

## Investigating the geoelectrical response of hydrocarbon contamination undergoing biodegradation

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[1] A newly proposed geoelectrical model for hydrocarbon contaminated sites predicts high conductivities coincident with the contaminated zone as opposed to the traditionally accepted low conductivity. The model attributes the high conductivities to mineral weathering resulting from byproducts of microbial redox processes. To evaluate this conductive model, in situ vertical conductivity measurements were acquired from a light non-aqueous phase liquid (LNAPL) contaminated site. The results showed high conductivities coincident with the zone of contamination and within the smear zone influenced by seasonal water table fluctuations. We infer this zone as an active zone of biodegradation and suggest significant microbial degradation under partially water saturated conditions. A simple Archie's Law analysis shows large pore water conductivities necessary to reproduce the bulk conductivity measured at the contaminated location. This study supports the conductive layer model and demonstrates the potential of geoelectrical investigations for assessing microbial degradation of LNAPL impacted soils. *INDEX TERMS*: 5109 Physical Properties of Rocks: Magnetic and electrical properties; 0915 Exploration Geophysics: Downhole methods; 1831 Hydrology: Groundwater quality. **Citation**: Werkema, Jr., D. D., E. A. Atekwana, A. L. Endres, W. A. Sauck, and D. P. Cassidy, Investigating the geoelectrical response of hydrocarbon contamination undergoing biodegradation, *Geophys. Res. Lett.*, 30(12), 1647, doi:10.1029/2003GL017346, 2003.

### 1. Introduction

[2] Studies conducted on the geophysical detection of hydrocarbon contaminants have based interpretation on the insulating layer model [e.g., *Lien and Enfield*, 1998]. This interpretation is intuitive as hydrocarbons that displace the groundwater are electrically resistive. However, recent findings at sites impacted with hydrocarbons for decades show a conductive response, characterized by low apparent resistivities/high conductivities [e.g., *Atekwana et al.*, 2000] and attenuated GPR reflections [e.g., *Bermejo et al.*, 1997].

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[3] In view of these field observations, a new conceptual model (herein named the conductive layer model) linking the conductive response to the effects of biodegradation processes has been proposed [*Sauck*, 2000]. High bulk conductivity is hypothesized to be caused by high pore water conductivity due to higher total dissolved solids (TDS) in groundwater which resulted from enhanced mineral weathering accompanying the production of carbonic and organic acids during biodegradation. The role of organic acids and microbial activity in promoting mineral dissolution in hydrocarbon contaminated aquifers is well documented [e.g., *McMahon et al.*, 1995]. This study is driven to evaluate the conductive and insulating layer models and to advance the understanding of the geoelectrical response at a site impacted with light non-aqueous phase liquid (LNAPL) contamination.

[4] Vertical conductivity profiles are used to measure the vertical geoelectrical distribution. Because of the difficult task in geochemical sampling from the immiscible contaminant zone under saturated and partially saturated conditions, vertical geoelectrical profiles may provide an indirect observation of the processes in this zone. The profiles are analyzed using simple Archie's Law relationships to compare the two competing models.

[5] The study site is adjacent to a former refinery, the Crystal Refinery in Carson City, Michigan, which leaked mostly jet and diesel fuel, since 1945. The geology consists of 4.5 to 6.1 m of glacially derived unconsolidated fine to medium grained sands, coarsening at and below the water table to gravel and underlain by a 0.61 to 3.05 m thick clay aquitard unit. Due to topographic variations, depth to groundwater ranges from approximately 1 to 4 meters. Contamination occurs in the residual, free, and dissolved phases as defined previously [*U.S. EPA*, 1992] and applied to LNAPL. In 1994, the free phase plume (referred here as the plume core) was approximately 229 m long and averaged 82 m wide with a thickness between 0.3 to 0.6 m and an estimated volume of 167,200 liters [*Snell Environmental Group*, 1994]. The fringe zone, characterized by residual and dissolved phase hydrocarbons, is approximately 70 meters beyond the edge of the plume core.

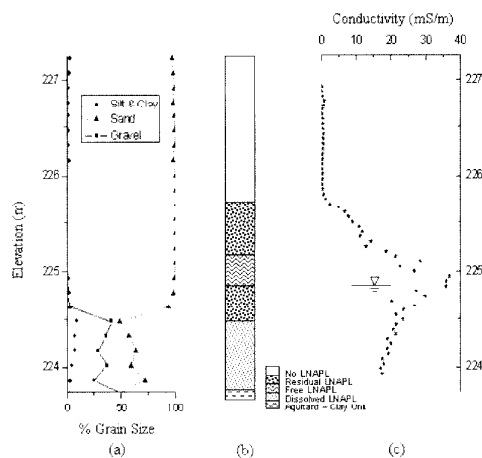
[6] Recent geochemical investigations suggest that intrinsic biodegradation is occurring in groundwater at the site [*Legall*, 2002]. Microbial studies of soil cores collected monthly for one year and completed to depths within the saturated zone have documented microorganisms capable of degrading hydrocarbon and show orders of magnitude increase in alkane degrading microorganisms in the hydrocarbon impacted zones [*Cassidy et al.*, 2002; *Werkema et al.*, 2000]. Methanogenesis is the dominant redox process within the core of the contamination, while sulfate, iron, and

manganese reduction occur at the fringes of the contamination [Legall, 2002]. Volatile organic acids and biosurfactants have been detected in the contaminated groundwater at this site [Cassidy *et al.*, 2002].

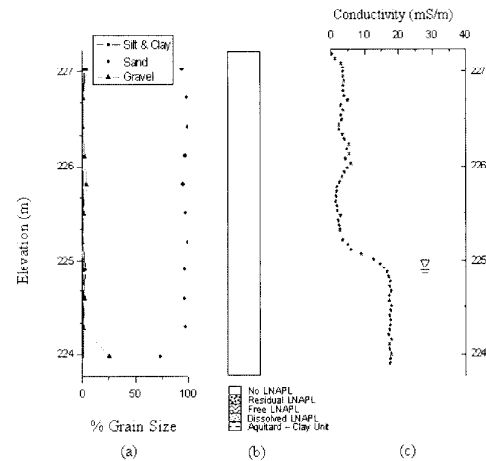
## 2. Results

[7] Apparent resistivity data were collected using in situ vertical resistivity probes (VRPs) installed in contaminated and uncontaminated portions of the aquifer. A total of ten VRPs (4 in free phase, 4 in residual and dissolved, and 2 in uncontaminated locations) were installed from the ground surface to depths at or near the top of the clay aquitard. Measurements were collected monthly for 15 months using a Wenner array with 5.08 cm spacing and collected at 5.08 cm increments. The results are repeatable, showing some fluctuations due to natural hydrologic events. Those data, the collection methodology, sediment cores, grain size analysis, LNAPL distribution, and the water level data have been described elsewhere [Werkema, 2002]. Representative VRP profiles from September 2000 are shown in terms of conductivity in Figures 1 and 2. Those figures include the grain size and LNAPL distribution from cores collected within a 50–100 cm radius from the VRP installations [Werkema, 2002].

[8] The grain size distribution determined the percentage gravel (>4.8 mm), sand (4.8–0.06 mm), and silt/clay (<0.06 mm) fractions after drying to a constant weight at 105°C and using sampling intervals of either 15 or 30 cm. Figure 1 is the conductivity profile within the core of the plume. At approximately 225.7 m elevation and coincident with the first encounter of contamination, the conductivity profile (Figure 1c) shows a steep increase from approximately 0.3 mS/m to 15 mS/m over a 0.5 m elevation change. Decreasing in elevation, the conductivity profile progressively increases reaching a maximum of approximately 37 mS/m at 224.9 m. This point correlates with the free (i.e., floating) LNAPL layer (Figure 1b) and occurs near the water table-free LNAPL interface. Below this conductivity maximum, the profile decreases to approximately 18 mS/m



**Figure 1.** Profiles for the Contaminated Location, (a) Grain Size Distribution, (b) LNAPL Distribution, (c) Conductivity Profile.



**Figure 2.** Profiles for the Uncontaminated Location, (a) Grain Size Distribution, (b) LNAPL Distribution, (c) Conductivity Profile.

through the saturated zone that contains dissolved LNAPL and a zone of submerged residual LNAPL (Figure 1b). This subaqueous immiscible phase represents LNAPL adsorbed on the soil grains at lower water levels [Werkema, 2002] that occurs from 224.8 m to approximately 224.5 m elevation. The grain size data in Figure 1a shows a change in grain size from predominantly sand to sand and gravel occurring at 224.5 m elevation. This change occurs 0.5 m below the zone of maximum conductivity suggesting that the conductivity profile is not significantly affected by variations in lithology. The clay aquitard was reached by the VRP at approximately 223.7 m.

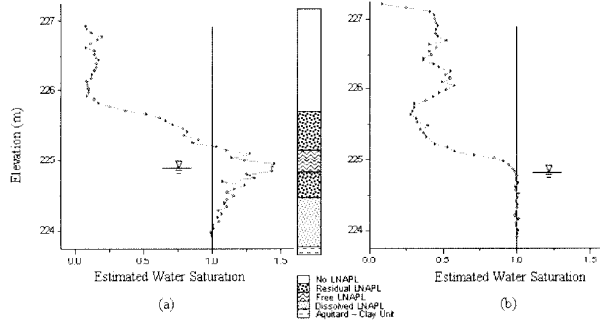
[9] The conductivity profile at an uncontaminated location (Figure 2c) shows a gradual increase due to the presence of the transition zone above the saturated zone (~225 m). Below the water table, the conductivity values remain at the relatively constant maximum value of approximately 17 mS/m. Those data reveal no steep conductivity gradients or zone of maximum. In fact, over a two fold increase in maximum conductivity was observed at the contaminated location relative to this uncontaminated location. This location also shows a uniform grain size distribution until approximately 224 m elevation (Figure 2a) that appears to have little effect on the conductivity profile. The clay aquitard was not reached by this VRP.

## 3. Analysis

[10] The empirical Archie's Law [Archie, 1942] is given by

$$\sigma_e = a \phi^m S_w^n \sigma_w, \quad (1)$$

where  $\sigma_e$  is the effective conductivity of the medium,  $\phi$  the porosity,  $S_w$  the water saturation,  $\sigma_w$  the pore water conductivity,  $m$  the cementation exponent,  $n$  the saturation exponent and  $a$  is an empirical factor. Since grain size analysis revealed no appreciable amounts of silt or clay (Figures 1a and 2a) Archie's Law is applicable. To analyze the conductivity profiles at both locations, we have assumed the only variables are water saturation ( $S_w$ ) and pore water



**Figure 3.** Estimated Water Saturation Profiles (a) Contaminated Location including LNAPL Distribution. (b) Uncontaminated Location. Vertical line shows  $S_w = 100\%$ .

conductivity ( $\sigma_w$ ). This approach implicitly assumes the porosity and pore structure are uniform throughout the aquifer (i.e.,  $\phi$ ,  $a$ ,  $m$  and  $n$  are constants).

[11] Our first analysis assumes changes in conductivity were due entirely to variations in  $S_w$  while  $\sigma_w$  remains constant. This approach is consistent with the insulating layer model for LNAPL pools as the resistive LNAPL displaces the more conductive water decreasing water saturation. Consider the effective conductivity,  $\sigma_e(z)$ , at elevation  $z$  along the VRP profile and the effective conductivity in the uncontaminated saturated zone,  $\sigma_e^{sat}$ . From equation (1) the apparent water saturation  $S_w(z)$  required to account for the effective conductivity  $\sigma_e(z)$  is given by

$$S_w(z) = \sqrt[n]{\sigma_e(z)/\sigma_e^{sat}}. \quad (2)$$

When no independent information is available,  $n$  is commonly assumed to be 2 [Schön, 1996]. The uncontaminated saturated zone conductivity profile suggests that the average effective conductivity is  $\sigma_e^{sat} = 17.4$  mS/m.

[12] Figure 3a, shows excessively high calculated water saturation  $S_w(z)$  values (up to 150%) that are coincident with the zone of free LNAPL that occurs near the water table. These excessively high water saturation values remain greater than 100% throughout the free LNAPL layer and below through the subaqueous residual LNAPL layer and dissolved LNAPL zone to approximately 224 m elevation. In comparison, Figure 3b from the uncontaminated site clearly shows a typical water saturation profile. While Figure 1a does show grain size increase at approximately 224.6 m, which may result in an increase in the porosity and possibly contribute to the increasing conductivity, we note that this elevation is well below the zone of enhanced conductivity as presented in Figure 4.

[13] According to the insulating layer model, unrealistically high water saturations (i.e.,  $\sim 150\%$ ) are required to account for the VRP conductivity measurements in the contaminated zone. This is inconsistent with the displacement of pore water by LNAPL which is expected to lower the water saturation. Hence, we infer that varying water saturation in the insulating layer model cannot account for the anomalously high conductivity in the contaminated zone.

[14] Next, we examine the effects of changing pore water conductivity,  $\sigma_w$ . To perform this analysis, we assume the

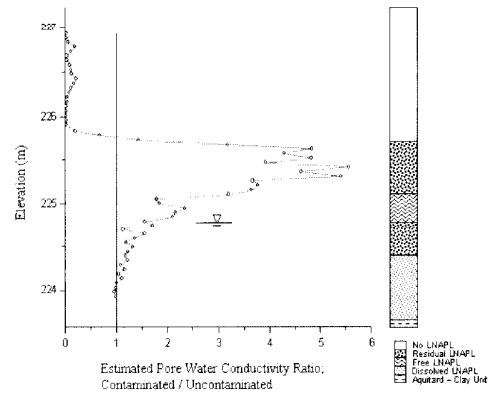
water saturation profile relative to the water table,  $S_w(z)$ , is the same at both locations. Hence, the conductivity profiles for each location were aligned such that the water table positions were coincident prior to performing this analysis.

[15] It follows from Archie's Law that the pore water conductivity ratio between the contaminated and uncontaminated locations ( $\sigma_w^c(z)$  and  $\sigma_w^{uc}(z)$ , respectively) at a given depth relative to the water table is given by

$$\frac{\sigma_w^c(z)}{\sigma_w^{uc}(z)} = \frac{\sigma_e^c(z)}{\sigma_e^{uc}(z)}, \quad (3)$$

where  $\sigma_e^c(z)$  and  $\sigma_e^{uc}(z)$  are the effective conductivity profiles at the contaminated and uncontaminated locations. Obviously, our assumption about  $S_w(z)$  will lead to an overestimate of  $S_w$  in the contaminated aquifer material where the immiscible contaminant has displaced the pore water. This approach will underestimate  $\sigma_w^c(z)$  over the contaminated region. Hence, this analysis yields a lower limit for the pore water conductivity in the LNAPL impacted zone required to satisfy the conductivity measurements.

[16] The estimated pore water conductivity ratio,  $\sigma_w^c(z)/\sigma_w^{uc}(z)$  is presented in Figure 4; four important observations are made from this figure. First, the highest estimated pore water conductivity suggests a 5.5 fold increase over equivalent uncontaminated locations. Second, the zone of elevated conductivity (approximately 1.25 m thick) occurs within the tension saturated zone and extends into the upper parts of the saturated zone (224.5–225.75 m). This region of elevated conductivity is essentially coincident with the hydrocarbon smear zone resulting from water table fluctuations. Third, the zone of maximum elevated conductivity occurs above the water table and within the upper residual LNAPL zone (225.7–225.2 m). If the high conductivity is the result of biodegradational processes, then we infer from this observation that the residual product zone is the site of most active biodegradation. Previous investigations at this contaminated location support this inference and show the alkane degrading population maximum [Werkema et al., 2002]. Additionally, geochemical studies show an influx of nutrients which could result in greater biological activity



**Figure 4.** Estimated Pore Water Conductivity Ratio Profile: Contaminated/Uncontaminated. Vertical line at 1 is the reference base line.

and is consistent with high CO<sub>2</sub> concentrations observed within this zone [Legall, 2002]. Lastly, the spatial variability (vertically) of the conductivity profile within the zone of LNAPL impact corresponds to the elevations of the different LNAPL zones and not to changes in grain size.

#### 4. Discussion and Conclusions

[17] This study found that variations in water saturation (i.e., the insulating model) could not account for the observed conductivity profiles. Further, analysis found the conductive layer model required a minimum 5.5 fold increase in pore water conductivity relative to the uncontaminated location to explain the conductivity profiles. This increase is consistent with a laboratory slurry experiment that showed a factor of 6 increase [Cassidy *et al.*, 2001]. We further show that for the contaminated location, less than a 1.5 fold increase in pore water conductivity occurs below the water table, which agrees with geochemistry data that shows groundwater conductance  $\sim 1.4$  times greater [Legall, 2002]. Legall [2002] further showed elevated concentrations of Si, Ca, Mg, Na, HCO<sub>3</sub><sup>-</sup> at the contaminated locations relative to uncontaminated conditions. This is consistent with enhanced dissolution of the aquifer minerals. The above findings are supported by McMahon *et al.* [1995] that showed the concentration of dissolved organic acids from microbial degradation of hydrocarbons positively correlated with dissolved silica. Finally, elevated populations of oil degrading bacteria have been documented at this field site coincident with the zone of elevated conductivity [Werkema *et al.*, 2000], which suggest a possible link between the conductive pore water and the biological activity.

[18] The conductivity increase correlated with locations of LNAPL contamination is observed at other sites where the geology is uniform sand [Bermejo *et al.*, 1997] and heterogeneous glacial deposits [Atekwana *et al.*, 2002]. Therefore, this conductivity increase is not unique to this site or this work. Furthermore, a conductivity increase associated with LNAPL contamination has recently been reported by other investigators [Shevvin *et al.*, 2003; Bradford, 2003].

[19] The findings of this study not only corroborate the conductive layer model and provide an indication into the biologically driven mechanism, they suggest that the vertical position of the high conductivity anomaly occurs in partially water saturated conditions above the water table. The fluctuating water table likely smears the LNAPL potentially making it more readily available for microbial activity [Lee *et al.*, 2001]. If the magnitude of conductivity observed in this study is an indirect measure of biological activity through changes in pore water geochemistry, then our geophysical data suggests that the zone of most active biodegradation occurs above the water table and not below as is conventionally studied. Thus, this zone of enhanced conductivity, observed geophysically, can be more effectively investigated for geochemical and/or biological processes.

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