

Crystal Refinery

Case Study Abstract

Crystal Refinery Carson City, MI

Site Name and Location: Crystal Refinery Carson City, MI	Geophysical Technologies: Ground Penetrating Radar (GPR) Electrical resistivity	CERCLIS # Not Applicable
Period of Site Operation: 1935 to early 1990s		Current Site Activities: Groundwater pump and treatment system via French drains/capture trenches
Operable Unit: Not Applicable		
Point of Contact: David Monet, Geologist Environmental Response Division MI DEQ 245 Colrain, SW Wyoming, MI 49548-1013 (616) 246-1739		
Geological Setting: Alluvial sand and loam soils overlay a shallow, fine to coarse sand aquifer separated from deeper aquifers by a clay aquitard. Bedrock occurs at 350 ft bgs and is composed of sandstone, shale, limestone, siltstone, and clay.		
Technology Demonstrator: William A. Sauck, PhD Department of Geosciences Western Michigan University Kalamazoo, MI 49008 (616) 387-4991 sauck@wmich.edu		
Purpose of Investigation: Investigation of the hypothesis that electrical properties of the zone impacted by a hydrocarbon plume in a natural environment change over time from electrically resistive to electrically conductive due to biodegradation, and that this shift in conductivity can be measured using geophysical methods.		
Number of Images/Profiles Generated During Investigation: 1 GPR profile, 1 dipole-dipole resistivity profile, 1 vertical resistivity probe profile and associated soil boring		
Results: The investigation confirmed the hypothesis that an older light non-aqueous phase liquid hydrocarbon plume in the natural environment will shift the bulk resistivity of the impacted zone from high resistivity to low resistivity over time.		
Project Cost: Estimated total cost for the investigation of this type was approximately \$5,795.		

EXECUTIVE SUMMARY

The Crystal Refinery is located in northwest Carson City in central Michigan. To the north and northwest there is a pine forest, and to the east and southeast, there are agricultural lands, residences, and commercial businesses. Site topography is characterized by rolling hills and uniformly western sloping plains. The geology at this site was created by two types of moraines created during the Wisconsin Glacial Period; a ground moraine and two end morainic ridges. The soil in the ridges is composed of clay, while soils deposited by glacial outwash in the ground moraine are sands and loams. The alluvial soils overlay a shallow, fine to coarse sand aquifer which is separated from deeper aquifers by a clay aquitard.

For this geophysical investigation two methods were used. The first was ground penetrating radar (GPR), which uses high-frequency radio waves to determine the presence of subsurface objects and structures. The second method was electrical resistivity, which injects electric currents into the earth through a pair of current electrodes, and the potential difference is measured between a pair of potential electrodes. The investigator chose GPR and electrical resistivity as the best methods to recognize the geoelectric properties of the volume of earth containing a hydrocarbon contaminant plume.

The GPR profile revealed a strong and continuous reflector which was interpreted as the water table at a depth of 10-18 feet. This is in agreement with known water table measurements. A second reflector was visible in the profile just above the water table from the west to approximately 100 meters (m). Depths to this reflector are computed as 2.7 m in the west down to 5.5 m at its lowest point. Soil boring data indicate that this reflector is coincident with the top of a layer containing residual product and exhibiting oil staining and a strong gasoline odor. The dipole-dipole resistivity profile demonstrated high resistivity in the vadose zone and a gradient to low resistivity. The areas of low resistivity were interpreted as the saturated zone and the clay aquitard beneath it. The vertical resistivity probe was placed in a known area of free product. The vertical resistivity probe revealed high resistivity in most of the vadose zone, in correlation with the dipole-dipole profile. However, near the base of the vadose zone and in the uppermost part of the saturated zone, a pronounced resistivity minimum was encountered.

This investigation was done as a field demonstration by Western Michigan University and all the equipment was owned by the University. Therefore, there were no direct labor and equipment costs associated with this geophysical investigation. However, the estimated cost of initiating such an investigation using three different geophysical methods would cost approximately \$6,000.

Biodegradation of mature LNAPL plumes can produce geochemical changes in the materials at the capillary fringe that mobilize inorganic compounds from the subsurface materials. The change in pH and ion charge of the materials increases the conductivity of the subsurface materials. This increase in conductivity can be detected using electromagnetic methods, such as ground penetrating radar [2]. Light hydrocarbon free-product and associated dissolved plumes are dynamic systems. Therefore the application of geophysical techniques to investigations such as this should be conducted in conjunction with geochemical investigations [2].

SITE INFORMATION**Identifying Information**

Crystal Refinery
Carson City, MI 48811

Background [2]

Physical Description: Crystal Refinery is located on North Williams Street in northwest Carson City in central Michigan. Carson City is a small rural town and the site is located in a residential and commercial area. The Carson City Park is located on the southern border of the site, and Fish Creek forms the western border. To the north and northwest there is a pine forest, and to the east and southeast, there are agricultural lands, residences, and commercial businesses (Figure 1). The center of Carson City is located approximately 3,000 feet to the southeast of the site. The site is approximately 32.5 acres and consists of two separate parcels. The larger southern parcel contains the petroleum refinery, storage tanks, lagoons, loading docks, and several buildings. The northern parcel contains storage tanks, a valve station, and a disposal area. Both parcels are partially fenced and gated. Site topography is characterized by rolling hills and uniformly western sloping plains. Between the two parcels is a cemetery. South of the southern parcel is a city park.

Site Use: Crystal Refinery began processing crude oil in 1935 and operated until the early 1990s. The site received crude oil from both an underground pipeline and railroad cars. The average production of the refinery was approximately 84,000 gallons of oil per day. Total tank storage capacity, including above-ground storage tanks (ASTs) and underground storage tanks (USTs), was an estimated 10,000,000 gallons. Between 1957 and 1962, two additional ASTs were constructed on the northern parcel, adding 2,000,000 gallons to the total tank storage capacity.

Eight cooling lagoons on the southern parcel received waste sludges from site operations. These sludges, copper chloride, Fuller's Earth, and styrene materials were transferred to and disposed of on the northern parcel until the mid-1970s. In 1970, four french drains were installed. Recovered oil and water from these drains was pumped to an oil/water separator. Remaining liquids were then pumped to a second separator and discharged into one of the lagoons. The site is currently inactive.

Release/Investigation History: Shortly after site operations began, an oil seep was discovered in the north recovery area. The Michigan Department of Natural Resources (MDNR) investigated this seep in 1945, however there is no information regarding the results of this investigation. In 1968, MDNR performed an evaluation of Crystal Refinery to determine the extent of oil contamination in groundwater. Twenty-two wells were installed, both on- and off-site, to establish the lateral extent of contamination and groundwater flow direction. A heavy oil slick was noted on the backwaters of Fish Creek at this time.

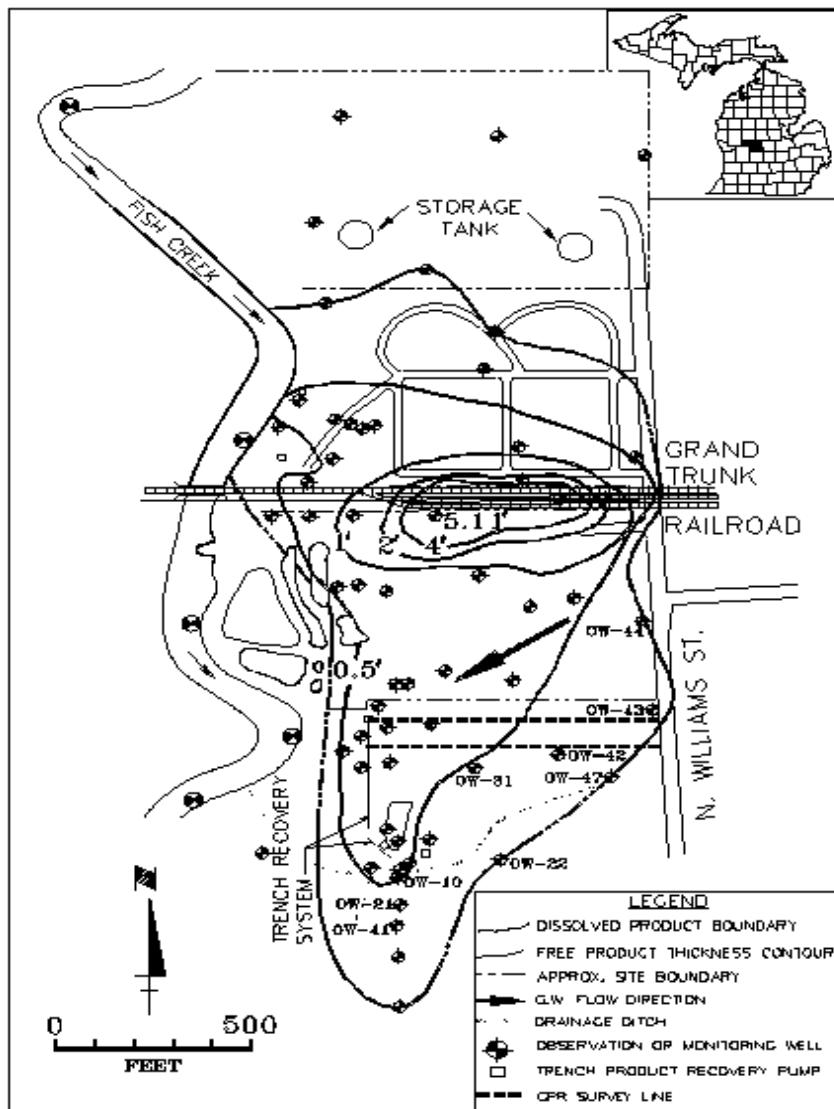
SITE INFORMATION

Figure 1: Crystal Refinery Site Map [2]

SITE INFORMATION

A large release of crude oil occurred in January, 1973 when a fractured check valve on a receiving line burst. Eighty-eight thousand gallons of crude oil flowed over frozen ground toward Fish Creek. Although some was intercepted on site, oil did enter Fish Creek. The ensuing cleanup was performed by Crystal Refinery.

In 1982, Crystal Refinery conducted a hydrogeological investigation required by MDNR. More wells were installed to evaluate both the lateral and vertical extent of contamination. This investigation estimated that as much as 4,000,000 gallons of oil might be present in the groundwater, 117,000 cubic yards of soil might be seriously impacted by oil contamination, and 86,000 cubic yards of soil may have been marginally impacted. In 1983, Crystal Refinery installed purge wells in an attempt to address the groundwater contamination. Water pumped from the wells was skimmed, sent to a separator, and then to one of the lagoons.

A 1989 EPA visit to the site documented degradation of containment measures, such as erosion around the lagoons and degradation of insulation in storage tanks. EPA instructed Crystal Refinery to address these conditions, and in 1992, MDNR required the development of a remedial action plan (RAP) addressing both groundwater and soil contamination. A RAP was completed in 1992 addressing only groundwater issues. MDNR accepted the RAP as an interim response, but stated it was inadequate until soil concerns were addressed. Since 1993, Crystal Refinery has continued to address groundwater, but has not performed any remedial measures addressing soil contamination. The EPA razed (removed) all above-ground facilities in Fall, 1998.

Regulatory Context: MDNR has been the lead agency in overseeing and approving the Crystal Refinery activities and decisions. However, in April 1997, MDEQ (formerly MDNR) referred the site to the US EPA Region 5 Emergency Response Branch.

Site Logistics/Contacts**Federal Lead Agency:**

US EPA Region 5 Emergency Response
Branch

State Lead Agency:

Michigan Department of Environmental
Quality

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MEDIA AND CONTAMINANTS**Matrix Identification**

Type of Matrix Sampled and Analyzed: Subsurface soils and groundwater

Site Geology/Stratigraphy

The geology at this site was created by two types of moraines created during the Wisconsin Glacial Period; a ground moraine and two end morainic ridges. The soil in the ridges is composed of clay, while soils deposited by glacial outwash in the ground moraine are sands and loams. The alluvial soils overlay a shallow aquifer composed of fine to coarse sand. The shallow aquifer is separated from deeper aquifers by a clay aquitard. The thickness of the shallow aquifer ranges from 15 feet in the western portion of the site to 30 feet in the eastern portion. Bedrock occurs at 350 feet below ground surface and is formed by the Jurassic and Saginaw Formations. The bedrock is composed of primarily sandstone, shale, limestone, clay, and siltstone.

Contaminant Characterization

Primary Contaminant Groups: The contaminants of concern are residual oil and hydrocarbons both as dissolved phase and free product. Hydrocarbons are present as light, non-aqueous phase liquids (LNAPLs). Both crude oil (north) and refined products (south).

Matrix Characteristics Affecting Characterization Cost or Performance [2]

Some fading of the ground penetrating radar (GPR) reflections occurred and may have been related to enhanced soil conductivities which limit the effective depth of penetration of the radio waves. Some of the problems affecting the performance of the electrical resistivity data interpretations were related to equivalence and suppression. Lower resistivities at the fringes of survey lines may have been the result of a shallower water table to the west, and, to the east, lower resistivities may have been caused by the presence of road salt. Other factors such as the surface conditions, and subsurface distribution of conductive zones may also play an important role in controlling the electrical signature of surface geophysical measurements at hydrocarbon impacted sites.

GEOPHYSICAL INVESTIGATION PROCESS**Investigation Goals**

The geophysical investigation was undertaken in November 1997 as part of academic research for Western Michigan University's Department of Geology. The purpose of the investigation was to test the proposition that the electrical properties of the soil moisture intermingled with a hydrocarbon plume change over time from electrically resistive to electrically conductive. The conventional model, based on controlled spill and lab experiments, is that groundwater and soils contaminated with hydrocarbons exhibit lower electrical conductivity and lower relative permittivity than the surrounding uncontaminated media. The hypothesis tested in this study is that hydrocarbon spills in the natural environment will change the bulk properties of the impacted zone from electrically resistive to electrically conductive over time due to biodegradation of the hydrocarbons. Conductivity is enhanced by the leaching of inorganics from the soil and aquifer materials by organic acids produced by microbial activity during degradation of the hydrocarbons [1].

Geophysical Methods [2]

For this geophysical investigation two methods were used. The first was GPR, which uses high-frequency radio waves to determine the presence of subsurface objects and structures. A GPR system radiates short pulses of high-frequency electromagnetic (EM) energy into the ground from a transmitting antenna. This EM wave propagates into the ground at a velocity that is related to the electrical properties of subsurface materials (specifically, the relative dielectric permittivity of the materials). When this wave encounters the interface of two materials having different dielectric properties (i.e., soil and water), a portion of the energy is reflected back to the surface, where it is detected by a receiver antenna and transmitted to a control unit for processing and display. The major principles involved for GPR are similar to reflection seismology, except that EM energy is used instead of acoustic energy and the propagation times are much shorter.

The GPR survey was conducted using the Geophysical Survey Systems Inc. (GSSI) Subsurface Interface Radar-10A+ (SIR-10A+) with 300 MHZ bistatic antennae. The modulation frequency was set at 300 MHZ with a recording time of 160 nanoseconds (ns). The survey used a constant gain setting and a 3-scan moving average horizontal filter. The GPR system was towed for 230 meters along two lines 20 meters apart at 15 and 35 meters south of the refinery boundary (Figure 1).

The second geophysical method used was electrical resistivity. During resistivity surveys, current is injected into the earth through a pair of current electrodes, and the potential difference is measured between a pair of potential electrodes. The current and potential electrodes are generally arranged in a linear array. Common arrays include the dipole-dipole array, pole-pole array, Schlumberger array, and the Wenner array. The apparent resistivity is the bulk average resistivity of all pore fluids, soils and rock influencing the flow of current. Resistivity is the inverse of conductivity. It is calculated by dividing the measured potential difference by the input current, and multiplying by a geometric factor (specific to the array being used and electrode spacing).

GEOPHYSICAL INVESTIGATION PROCESS

Models of the variation of resistivity with depth can be obtained using model curves or forward and inverse modeling computer programs.

Electrical resistivity was measured with the Iris Syscal R2 Deep Resistivity-IP System using the axial dipole-dipole array configuration with dipole separations between 1 and 5 and the Wenner array configuration with a 2-inch electrode spacing for vertical resistivity measurements in the vertical probes. Both the dipole-dipole and vertical profiling (not along a line, but a single point) were conducted along a line 20 meters south of the refinery. The Iris Syscal R2 Deep Resistivity-IP System is menu-driven and has internal storage memory and weighs approximately 6 kilograms.

GEOPHYSICAL FINDINGS**Technology Calibration**

No calibration was reported as being necessary for this investigation. However, for the resistivity system calibration is usually done digitally by the microprocessor based on correction values stored in memory. The correction values are found in final production testing and are also established during later periodical recommended yearly checks at authorized service centers. Vertical probes have been calibrated in a water tank to determine the correction factor for the body of the probe (2" OD PVC cylinder-perfect insulator).

Investigation Results [2, 3]

The GPR profile revealed a strong and continuous reflector occurring at 40 ns near the west end and 70 ns further east along the profiles (Figure 2). This reflector is interpreted as the water table and a depth of 3.5 to 5.5 m was computed. This is in agreement with known water table measurements. Another, parallel, reflector is visible in the profile just above the water table from the west to approximately 100 meters. At 100 meters, this reflector dips to the east and then merges with the W.T. reflector at 140 meters. After 160 meters, this reflector is visible as a separate event again and rises to 50 ns. Depths to this reflector are computed as 2.7 m in the west down to 5.5 m at its lowest point at 140 meters east. Soil boring data indicate that this reflector is coincident with the top of the layer containing residual product and exhibiting oil staining and a strong gasoline odor. The appearance of this reflector on the GPR profile may be due to viscous residual product in the vadose zone blocking sediment pore space and altering the permeability.

The dipole-dipole resistivity profile demonstrates high resistivity in the vadose zone and a downward gradient to low resistivity (shown as lighter shades in Figure 3). The areas of low resistivity are interpreted as the saturated zone and the clay aquitard beneath it. The fact that no anomalous features attributable to the free product plume were observed is possibly due to problems of equivalence and suppression associated with resistivity interpretations.

The vertical resistivity probe is located in a known area of free product. The vertical resistivity probe revealed high resistivity in the vadose zone (staying around 1000 Ohm-meters on a log

GEOPHYSICAL FINDINGS

scale), in correlation with the dipole-dipole profile. However, at approximately 3.8 m bgs, electrical resistivity suddenly decreases to 15 Ohm-meters. This is lower than background water resistivities of 30 Ohm-meters. According to soil boring data, this zone of low resistivity begins just above the water table and is coincident with the layer containing free product observed between the upper reflector and the W.T. reflector in the GPR survey. This is interpreted to confirm that a natural environment zone which has been saturated with hydrocarbon for a period of time (in this case, 50 years) exhibits an increased conductivity (decreased resistivity), contrary to the conventional model that it will display conductivities less than the uncontaminated areas.

Results Validation [2]

Geochemical data, including dissolved oxygen, pH, and specific conductance was collected from five on-site wells (Table 1). The locations of these wells can be seen in Figure 1. The high measurements of dissolved oxygen and low conductivity in OW-10 and OW-21 indicate minimal impact by hydrocarbon contamination. Similar measurements in OW-43 showed low dissolved oxygen and the highest conductivity. This well is located at the margin of the dissolved phase plume, as is OW-44. Measurements in OW-31 revealed the lowest dissolved oxygen and a corresponding high conductivity. The variations in measurements are attributed to varying rates of biodegradation. Waters from below the impacted zone were 3-5 times more conductive than background. The low dissolved oxygen rates correlate with high conductivities and indicate microbial activity is breaking down the hydrocarbons. The use of ambient dissolved oxygen ultimately results in (involves bacterial process, then chemical leaching process) elevated conductivities.

GEOPHYSICAL FINDINGS

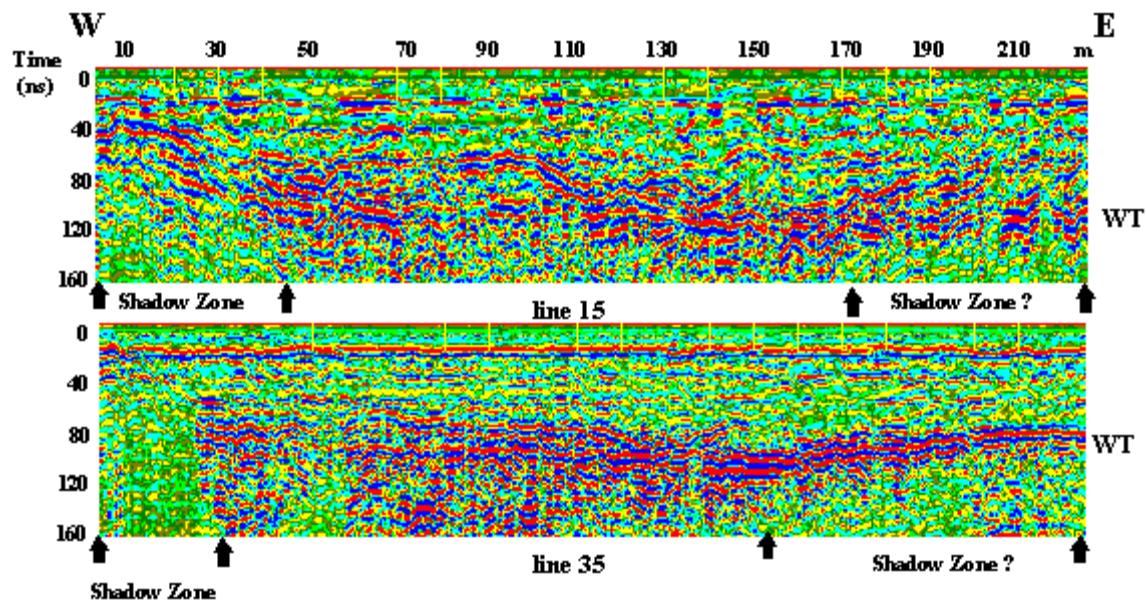


Figure 2: Ground Penetrating Radar Profiles of Line 15 and Line 35 [2]

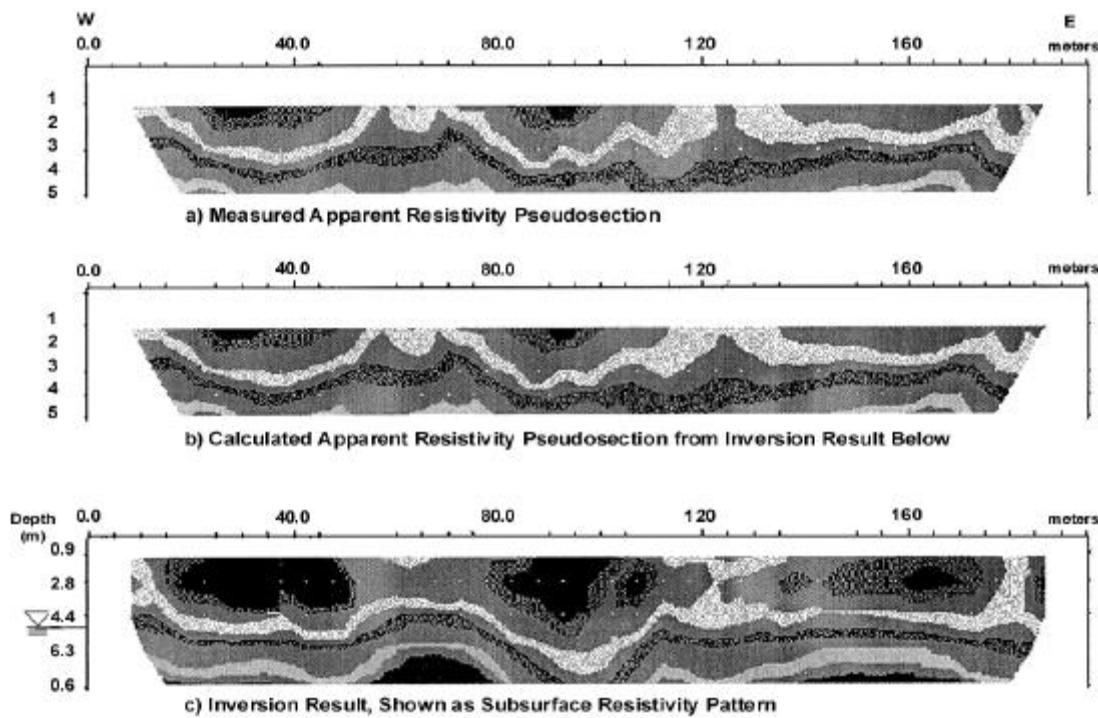


Figure 3: Resistivity Pseudosections [2].

GEOPHYSICAL FINDINGS

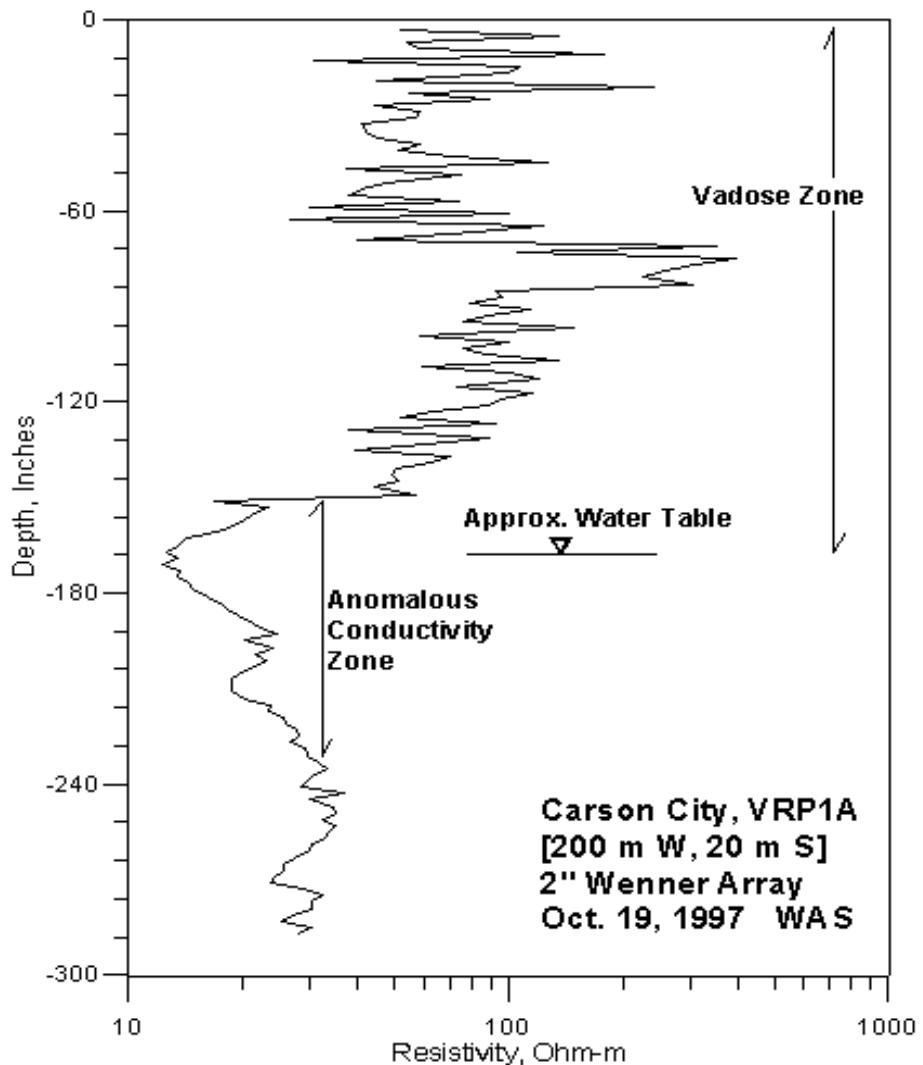


Figure 4: Vertical resistivity probe located at 0.0 mE, 20 mS, 2" Wenner Array, semi-log scale [2].

GEOPHYSICAL FINDINGS**Table 1: Geochemical Data Used in Results Validation**

Well ID	Dissolved Oxygen (mg/L)	pH	Specific Conductance (mS/m)
OW-10	7.2	6.4	32
OW-21	7.2	7.1	30
OW-31	0.3	6.37	93
OW-42	0.7	7	90
OW-43	0.6	6.76	158
OW-44	1.2	6.5	101

LESSONS LEARNED

The lessons learned during this investigation are the following:

- Biodegradation of mature LNAPL plumes can produce geochemical changes in the materials at the capillary fringe or zone of mixing that mobilize inorganic compounds from the subsurface materials. The change in pH and ion charge of the materials increases the conductivity of the subsurface materials. This increase in conductivity can be detected using electromagnetic methods, such as ground penetrating radar. This phenomenon will be limited to “mature” plumes, and depending on the specific chemical nature of the plume and the viability of the indigenous microbial population, may not be observed at all sites [2].
- Ground penetrating radar was able to clearly identify the water table and the top of the impacted zone [2].
- No anomalous regions which can be attributed to the free product plume could be observed along the horizontal resistivity profile. This was likely due to the problems of equivalence and suppression, which often plague resistivity interpretations [2]. However, electrical resistivity data from fixed vertical resistivity probes showed resistivity minima which coincide with GPR shadow zones with relation to the depth of the water table.
- Light hydrocarbon free-product and associated dissolved plumes are dynamic systems. Therefore the application of geophysical techniques to investigations such as this should be conducted in conjunction with geochemical investigations [2]. This will result in a better understanding of site conditions.

REFERENCES

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- Atekwana, E., W.A. Sauck, and D.D. Werkema, Jr. *Characterization of a Complex Refinery Groundwater Contamination Plume Using Multiple Geoelectric Methods*. Proceedings of the Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP 1998), pp. 427-436.
- Sauck, William A. *A Conceptual Model for the Geoelectrical Response of LNAPL Plumes in Granular Sediments*. Proceedings of the Symposium on the Application of Geophysics to Engineering and Environmental Problems (SAGEEP 1998) pp. 805-817.
- Personal communication with Phil Sirles of Microgeophysics. Wheat Ridge, CO. December 10, 1998.

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