DNAPL Remediation at Camp Lejeune Using ZVI-Clay Soil Mixing

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ABSTRACT: Site 88 at Camp Lejeune, NC is the former Base dry cleaners. Historical activities have resulted in a release of dry cleaning solvents especially perchloroethene (PCE). A 10,000 square foot source area was delineated using membrane interface probe (MIP) technology, and soil and groundwater sampling. The contamination extended from the water table (roughly 7 feet below ground surface (bgs)) down to 20 feet bgs. At 20 feet bgs, there is a clayey-silt layer that prevents further downward migration of dense-nonaqueous phase liquid (DNAPL). The estimated volume of contaminated soils was 7,000 cubic yards. DNAPL was observed in several wells at the site.

Soil mixing with zero-valent iron (ZVI) clay addition was implemented at the site in February 2005. The ZVI treated the chlorinated solvents, while the clay created a low permeability zone that limited flow of groundwater into and out of the treated area. A treatability study indicated a PCE half-life on the order of 30 days would be achieved with ZVI concentration of 2 percent and bentonite of 1 percent.

The project included site preparation, removing and re-routing utilities, abandoning monitoring wells, removing soil and concrete debris, soil mixing, site stabilization, utility installation, construction of a parking lot, and monitoring. Since the site was located in a highly developed portion of the base, monitoring well and utility removal had to be complete prior to mixing.

The soil mixing was completed during a 17-day period in February 2005. A crane was used to turn a 10-ft auger while injecting the slurry of ZVI and clay. A total of 200 tons of ZVI and 100 tons of bentonite were mixed to create 146 overlapping columns. Off-gas was treated with activated carbon. After allowing approximately six weeks for settlement, 196 tons of cement were added to the top five feet of soil over the treatment area to stabilize the site for a parking lot.

The results of the treatment are encouraging. One year after the treatment, PCE soil concentrations were significantly reduced with average concentrations of over the entire treatment area being reduced by 82%, with a median concentration reduction of 99%. Reductions were lower in about 1/5 of the area where mobile DNAPL had been present prior to treatment. Reductions in soil concentrations were 61% in this area and were 99% in the remaining 4/5 of the treated area. Overall reduction based on a weighted average of these results is 91%. ZVI was still present in the treatment area, so that continued treatment should occur. Groundwater concentrations of PCE were reduced by greater than 96% in the treatment area, but DCE concentrations did increase significantly in one groundwater well.

Downgradient water quality improved after the treatment, with PCE reduction of 67 and 90%. Hydraulic conductivity within the treatment area was reduced 50 to 400 times (one to two orders of magnitude) with a post-treatment hydraulic conductivity of 0.013 ft/day, so that there should be a significant reduction in mass flux from the treated area.

INTRODUCTION

MCB Camp Lejeune is located in Onslow County, North Carolina. The site consists of the former Building 25, and the surrounding paved and grassy areas. Building 25 was used as a dry cleaning facility since the 1940's. Tetrachloroethene (PCE) was used as the drying cleaning agent since the 1970's. The PCE was stored in one 150-gallon above ground storage tank (AST) adjacent to the north wall of Building 25. PCE was reportedly stored in the AST from the 1970's until the mid-1980's. During this time, facility employees have reported that spent PCE was disposed of in floor drains which were connected to the sanitary sewer system. In March 1995, self-contained dry cleaning machines were installed in Building 25, eliminating the need for bulk storage of PCE, and the USTs and AST were removed.

The general profile of soils below Building 25 consists of alternating sands and silt turning into silty fine sands in the zone just above a low permeability silt and clay unit. The top of low permeability unit exists at roughly 20 ft bgs. The silty find sands were found to have the highest concentrations of PCE and were targeted for this effort.

Groundwater is at a depth of approximately seven feet below ground surface. In general, groundwater flow is east to west across the source area, with components flowing to the southwest and northwest.

The estimated source zone is based primarily on investigation with a Membrane Interface Probe (MIP), soil sampling, and groundwater sampling. The source area around Building 25 was approximately 10,000 square feet with treatment volume of approximately 7,000 cubic yards (cy). The depth of contamination extends into to the silty clay layer for a total depth of approximately 20 ft bgs.

An engineering evaluation/cost assessment (EE/CA) followed by a non-time critical removal action (NTCRA) was undertaken with the objective of removing or treating as much DNAPL from the source area as is practical and cost effective. Other remedial action objectives (RAOs) were to reduce exposure and risk to human and ecological receptors, and to reduce the potential for contaminant mass flux from the source zone to groundwater. Based on potential effectiveness, implementability, and cost, shallow soil mixing with a ZVI-Clay slurry addition was the selected remedial technology for the DNAPL source area located around Building 25.

Technology Description

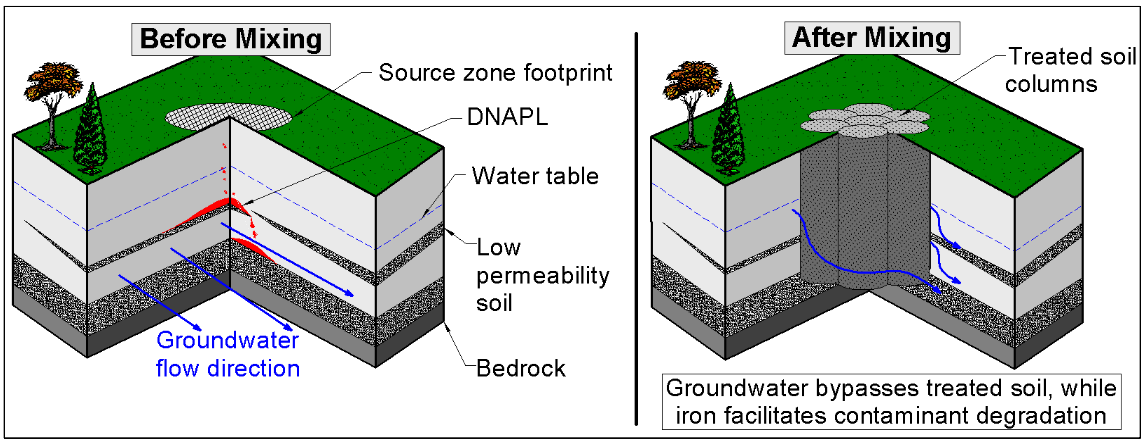
Shallow soil mixing is an in-situ technology that uses a large auger system with the ability to deliver zero-valent iron and clay (ZVI–Clay) slurry into the soil while mechanically breaking up and mixing the soil. Shallow soil mixing distributes the DNAPL source zone into a homogenous mixture of soil, clay, iron, and target contaminants by turning a large diameter auger while cycling up and down throughout the mixing column.

The clay reduces the hydraulic conductivity of the treated media. This provides source containment. Inclusion of clay also: 1) facilitates drilling, 2) provides a high viscosity delivery fluid (necessary for suspension of the ZVI) improves the uniformity of subsurface mixing, 4) reduces inflow of competing electron acceptors (e.g., dissolved oxygen and nitrate), 5) increases residence time for the reaction to proceed, 6) enhances capillary rise precluding air entry into treated material above the water table, and 7) constrains adverse migration of dense non-aqueous phase liquids.

DuPont and the University of Waterloo (Wadley et al., 2005) pioneered this technology in the 1990s and early 2000s. In 2003, DuPont donated patents for the technology (Batchelor et al. 1998 and 2002) to Colorado State University (CSU).

ZVI is a strong reducing agent and its properties are well suited to the treatment of many common chlorinated contaminants. Under certain groundwater conditions, elemental iron is oxidized to ferrous iron, releasing two electrons in the process. These electrons participate in a variety of reactions leading to the transformation of the target contaminant.

The reaction proceeds through two known pathways. In the beta-elimination pathway, the formation of partially dechlorinated products such as dichloroethene (DCE) and VC is avoided, and PCE and TCE are transformed directly to ethene via the production of some short-lived intermediates, such as chloroacetylene and acetylene. Most experts believe that chlorinated solvents degrade primarily through the beta-elimination pathway when exposed to iron. Very little DCE or VC have been found in laboratory or field studies with iron, indicating the dominant mechanism is probably beta-elimination. In the hydrogenolysis, or sequential reductive dechlorination pathway, one chlorine atom is removed in each step, so that TCE degrades to *cis*-1,2 DCE, then to VC, and finally to ethene and ethane (Environmental Restoration Technology Transfer (ERT2) Webpage).



TREATABILITY STUDY

CSU conducted laboratory studies that characterized the potential to treat PCE and associated degradation intermediates using ZVI-clay. The experimental setup involved 1) admixing varying amounts and types of iron with bentonite clay and soils collected from Site 88 and 2) measuring concentrations of target compounds at 3, 7, 14, 31 and 59 days.

Results of the treatability study indicated an approximate 75% decrease in PCE over the 59-day study. Half-life estimates ranged from 20 to 30 days. Extrapolating the observed degradation rates through time, it appeared that the vast majority of PCE can be depleted in a period of a year or less. Also, significant accumulation of TCE, DCE isomers, or VC was not observed.

Studies with 1, 3, 5 and 7 % Peerless™ iron (dry soil weight basis) indicated faster rates of degradation with greater amounts of iron. However, similar overall decreases were not observed after 59 days. The optimum mixing blend to be injected into the DNAPL source area was a grout containing 2% ZVI-clay and 1% bentonite.

IMPLEMENTATION

All utilities located within the treatment area were rerouted or abandoned. The utilities rerouted include: water (220 ft), electric (285 ft), storm sewer (100 ft), and steam (215 ft). In addition, 19 groundwater monitoring, extraction, and recovery wells within the treatment area were abandoned.

Slurry injection and mixing will create a fluff or increase in soil volume. The amount of resulting fluff is a function of the soil type, injection volume, reagent type, and operating conditions. To contain this fluff, roughly 1,000 cy of soil was removed prior to mixing for disposed at the Base landfill. The area of excavation was extended outward laterally from the treatment area boundary in order to keep the excavation area to a depth of 3 ft or less.

Soil mixing activities were conducted from February 11, 2005, until February 28, 2005. The soil mixing was performed using a 10-foot diameter auger. A 150-ton Manitowoc 4000 W series crane, and a 300,000 foot-pound rotary torque drill rig were used to mix the soil. ZVI-clay slurry was pumped through the hollow Kelly Bar connected to the auger. The auger was equipped with injection ports to inject the slurry into the soil at the point of mixing. As the auger rotated, the slurry was pumped and mixed with the in-situ soils. The auger's continued rotation and downward movement provide homogeneously-mixed columns to the desired depth. Eight or more up and down strokes were used to mix each column.

The centers of the columns were positioned in the treatment area so the columns overlapped to treat 100% of the area. The center points of each column were laid out each day prior to drilling using a sub-meter accurate Global Positioning System (GPS) unit. During soil mixing activities, 146 columns were advanced to 20 ft. and approximately 7,050 cy of impacted soil was treated.

A batch plant was constructed on site to prepare the iron-bentonite slurry mixture to the project specifications. The slurry was produced in a high-shear mix plant, capable of producing up to 1,000 gallons of ZVI-clay per batch. The soil mixing process consisted of four batches. Batches one, two, and three, consisted of three 100-pound (lb) bags of bentonite and 400 gallons of water each. Batch four consisted of one 100-lb bag of bentonite and one supersack of either 2,500 lbs or 2,230 lbs of iron filings, each column was mixed a minimum of six times. For each 10 ft diameter column, approximately 124 lbs of iron and 62 lbs of bentonite were blended per vertical foot of soil. This achieved the specified 2% iron and 1% bentonite addition to the soil by weight.

Fugitive emissions had the potential to occur during the soil mixing. These emissions were captured from the mixing zone by a 14 ft diameter removable hood. The removable hood was an open bottom cylinder that covered the surface of the mixing zone while mixing is preformed directly beneath. Negative pressure was kept on the headspace of the hood using a 1,800 cubic feet per meter variable speed vacuum unit, pulling any vapors and dust to a vapor treatment system. Components of the vapor treatment system include a high efficiency particulate air (HEPA) filter for dust particle removal, a 3,000 lb. granular activated carbon filter and a discharge stack.

The uniformity of the mixing was monitored in the field by collecting soil samples immediately after mixing and analyzing for iron using a magnetic separation process. Iron contents ranged from 2.4 to 5.7 percent suggesting that uniform mixing was achieved.

SITE RESTORATION

Upon completion of the shallow soil mixing activities, stabilization of the soil was required in order to proceed with construction of the parking lot. Stabilization activities took place between April and June 2005. Stabilization was performed by mixing cement into the top 5 to 10 feet of the treatment area.

The treatment area was stabilized using the predetermined 5% Portland cement mix ratio, and mixed to 5 ft bgs. Mixing was conducted by adding one ton of cement to a 10 ft by 10 ft area, over the entire treatment area. After stabilization, a significant portion of the treatment area was stable with this cement ratio and at this depth, while the center of the treatment area was still soft. The center of the treatment area was then divided into a grid pattern, with twenty eight 15 ft. by 15 ft. grids. Each grid was then stabilized to 10 ft bgs with 6% Portland cement. In total, 190 tons of cement was used to stabilize the treatment area.

In order to restore the nearby buildings back to working condition, buried water lines (130 ft), buried steam lines (230 ft), and overhead electrical lines (300 ft) were installed.

After completion of the soil mixing and site stabilization, a parking lot was constructed over the site. Approximately 38,000 square feet was paved for the parking lot, requiring approximately 1,450 tons of asphalt creating 65 parking spaces. Other improvements include stormwater drainage, with approximately 400 ft of drainage pipe installed including necessary manholes and junction boxes, parking lot markings, bumpers, etc.

MONITORING/RESULTS

The performance of the project was evaluated through monitoring of soil gas, soil, and groundwater sampling and analysis. Baseline and historic data was compared to data collected after soil mixing.

Soil Gas Sampling - Prior to soil mixing, soil gas sampling probes (Geoprobe® PRT systems) were installed at three locations to a depth of 5 ft bgs. The Geoprobe® PRT system contains Teflon® tubing that attaches the PRT gas sampling adapter to a series of sample valves, a vacuum gauge, and flow controller in order for the gas to enter the one liter summa canister.

Laboratory analysis indicated the presence of PCE, TCE and VC in all the base line soil gas samples. The highest concentration of PCE and TCE were 1,400,000 micrograms per cubic meter ($\mu g/m^3$) and 4,500 $\mu g/m^3$, respectively.

Seven months after treatment, soil gas samples were collected at the same locations. Analytical results indicate significant reduction in VOC concentrations. PCE concentrations were reduced by 83 to 99.97 percent.

Soil Sampling - Twenty confirmatory soil samples were collected within ten different mixing columns at two depths in the treatment area. The samples were taken the day of or the day after mixing. The PCE concentrations ranged from 420 mg/kg to 2,700 mg/kg, with an average of 1,097 mg/kg . It should be noted that the concentrations from samples collected immediately after mixing had a much smaller range and thus better “baseline” compared to pre-mixed samples because of the significant vertical variability in the contaminant distribution prior to mixing.

Soil sampling was conducted throughout the duration of the project including: February, April, August, October 2005, and February 2006. For purposing of evaluating the data, the treated area was divided into the area where mobile DNAPL was generally observed prior to mixing (about 1/5 of the area) and the rest of the area. The area with mobile DNAPL was also where a pilot test of Surfactant Enhanced Aquifer Remediation (SEAR) was performed (Duke, 2000).

Significant PCE reduction was observed across the site. Table 1 summarizes the data while Figure 1 illustrates the change in the weighted average PCE concentration with time. A reduction of the average concentrations of 82% was achieved. In areas where mobile DNAPL was observed prior to treatment, the reduction was less than other portions of the site (61 percent). The other, non-mobile DNAPLs areas of the site had 99 percent reductions. Overall reduction based on a weighted average of these areas is 91%. The range of the data from the last sampling round from this area was from 0.19 to 0.75 mg/kg, which suggest very good uniformity. DCE concentrations were generally less than 50 mg/kg and vinyl chloride non-detect, so that beta-elimination, with complete dechlorination was likely the predominate pathway.

Table 1 – Soil PCE Concentration Summary (mg/kg)

	Overall Average Concentration	Average of Non-Mobile DNAPL Areas	Average of Mobile DNAPL Areas
1 Day Post Treatment	1,097 [24 samples, 10 locations, 2 or 3depths]	1,066 [19 samples, 12 locations, 2 or 3 depths]	1,183 [5 samples, 3 locations, 2 depths]
360 Days Post Treatment	199 [21 samples, 7 locations, 3 depths]	0.43 [12 samples, 4 locations, 3 depths]	463 [9 samples, 3 locations, 3 depths]
% Reduction	82	>99	61
% of total area	100	78	22

It is not clear why the mobile DNAPL area exhibited poorer performance at one year.

Soil samples from October 2005 were analyzed by CSU to measure the iron content. The average iron content was 0.84% and 1.29%. These values indicate that ZVI is still present and available for treatment so that further reductions in the mobile DNAPL area are anticipated.

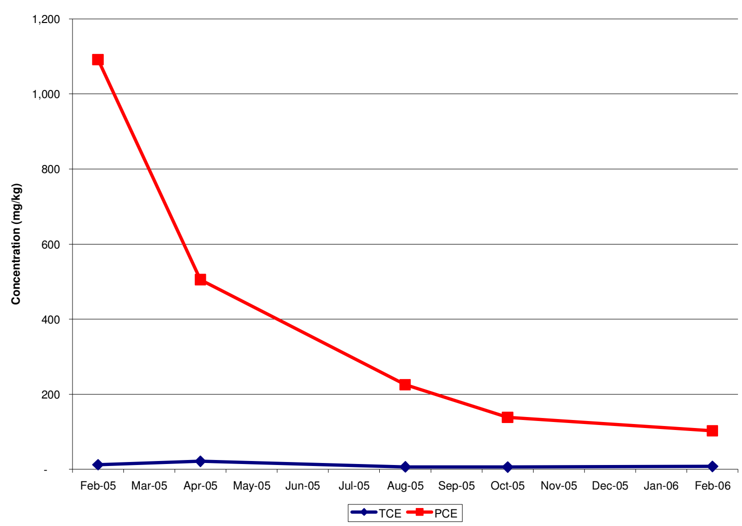


Figure 1. Average PCE and TCE Soil Concentrations (mg/kg) Over Time

Groundwater Sampling - Groundwater sampling in 2004 from wells within the treatment area, but without DNAPL had average PCE, TCE, and DCE concentrations of 64 mg/L, 37 mg/L, and 39 mg/L respectively. Wells that historically contained DNAPL were not sampled as part of this effort.

After mixing, four new monitoring wells were installed within and below the treatment area. In addition, five monitoring wells were installed around the treatment area (3 downgradient and 2 upgradient) prior to mixing to observe if any changes or contaminant migration would occur during mixing.

PCE concentrations from one of the shallow monitoring well in the treatment area (in the non-mobile DNAPL area) were below detection limits 12 months after treatment, while the other shallow well (in the mobile DNAPL area) had 1.5 mg/l of PCE. This is a reduction of approximately 96 percent based when the PCE concentrations are back extrapolated to February 2005. DCE concentrations increased to up to 390 mg/l in the well in the mobile DNAPL area suggesting some of the transformation that was occurring was due to reductive dechlorination. The deep wells showed no indication of increase in concentration.

The downgradient wells, which are 10-20 ft from the treatment area, have shown a reduction in PCE concentration during the project. In these wells, there was an initial increase in PCE during treatment, however the concentration has fallen by 67 and 90% one year from the baseline sampling (from roughly 22 and 25 to 7 and 2.5 mg/l PCE, respectively), with little increase in DCE or vinyl chloride.

Aquifer testing (slug tests) was conducted on wells inside and outside the treatment area. Hydraulic conductivities of the upgradient and downgradient wells are on the same order of magnitude, 0.12 ft/day and 0.67 ft/day respectively. In contrast, the hydraulic conductivity value for the treatment area well is an order of magnitude lower, 0.013 ft/day or $4.6x10^{-6}$ cm/s.

OBSERVATIONS/CONCLUSIONS

Observations made based on the results of the Site 88 NTCRA are as follows:

- Within the treatment area PCE concentrations within the soil were significantly reduced after one year. Reduction was as follows:
  - ❖ Average concentrations of entire treatment area – 82%
  - ❖ Mobile DNAPL area – 61%
  - ❖ Non-mobile DNAPL area – 99%
  - ❖ Weighted average (22% NAPL area, 78% non-NAPL area) – 91%
- Reduction of areas with observed mobile DNAPL was less than areas that had no mobile DNAPL. Reasons may include:
  - ❖ A much higher initial concentration that was not detected during initial sampling.
  - ❖ Slower reaction kinetics associated with DNAPL
  - ❖ DNAPL possibly coating the ZVI, thus hindering the reaction
  - ❖ Impacts of the residual SEAR chemicals
  - ❖ DNAPL being slow to dissolve into water, thus slowing the reduction reaction
- ZVI is still present in the treatment area, so that continued treatment should occur.
- Soil gas analysis indicates a reduction of PCE concentration within the treatment area has an average reduction of 99% seven months after mixing.
- Groundwater concentrations of PCE were reduced by more than 96% in the treatment area.
- DCE concentrations did increase significantly in one groundwater well within the treatment area.
- Downgradient water quality appears to have improved from the treatment process with PCE reduction of 67 and 90%.

- Hydraulic conductivity within the treatment area was reduced 50 to 400 times (one to two orders of magnitude) with a post-treatment hydraulic conductivity of 0.013 ft/day.
- There were no measurable air emissions during the treatment process. Contaminant vapors were easily captured with the hood and treated in an onsite carbon system.
- Treatment took approximately 3 weeks, and full implementation time was approximately 9 months. This total implementation time was from fencing the site and demolishing the slab to completing the parking lot.
- A new 38,000 square foot parking lot has been installed at the Base that has provided 65 new parking spaces and caps the treatment area.
- A significant amount of the project cost was associated with preparing the site and site restoration. These activities were necessary due to the age, location and end use of the site. Roughly 33 to 40% of the project costs were associated with these logistical issues.

NTCRA OBJECTIVES AND GOALS

The NTCRA was successful in meeting the established objectives and goals. Contaminant volume and mobility have been significantly reduced. Within the treatment area, the overall mass of the contaminant plume was reduced by greater than 90%. The mixing activities took place within three weeks once the site had been prepped, i.e. abandonment of utilities and excavation and removal of the foundation of former Building 25. Further, Site 88 has been fully restored, installing water, steam, and power lines to supply surrounding buildings as well as paving a new parking lot over the treatment area.

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