H_2$, which contains two chlorine atoms), then to chloroethylene (vinyl chloride), ($C2ClH_3$, which contains one chlorine atom) then to ethene ($C_2H_4$), then ethane ($C_2H_6$). During this process, chlorine atoms are released to solution as harmless chloride ions.

Reductive technologies to degrade PCE require that the oxidation-reduction potential (ORP, also referred to as "Eh") to be strongly reducing. As measured in millivolts (mV), complete reduction of PCE requires a range of approximately -220 to -240 mV. Employing reductive technologies means that substances may be injected into groundwater to establish sufficiently reducing conditions. In order for the Eh to reach -220 mV for complete reductive dechlorination of PCE, the competing electron acceptors such as oxygen ($O_2$), nitrate ($NO_3$), manganese (Mn), ferric iron (Fe+3), bicarbonate ($HCO_3$-) and sulfate ($SO_4$) must be satisfied. Knowing the concentrations of these constituents in the groundwater and the stoichiometry of the reduction reactions, one can calculate how much reductant would be required to achieve the desired Eh.




The Eh measured in the shallow groundwater system at the Maryland Square PCE Site (typically around 50 to 150 mV) averages well above the negative Eh values required for PCE degradation. The concentration of sulfate is as much as 3,700 mg/L at the site; very large amounts of reductant would be required.

## Geochemical conditions & concentrations of electron acceptors at the Maryland Square Site

| Parameter | Range for Maryland Square Groundwater | 1st Quarter, 2009 Groundwater | Units |
|---|---|---|---|
| Eh or ORP | -320 to 550 | 66 to 120 mV | mV |
| pH | 6.3 to 7.1 | 6.4 to 6.7 | pH |
| Temperature | 20 to 27 | 20 to 23 | °C |
| Specific conductance, SC | 900 to 9,100 | Average = 3,500 | µS/cm |
| Dissolved oxygen, DO | 0.7 to 8.0 | 0.7 to 3.8 | mg/L |
| Iron, Fe | 1.2 to 1.9 | -- | mg/L |
| Manganese, Mn | 0.02 to 0.05 | -- | mg/L |
| Bicarbonate, $HCO_3$ | 250 to 270 | -- | mg/L |
| Sulfate, $SO_4$ | 1,900 to 3,700 | -- | mg/L |
| Nitrate, $NO_3$ as N | 5.9 to 6.7 | -- | mg/L |

Eh or ORP (oxidation-reduction potential or simply, redox potential) is a measure of the oxidizing or reducing tendency of a system; measured in millivolts, mV
pH is a measure of hydrogen ion activity, but is commonly taken as describing whether a solution is acidic, neutral, or alkaline

SC is a measure of electrical conductivity of a solution, and is related to the dissolved ions or "saltiness" of the solution; measured in microsiemens per centimeter, µS/cm

All types of cleanup technologies that rely on reductive dechlorination are likely to be economically infeasible in the geochemical environment of the shallow groundwater system in the Las Vegas Valley. The geochemistry of the shallow groundwater system in Las Vegas is strongly aerobic, contains high concentrations (>3,000 parts per million [ppm]) of sulfate in some areas and is not conducive to degradation of PCE by chemical or biological reduction ("reductive dechlorination"). Partial dechlorination of PCE to TCE or cis-1,2-DCE or vinyl chloride is unacceptable because the toxicity of these daughter products may exceed that of PCE.

However, for completeness, several of these types of reductive dechlorination and bioremediation remedies are discussed briefly in the following paragraphs.

*In-situ Bioremediation or Anaerobic Biostimulation:* Biological approaches, both in-situ and aboveground, involve addition of a substrate/electron donor to promote and support indigenous bacteria capable of reductively dechlorinating PCE. In-situ methods require effective delivery and distribution of the amendment(s) to ensure contact with the contaminant and dechlorinating bacteria. This technology must be able to achieve and maintain a reduced environment that is conducive to complete PCE degradation.

*Anaerobic Biostimulation with Bioaugmentation:* This alternative is the same as anaerobic biostimulation with the addition of microorganisms that are capable of reductively dechlorinating PCE to ethene. The added bacteria must be able to adjust and control the environmental conditions to ensure survival and continued growth of the injected culture. This technology is better suited for a fence/barrier approach, but can be used plume-wide.

*Anaerobic Biowall:* This is a form of permeable barrier that uses solid-phase slow-release donors to support reductive dechlorination in, and downgradient of, the wall. This technology is a semi-passive approach that uses natural hydraulic gradients to move water through the treatment zone. Typically, plant materials including mulch, wood chips, manures, compost, cotton burrs, and a host of other organic-based materials are mixed with sands and gravels and placed into a trench that runs perpendicular to groundwater flow. Biowalls require substrate amendments once the more readily available substrates are released from the plant materials. Typical biowall designs include pipe systems to add those amendments. Hydraulic properties of biowalls are complex and can result in short circuiting or bypass.

*Hydrogen Release Compound (HRC):* The Regenesis company sells a product known as "HRC", which is injected into the subsurface to stimulate microbes and facilitate reductive dechlorination of PCE. This technology would encounter the same limitation as other in-situ reductive technologies.

*Permeable Reactive Barrier (zero-valent iron):* Permeable reactive barriers (PRBs) are a passive technology that relies on natural hydraulic gradient to move groundwater through the treatment zone. Zero-valent iron (ZVI) catalyzes the abiotic degradation of PCE, which is tied to the corrosion of the iron. The primary abiotic pathway takes PCE through dichloroacetylene to acetylene, avoiding cis-DCE and VC. However, as the iron corrodes, hydrogenolysis and biotic degradation promoted by the hydrogen that is released can form these reductive dechlorination daughter products. PRBs are constructed by placing the ZVI (either pure or mixed with sand) into an open trench, or injected under pressure into the formation. Barriers can be continuous with ZVI placed across the width of the plume, or they can be a funnel-and-gate configuration where impermeable barriers such as sheet pile or grout curtains direct groundwater to flow through a more localized mass of ZVI. High capital costs are generally offset by low operations and maintenance (O&M) costs. However, this technology suffers from the same limitations as the other reductive technologies if attempted at the Maryland Square PCE Site.

Air Sparging with Soil Vapor Extraction — In situ sparging offers the benefit of not bringing contaminated groundwater to the surface, but at the same time, this technology offers less direct plume control than the pump and treat alternative. However, air sparging systems are simple in design, require little O&M, require a small footprint and are relatively inexpensive.

In this remedy, air is injected through sparge points placed underground near the bottom of the contaminant plume. As the air bubbles move up through the formation, PCE transfers from the aqueous phase to the gas phase as the injected air migrates up to the unsaturated zone. Soil vapor extraction (SVE) to capture fugitive vapors is required for PCE applications to ensure that the PCE-laden vapor does not enter buildings or pose a human health risk. The off-gas from the SVE system may require treatment to remove PCE before discharging to the atmosphere, if regulatory levels for air emissions are exceeded.

Designing an in-situ sparging system requires that the vertical and cross-sectional profile of the PCE plume be well defined for optimum placement of the sparge points. Pilot testing must be conducted to determine the effective radius of influence of a sparge point and to define the initial and design operational parameters (i.e., number of sparge points, operating pressures and flow rates, etc.). Soil-gas permeability and radius of influence testing are performed to design an SVE system, so it adequately captures the vapors created by the sparging action.

Not all lithologies are conducive to successful remediation by air sparging. Low-permeability soils or highly stratified soils may cause air sparging to be ineffective, and there is the possibility of inducing migration of the contaminant. Thick and continuous layers of caliche may impede collection of sparged vapors; possibly resulting in fugitive contaminant vapors.

Ozone Sparging with Soil Vapor Extraction — Ozone is a strong oxidant that is known to oxidize PCE. Ozone injection is coupled with air sparging to both strip and chemically oxidize PCE. SVE is required when there is a potential for PCE stripping without complete oxidation, which can lead to vapor intrusion or other human health or ecological risk issues. SVE systems are designed to prevent uncontrolled vapor migration and typically extract larger volumes of vapor than are injected. The off-gas from the SVE will require treatment to remove PCE before discharging to the atmosphere if regulatory levels are exceeded.

If emitting the off-gas, an air permit will be required from the Clark County Department of Air Quality and Environmental Management (CCDAQEM). Ozone added to the injected gas flow has been shown to be effective for PCE destruction. Incorporating ozone injection would result in greater PCE destruction; however, it complicates the system design, requires additional operating and maintenance costs and adds to the capital cost.

Groundwater Extraction and Above-ground Treatment ("Pump and Treat") — This method offers both hydraulic containment and ex-situ treatment of extracted groundwater. In this remedy, extraction wells are situated to capture the PCE-contaminated groundwater from targeted areas along a transect of the plume, effectively stopping further migration of the portion of the plume that lies upgradient of the pumping wells. This process is called "hydraulic containment." The extracted groundwater is treated, then either reinjected or disposed of properly. There are many aboveground treatment options, including air stripping, granular activated carbon, and oxidation, among other treatments. The treated groundwater can typically be discharged to the storm water system under a NPDES permit or discharged to the sewer system under a POTW permit.

Standard pump and treat remediation is sometimes criticized as being too expensive and time-consuming, especially when cleanup levels are low, such as the

5 ppb MCL for PCE. However, this is a relatively dependable technology for capturing and treating large areas of contaminated groundwater. Pump and treat offers hydraulic containment of a migrating plume and can achieve significant reductions in contaminant concentrations. If applied with reasonable expectations (for example, a cleanup level of 100 ppb rather than 5 ppb), pump and treat can be a cost-effective remedy.

Successful application of pump and treat technology requires (1) establishment of realistic cleanup goals; (2) careful and detailed characterization of geologically complex sites, in order to design an optimal extraction system; (3) dynamic well-field management, with on-going evaluation of the operating well field; and (4) reinjection of treated groundwater to speed up flushing of the contaminants.

Phytoremediation — Phytoremediation may be an effective plume control technology at the Maryland Square PCE site if trees that are capable of "pumping" sufficient volumes of groundwater can grow and survive the local climatic conditions and tolerate the PCE concentrations and salinity of the groundwater. Cottonwoods, desert willows, cat claw acacias, and mesquite trees are all native to the area and have some potential for application. The ability of the trees to develop roots that intercept the water table would be a key factor in the technology's success. Establishing the trees so that their roots reach the water table and start to extract groundwater could take several years; therefore, phytoremediation could be part of a longer-term solution.

The trees would need to impart a hydraulic gradient that draws the plume to the root zone. The arid Las Vegas climate could optimize the evapotranspiration rate of the trees, which is the driving force of the pumping action. The trees could also add to the aesthetics of the landscaping.

Summary: Constraints to Cleanup of Groundwater The NDEP conducted a preliminary evaluation of the different types of technologies that may be used to remediate PCE-contaminated groundwater. Pilot studies and field testing are required to gather more detailed information to design the remedy. The cleanup of groundwater at the Maryland Square PCE Site is a technically complex problem for a number of reasons, including the following factors:

- Heterogeneous lithology of the sediments that host shallow groundwater make contaminant transport complex and cleanup somewhat unpredictable
- Geochemical conditions in the shallow groundwater system are unfavorable for natural or induced reductive dechlorination of the PCE and inhibit breakdown of PCE
- Infrastructure and buildings overlying the plume may limit treatment options
- Proximity to receptors (a residential area with two schools) make safety of the treatment a priority

- Presence of a golf course irrigation well with a compromised casing and well seal that lies in the centerline of the PCE plume creates an additional concern as a potential preferential pathway for vertical contaminant migration

The remedy must be designed to avoid spreading the plume, either by displacement by injected fluids or occlusion of porosity. Some form of hydraulic containment may be needed to prevent further migration of the PCE mass underneath the residential neighborhood. Clean water infiltrating or reinjected into groundwater immediately downgradient of the remedy (and upgradient of the neighborhood) would further decrease concentrations of PCE in the portion of the plume underlying the neighborhood.

**Summary: Key Limitations of Potential Remedies —** Several key points from the NDEP's evaluation of potential remedies include the following:

- Technologies that rely on anaerobic degradation (i.e., reductive dechlorination) are not likely to be economically feasible under the geochemical conditions of the shallow groundwater in Las Vegas; this limitation includes PRBs, biostimulation or bioaugmentation, HRC®, anaerobic biowalls, and other in-situ biodegradation strategies

- In situ chemical oxidation (ISCO) has the following issues that are challenges:
  - Unpredictable migration of oxidant solution injected into heterogeneous sediments
  - Unpredictable daylighting of the injected oxidant solution
  - Displacement of contaminated groundwater by the injected oxidant solution, with the potential to spread the plume
  - Blockage of porosity by precipitation of metals, such as manganese or iron oxides
  - Corrosion of underground infrastructure
  - Economic infeasibility, in that extremely large volumes of oxidant may be needed to remediate such a large contaminant mass spread over a large area
  - Mobilization of sorbed contaminant, resulting in increased concentrations of PCE in groundwater and soil gas downgradient of the treatment area
  - Safety
- Air sparging with SVE and ozone sparging with SVE could spread the plume if not properly designed; SVE should capture fugitive vapors released during the sparging. Both types of sparging are proven technologies, but lithologic heterogeneity makes any remedy difficult to design and air bubbles may block soil pores.
- Groundwater extraction and aboveground treatment requires on-going O&M and it is difficult to initially predict how long cleanup will take. However, this technology may offer hydraulic containment to prevent more PCE mass from migrating under the homes and PCE can be effectively destroyed in the extracted groundwater, under controlled, aboveground conditions. Cleaned groundwater can be re-injected to

prevent lateral expansion of the plume and to facilitate flushing of PCE-contaminated groundwater currently under the neighborhood.

**Groundwater Cleanup: Selection of a Final Remedy —** In selecting a final remedy for groundwater, the detailed evaluation of remedial alternatives will analyze data acquired during pilot testing and will consider the following criteria:

1. The potential for successful application (i.e., attainment of interim cleanup goals for PCE in groundwater) of the technology at the Maryland Square PCE Site based on hydrogeological and geochemical considerations.

2. The ability of the technology to control, reduce or eliminate the groundwater to vapor intrusion pathway in a reasonable time frame.

3. The ability of the technology to remove contaminant mass under controlled conditions.

4. Public health and safety concerns associated with implementing the technology in or near a residential area.

5. Public perception and acceptance issues.

6. Relative cost of implementation.

Technologies used for evaluating and cleaning up contaminated soil and groundwater at other dry cleaner sites across the country were summarized in a technology survey conducted by the SCRD;
see: http://www.drycleancoalition.org/tech/.