ERI Evaluation of Injectates Used at a Dry-Cleaning Site

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A former dry-cleaning site in Jackson, Tennessee, has undergone remediation to treat dense nonaqueous-phase liquid (trichloroethene [TCE] and tetrachloroethene [PCE]) contamination in the subsurface. The dry cleaning operation closed in 1977. In 2002, a series of injections were made at the site consisting of corn syrup, vegetable oils, and Simple Green®. In 2004, approximately 200 cubic yards of contaminated soil were excavated, and the bottom of the excavation was covered with sodium lactate.

In 2009, the site was characterized using proprietary electrical resistivity imaging (ERI; commercially available as Aestus GeoTrax Surveys™). Follow-up confirmation soil borings targeted anomalies detected via the geophysical work. The results indicate an extremely electrically conductive (less than 1 ohm-m) vadose zone downgradient from the injection wells, and extremely electrically resistive areas (greater than 10,000 ohm-m) in the phreatic zone near the injection area.

The sample data indicate that the electrically resistive anomalous zones contain moderate to high concentrations of undegraded dry-cleaning compounds. Electrically conductive anomalous zones are interpreted to be areas of biological activity generated by the amendments injected into the subsurface based on the extreme conductivity values detected, the chemical composition (i.e., PCE degradates are present), and the dominant vadose-zone location of the conductive zones. © 2012 Wiley Periodicals, Inc.

INTRODUCTION

The characterization of nonaqueous-phase liquid (NAPL)–contaminated sites is difficult, as there are many complicating factors relative to correctly understanding the distribution of NAPL products. NAPLs generally do not exist solely as free-phase product in the subsurface, but rather as a combination of free-phase zones with varying saturation levels and related dissolved-phase impacts. Degradation creates new compounds to monitor with new transport and risk properties. The variations in density and capillary forces create separation of the areas into blobs that are independent in their location from other areas on the site (Halihan et al., 2005a). Additionally, there are commonly multiple sources of NAPL impacts both temporally and spatially.

To further complicate the understanding of contaminant distribution in the subsurface, multiple remediation schemes are often attempted by multiple contractors and may include the injection of a range of treatment solutions in lightly monitored injection schemes. If these remediation schemes do not solve the problems for a site, the

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remaining subsurface distribution of original compounds, degradates, and injectates is a complicated three-dimensional distribution that changes over time.

Geophysical scanning techniques are seemingly the most reasonable approach for solving these types of complex site characterization issues. Unfortunately, the resolution and accuracy of the geophysical methods historically have not been sufficient to solve these site characterization problems and, thus, became suspect as potential methods to apply at these complicated sites.

Electrical resistivity imaging (ERI) technology has experienced significant advances in the last 20 years in both acquisition and processing (Daily et al., 2004). Some researchers have focused on improving the ERI process such that the improved methods can be used to image compounds such as undegraded NAPL, which exists in the subsurface as strong insulators (Halihan et al., 2005b). Also recently discovered is that when NAPL degrades as a function of bacterial processes, this process causes an increase in electrical conductivity, especially in the capillary zone, smear zone, and upper saturated zone (Atekwana & Atekwana, 2010).

When properly designed, a limited and focused drilling/sampling effort along with robust data integration allows the resistivity ranges encountered at a project site to be calibrated to provide an understanding of the spatial distribution of contaminated fluids and bioactivity across the survey domain.

ERI techniques have also been used to evaluate *in situ* chemical oxidation (ISCO) injections and have found that many injection programs are completed before practitioners realize that the injectate did not uniformly distribute itself in the subsurface (Albano et al., 2010; Halihan et al., 2011; Nyquist et al., 1999). The chemical reactions that occur after injection may not establish themselves as a geophysical signal for months to years after the injection, so understanding the initial distribution of injectate is only part of the puzzle relative to understanding overall success of an injection program.

An ERI scanning approach is not designed to be used alone and will normally not eliminate the need for drilling and sampling, which is typically a necessary and valuable component of a successful site characterization strategy. Specifically, drilling/sampling work that is focused on confirming the composition of anomalous zones allows calibration of the ERI electrical data/images back to the chemical/physical/biological properties of interest relative to regulatory standards and remedial design inputs. The ERI electrical images are effectively an amalgam of four individual signals. The intensity of the signals increases as follows: formation solids (soil and rock), groundwater, added fluids (contaminants and injectates), and bioactivity. When properly designed, a limited and focused drilling/sampling effort along with robust data integration allows the resistivity ranges encountered at a project site to be calibrated to provide an understanding of the spatial distribution of contaminated fluids and bioactivity across the survey domain.

Assessment of dense nonaqueous-phase liquid (DNAPL) sites using ERI can be successful yet presents new challenges. Experience on these sites indicates that soil and groundwater sampling data may be difficult to correlate to ERI images for a number of reasons including but not limited to the following:

- incorrect sampling interval choices;
- incomplete analytical suites (i.e., ERI "sees" bulk properties in the ground, so only testing for soil contamination and/or a limited analyte list may not provide sufficient data to correlate subsurface conditions observed in ERI datasets);
- effect of sampling and analytical methods (e.g., collection of filtered versus unfiltered groundwater samples, soil analytical data reported as dry-weight or wet-weight concentrations);

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- capillary effect (i.e., as a multiphase system, the NAPL phase does not enter the sampling device, either a well or direct-push screen, or is not extracted properly in the laboratory from a soil sample); and
- occurrence of a range of ongoing subsurface reactions, such as inorganic reactions and microbial degradation.

These complexities do not allow a simple approach of correlating a geophysical measurement to a concentration of a particular constituent as would be done on a simple site only impacted by chlorides for example. Instead, an evidence-based approach (analogous to the medical industry's evidence-based medicine) must be taken to determine the biogeochemical zonation of the subsurface that is mapped electrically and correlated to point chemical samples.

A former dry-cleaning site in Jackson, Tennessee, provided the opportunity to use proprietary ERI to evaluate the results of injecting a range of compounds into a site impacted by DNAPL and LNAPL compounds. This is an urban site that had multiple facilities over a range of time and, therefore, posed a significant challenge relative to site characterization. For this site, the project objectives were to determine if ERI could:

1. Locate areas impacted by NAPL that were previously uncharacterized,
2. Evaluate the efficiency of the previous injection programs, and
3. Provide an indication of biological activity in the subsurface.

SITE DESCRIPTION

The project site is a former dry-cleaning site, Boone Dry Cleaners, located in Jackson, Tennessee (Exhibit 1). The site operated as a dry cleaner between the mid-1940s and the mid-1970s, at which time it was converted to a welding facility. In 2003, a tornado destroyed the structure, and the site became a parking lot for a convenience store that is currently an operating retail gas station using underground storage tanks.

The upper ten feet of the site is a silt deposit with some sand and clay stringers, below which lies a sand unit. The site contained approximately 34 existing monitoring wells drilled to a depth of approximately 6 meters (20 feet) to evaluate the hydrogeology and distribution of contaminants. The water table on the site was approximately 2.75 meters (9 feet) below ground surface (bgs) in 2003. More current groundwater elevation data were not available but were assumed to be similar to levels from 2003. The hydraulic gradient trends toward the southwest. Site investigations have detected trichloroethene (TCE) and tetrachloroethene (PCE) from the dry-cleaning operation as well as their breakdown products and benzene, toluene, ethylbenzene, and xylene (BTEX) compounds presumably from the adjacent facilities with gasoline underground storage tanks.

Several phases of remedial action have been implemented at the site, including the injection of corn syrup, Simple Green®, and vegetable oil into the subsurface every two weeks between May and August 2002. The total volume of injectate is not known. A one-time injection of soybean oil occurred in December 2002. It is unknown how the mixture of injectate was chosen.

In December 2004, approximately 215 cubic yards of contaminated soil were excavated from the site, although the exact excavation location is unclear. The bottom of the excavation was covered in sodium lactate before being filled with #57 stone and clean

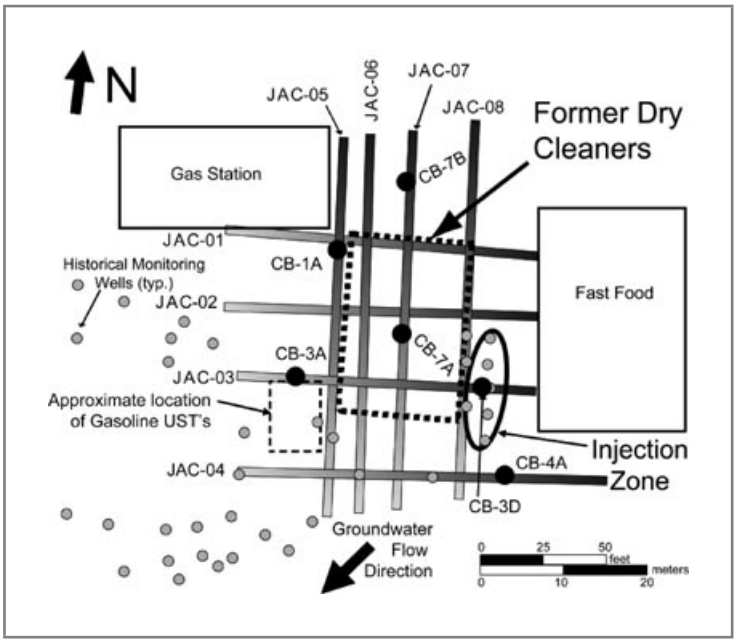

Exhibit 1. Map of former dry-cleaning site in Jackson, Tennessee

Location of former dry cleaners illustrated with dashed rectangle. Wells used as part of an injection scheme in 2002 illustrated with a solid oval. Location of eight ERI lines used to evaluate the site shown as heavy lines.

fill material. Subsequently, the excavation site was capped with a thick layer of concrete in some areas (approximately 2 to 3 feet).

Since the time of the injections, remedial activity has been limited and some groundwater sampling has occurred. Concerns that the remediation program may have missed some source areas and questions regarding the effectiveness of the remedial activities led to using a surface GeoTrax Survey™ ERI geophysical scanning program to evaluate the subsurface at the site in areas where the conceptual site model was poorly constrained by existing monitoring wells. Six confirmation borings were drilled to depths of 4.0 to 7.6 meters (13 to 25 feet) on the site to confirm the chemical composition of anomalous zones detected by the ERI work.

METHODS

Eight ERI were collected using the Halihan/Fenstemaker method (Halihan & Fenstemaker, 2004), which is available commercially as Aestus, LLC's GeoTrax Survey™ technology. The ERI activities were performed during night-shift work to minimize interference to daytime business and traffic flow at the adjacent convenience store/gas station (Exhibits 1 and 2).

Transect lines were surveyed and marked in the field, then electrode stakes were installed in the ground at specified, uniform intervals. The surveys were conducted using 56 electrodes at spacings ranging from 0.65 to 0.85 meters, yielding total line lengths ranging from 35.75 to 46.75 meters (117 to 153 feet). This layout facilitated data collection from the ground surface to depths of 7 to 9 meters (23 to 31 feet) bgs.

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Exhibit 2. Photograph of the deployment of ERI lines at former dry cleaners in Jackson, Tennessee

Work was conducted at night to avoid interfering with the adjacent businesses during the day. 56 electrode array being collected in centerline of image. Preparation for the next line is occurring to the left.

In grassy areas, electrodes were installed with a hand sledgehammer. In areas covered with asphalt and/or concrete, a rotary hammer drill was used to drill a 1/2-inch diameter hole, which allowed electrodes to be installed and contact material below the concrete. Once installed, electrical contact resistance was checked to ensure that the electrode stakes had good electrical contact with the ground. In some areas, the concrete cap was too thick to fully penetrate with rotary hammers, and the electrodes were installed in the drill holes that allowed the contact resistance to drop to an acceptable level for imaging through the concrete mass to soils below.

Following field data collection, the raw apparent resistivity data files were inverted using the Halihan/Fenstemaker method (Halihan & Fenstemaker, 2004). A final ERI image for each survey was developed that contains a gridded model of the electrical resistivity of the subsurface in units of ohm-meters. Changes in topography along the survey lines were accounted for during this data-processing work via land survey techniques using a total station.

To explore the horizontal distribution of resistivity values, plan-view depth slices from two different depths were created. A horizontal depth slice from 1.6 m bgs was generated to look at changes in the vadose zone, while a horizontal depth slice from 5.4 m bgs was generated to look at changes below the water table in the phreatic zone. Each horizontal depth slice was generated by taking ERI data at each respective depth from each of the eight surveys, and then compiled into a data set for each depth. The data sets for each depth were then gridded using kriging and contoured using Surfer® software (Golden Software, Inc., Golden, Colorado).

Six confirmation borings were drilled through both strongly electrically conductive and strongly electrically resistive anomalies detected via the ERI work. Confirmation borings were installed using direct push techniques. A temporary well screen was placed so that groundwater grab samples could be collected. Data collected during confirmation boring activities included geologic logs, PID readings, groundwater analytical data, and soil analytical data. The soil and groundwater samples were tested for TCE, PCE, and

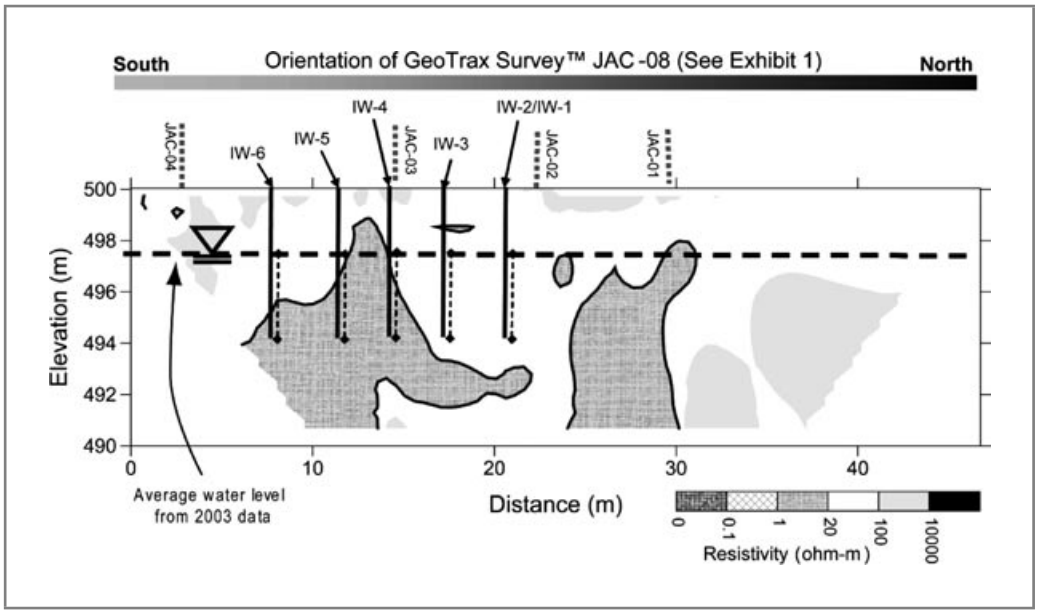

Exhibit 3. Electrical resistivity image of survey JAC-08

ERI cross-section (pseudosection) is illustrated with the location of injection wells, the average water-table elevation, and the location of cross lines. The profile on the right side of the image at approximately 40 meters horizontal distance illustrates the interpreted background electrical properties of the site. The lower resistivity (more conductive) 1 to 20 ohm-meter regions to the left are interpreted to be related to the injection process.

related breakdown (i.e., daughter) products, BTEX compounds, and basic groundwater chemistry.

RESULTS

The proprietary ERI data demonstrate a wide range of resistivity values in the inverted model resistivity data. In the area where the injections took place, values range from approximately 3 to 1,200 ohm-meters (Exhibit 3, Survey JAC-08). The data show dominantly vertical trends near the injection wells instead of the expected horizontal trends that would be generated by the native geology, which is horizontally bedded. The sandy interval below 3 meters (10 feet) is greater than 100 ohm-meters in the area north from the injection wells (gray colors on right side in Exhibit 3) but is more conductive (less than 20 ohm-meters) in the area where the injections occurred (stippled area on the left side in Exhibit 3). The increase in conductivity generally occurs beneath the water table in the injection zone.

Downgradient from the injection zone, resistivity values span seven orders of magnitude, from less than 0.1 ohm-meter to greater than 100,000 ohm-meters (Exhibit 4, Survey JAC-07). This trend is apparent in several lines downgradient of the injection zone. The highly electrically conductive area (less than 1 ohm-meter) tends to occur in the vadose zone just above the water table and extends below the water table in

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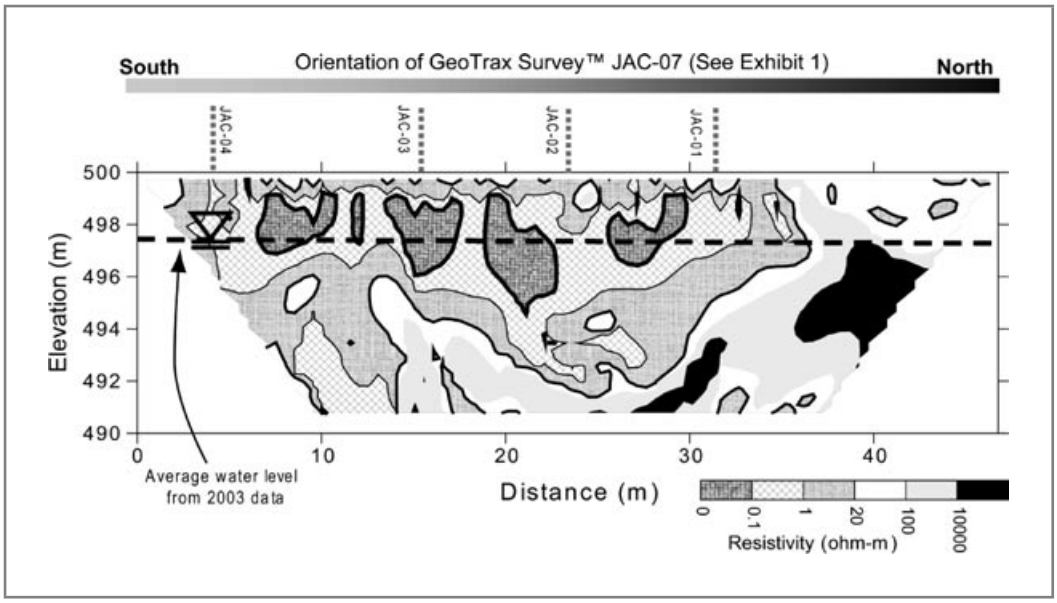

Exhibit 4. Electrical resistivity image of survey JAC-07

ERI cross-section (pseudosection) is illustrated with the location of injection wells, the average water-table elevation, and the location of cross lines. The high resistivity (i.e., greater than 10,000 ohm-meters) black regions on the right side of the image have been correlated with undegraded TCE and PCE. The low resistivity (high conductivity, less than 20 ohm-meters) regions, which occur dominantly in the vadose zone, are correlated with TCE and PCE, along with significant quantities of degradates. This low resistivity (extremely conductive) signature is interpreted as being generated by microbial activity.

some areas. The highly conductive area tends to be broken into five to six separate pieces (dotted areas on Exhibit 4) that roughly correspond to the number of injection wells (screened intervals shown on Exhibit 3).

The highly resistive areas (greater than 10,000 ohm-meters) tend to be located laterally adjacent to the injection-well flowpath and vertically below the injection-well flowpath (Exhibit 4). In the laterally adjacent highly resistive areas, the resistive areas occur both above and below the water table, but the majority of these areas are below the water table (Exhibit 4). The resistive areas are interpreted as resulting from pore spaces with high saturations of DNAPL, while the extremely conductive areas are interpreted as a microbial bloom in the unsaturated zone due to either injected compounds or the sodium lactate addition to the source area.

The horizontal depth slice in the vadose zone (1.6 meters bgs, 5.2 feet) illustrates the location of the interpreted microbial bloom in the vadose zone. The injectate plume appears to have spread more in the north/south direction than the east/west direction with a portion located upgradient from the injection zone. Small, highly resistive blob-shaped anomalous zones are visible near the edges of the conductive plume (Exhibit 5). This conductive area is connected to the injection-well location, but the values are most conductive downgradient of the injection wells.

The horizontal depth slice in the phreatic zone (5.4 meters bgs, 18 feet) occurs below the water table (Exhibit 6). This depth slice illustrates the higher volume of highly

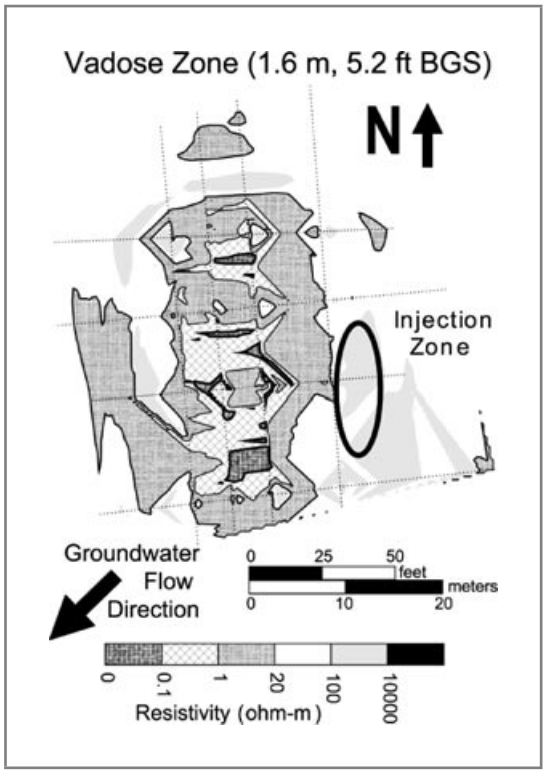

Exhibit 5. Interpolated horizontal depth slice of ERI data interpolated from GeoTrax Surveys™ at 1.6 meters (5.2 feet) below ground surface

The location of the injection zone is illustrated with a dark oval, but the injection occurred below the elevation of this depth slice. The resistivities associated with the center of the image are below 1.0 ohm-meter, which is extremely conductive for a freshwater environment. Additionally, the region exists with little relationship to the regional groundwater flow direction.

resistive anomalies in the subsurface at the edges of the survey area, with some conductive areas to the west and northwest of the injection wells. These data indicate that DNAPL may have existed beyond the survey area prior to injection, or that the injection activities may have pushed DNAPL out to the survey boundaries.

Chemical sampling of groundwater and soils indicates that the background fluids for the site are fresh with chloride concentrations of less than 20 mg/L. The background chemistry for major ions does not provide any reasonable interpretation for the extremely high or extremely low resistivity areas in the dataset due to the concentration of these ions. However, the concentration of iron species is highly variable and may be indicative of bioactivity for the site. Correlation of resistivity values at the middle of the screen interval from confirmation borings with TCE- and PCE-related constituent groundwater chemistry indicate highly resistive areas correspond to areas with minimal degradation of PCE (Exhibit 7). Confirmation borings with molar concentrations of PCE greater than *cis*-1,2-dichloroethene (DCE) corresponded with midscreen resistivity values of greater than 1,000 ohm-meters (PCE/DCE molar ratio greater than 1). The extremely resistive values had PCE/DCE ratios above 10.

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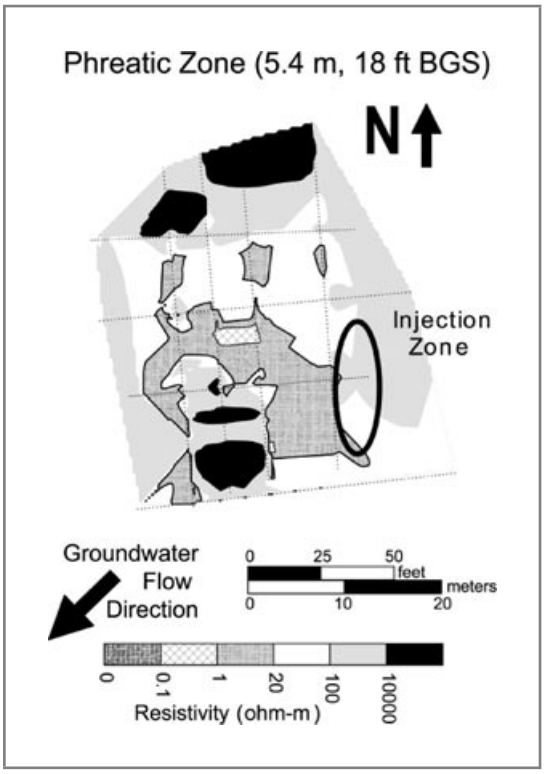

Exhibit 6. Interpolated horizontal depth slice of data taken from GeoTrax Surveys™ at 5.4 meters (18 feet) below ground surface

The location of the injection zone is illustrated with a dark oval and injected into the horizon associated with this depth slice. The resistivities associated with the center of the image are below 20 ohm-meters, which is interpreted as a signature of the injectate path. This region has little relationship to the regional groundwater flow direction. The large black resistivity body down the regional hydraulic gradient has been correlated to undegraded TCE and PCE that was not affected by the injection program.

BTEX compounds were detected along with PCE in some of these areas (CB-3A, -3D, and -4A) and may cause an increase in conductivity compared to an areas impacted with only PCE (CB-7B; Exhibit 7). The presence of BTEX would be expected to speed the degradation of PCE to daughter products as the hydrocarbons act as electron donors. The conductive areas correspond to areas with degraded PCE/TCE but have little to no BTEX concentrations in the groundwater samples, such as in CB-4A and CB-7A (Exhibit 7). The PCE/DCE molar ratio in these areas is below unity.

A plot of the PCE/DCE molar ratio from groundwater analytical data (from confirmation borings) against resistivity of the confirmation boring midscreen interval shows that lower ratios correspond well to more conductive areas (0.01 to 1.0 ohm-m), while higher ratios correspond to more resistive areas (100 to 1,000,000 ohm-m; Exhibit 8). These results are expected, because as biological activity increases, conductivity and degradation products such as DCE increase (as DCE amounts increase in relation to PCE, the ratio becomes smaller). Areas with less degradation tend to stay

Boring Name	MCL's	CB-1A	CB-3A	CB-7B	CB-3D	CB-4A	CB-7A
Distance along ERI survey (m)		14.0	4.9	39.3	28.7	31.7	20.7
Mid Screen Depth (m)		3.2	3.7	5.3	5.5	6.9	3.2
TCE/PCE Parameters (µg/L)							
Tricholoroethene (TCE)	5	U	0.670J	0.610J	1340	62.6	317
Tetrachloroethene (PCE)	5	3.97	97.9	39.2	43000	187	925
cis-1,2-Dichloroethene (DCE)	6	U	0.930J	1.45	4310	211	1070
Vinyl Chloride	0.5	U	U	U	2.28	13.8	1.16
PCE/DCE molar ratio		U	62	16	5.8	0.52	0.51
BTEX Parameters (µg/L)							
Benzene	1	U	1.32	U	1.52	0.62	U
Toluene	150	U	0.69	U	U	U	U
Ethylbenzene	300	U	6.66	U	0.62	U	U
Total Xylenes	1750	U	13.59	U	5.18	U	U
Other Constituents (mg/L)							
Chloride	250	4.3	8.3	16	NS	9.8	11
Nitrate	10	1.9	0.19	U	NS	0.95	U
Nitrite	1	0.022	0.0067J	0.0061J	NS	U	0.0077J
Sulfate	250	170	150	51	NS	84	100
Sulfide	NE	U	NS	U	NS	NS	U
Total Organic Carbon	NE	1	4.4	3.4	NS	1.9	2.1
Ferrous Iron	NE	0.47	29.2	39.3	NS	7.94	18.6
Iron	0.3	1.99	79.4	58.6	NS	85.1	17.3
ERI data (ohm-meters)							
Geometric mean resistivity along screen		1,010	12,879	168,663	1,875	24.3	0.04
NS- not sampled, U- undetected, J- estimated value from laboratory, NE- not established							

Exhibit 7. Groundwater chemistry and ERI data from screened intervals of confirmation borings

High resistivity zones are highlighted with dark shading. Low resistivity zones are highlighted with a hatch pattern.

more resistive, which is reflected in the higher PCE/DCE ratio. A power law function fits the data with a goodness of fit of 0.73 (Exhibit 8).

DISCUSSION

The high-resolution ERI data were successful at delineating areas with higher TCE and PCE concentrations at the site. The impacted areas were not successfully delineated by the previously existing monitoring-well network due to low data density inherent with this methodology. Additionally, the ERI data and confirmation drilling data indicate that the vertical extent of contamination has likely not been bounded. With the range of resistivity values in the dataset, the site provides a good test area for using ERI to observe biochemical changes, as the data indicate that strong signals are generated by TCE and PCE reactions.

The electrical signals from impacted areas appear to differ strongly in weathered and unweathered TCE and PCE. While a power law relationship exists across the resistivity range, two different mechanisms likely generate the strongly electrically conductive and strongly electrically resistive signals. Specifically, it appears as though weathered areas are

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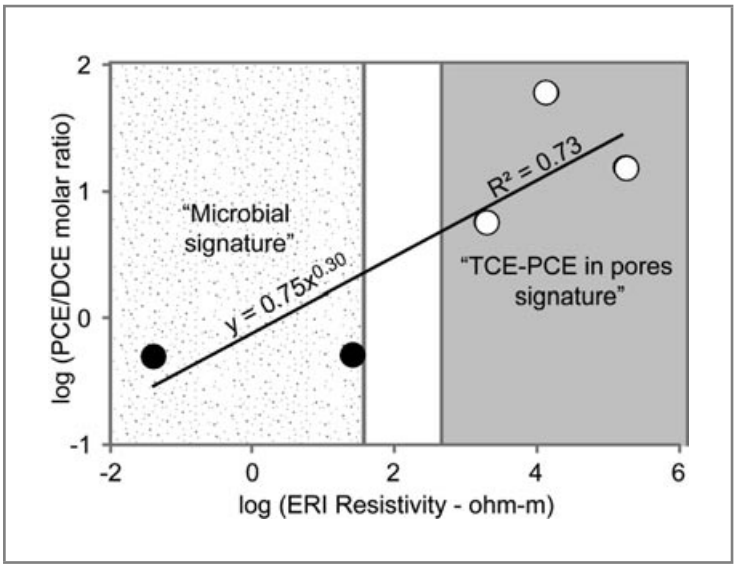

Exhibit 8. Graph of ERI resistivity values against PCE/DCE molar ratios

While the data provide a statistically significant trend, the cause of the signature is interpreted as being generated by two different mechanisms. Low PCE/DCE molar ratios (less than unity or a log value of zero) generate a low resistivity signature due to microbial processes, while high PCE/DCE molar ratios generate a high resistivity due to higher DNAPL saturations in the pore space.

electrically conductive and are present predominantly in the vadose zone. The magnitude of resistivity measurements are extremely low and often correspond to values well below what would be typical for native groundwater or diluted injectate.

Therefore, these areas are interpreted as microbial blooms associated with degradation of TCE and PCE in the presence of the injected treatment solutions. This conclusion is consistent with what would be expected based on laboratory and field results showing increased conductivity for zones of microbial degradation (Atekwana & Atekwana, 2010). To date, no microbial analysis has been performed on the samples to confirm the interpretation or to determine which species are present.

Compounds such as PCE and TCE are inherently electrically resistive, and are expected to appear in ERI surveys as highly resistive anomalies. The strongly electrically resistive zones associated with the undegraded TCE and PCE areas at this site are more resistive with values ranging from thousands to hundreds of thousands of ohm-meters. These high resistivity values may be caused by the pore structure of the sands on the site. No pore structure data are available to confirm this interpretation. The high electrical resistivity anomaly at confirmation boring CB-3D was confirmed to have significant dissolved-phase PCE (43,000 μg/L), which is indicative of free-phase concentrations, illustrating that saturations can be very high in these zones (Exhibit 7).

The results of the ERI work confirmed that a monitoring-well investigation of this site could provide only limited results, and suggest that future samples collected only in the saturated zone with monitoring wells would yield a limited understanding of the contaminant distribution in groundwater at this site. The ERI data detected a wide range of resistivity values that allowed drilling targets to be focused in areas with high contaminant levels, as well as areas with a significant degree of degradation.

Collecting ERI data over time (i.e., transient ERI data) would be useful for evaluating the response of the injection area for bioactivity, as well as the geometry of highly resistive areas demonstrated to be zones with high saturation of DNAPL. Because many of the highly resistive anomalies extend to the bottom of the ERI images, data from longer ERI lines with a greater imaging depth would provide data to assess the vertical extent of the remaining TCE and PCE on the site.

CONCLUSIONS

Proprietary ERI data were collected at a former dry-cleaning site impacted by PCE, TCE, and related daughter products. This work achieved the project objectives by locating previously uncharacterized areas (both laterally and vertically) in the subsurface containing moderate to high concentrations of PCE and TCE, evaluating the efficiency of the previous injection program, and providing an indication of bioactivity.

Specifically, the results indicate that the highly electrically resistive areas correspond to zones containing moderate to high concentrations of largely unweathered TCE and PCE. The highly electrically conductive zones in the subsurface correspond to the presence of moderate to high levels of weathered PCE and TCE and daughter products, and largely reside in the vadose zone.

The shift from highly resistive to highly conductive areas appears to indicate the presence of a strong bacterial bloom due to the biological activity presumably enhanced by the injectates interacting with the chlorinated solvent compounds at the site. These findings indicated that the injection program was partially successful in accelerating degradation of PCE and TCE at the site, particularly in the vadose zone. However, the ERI detected residual undegraded PCE and TCE contamination below the vadose zone and lateral to the injection plane.

The ERI dataset was used as a high data density framework to integrate historical monitoring-well data and boring data. The collective results confirm that monitoring wells alone were insufficient to adequately characterize this former dry-cleaning site.

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