

In-situ apparent conductivity measurements and microbial population distribution at a hydrocarbon-contaminated site

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ABSTRACT

We investigated the bulk electrical conductivity and microbial population distribution in sediments at a site contaminated with light nonaqueous-phase liquid (LNAPL). The bulk conductivity was measured using in-situ vertical resistivity probes; the most probable number method was used to characterize the spatial distribution of aerobic heterotrophic and oil-degrading microbial populations. The purpose of this study was to assess if high conductivity observed at aged LNAPL-impacted sites may be related to microbial degradation of LNAPL. The results show higher bulk conductivity coincident with LNAPL-impacted zones, in contrast to geoelectrical models that predict lower conductivity in such zones. The highest bulk conductivity was observed to be associated with zones impacted by resid-

ual and free LNAPL. Data from bacteria enumeration from sediments close to the resistivity probes show that oil-degrading microbes make up a larger percentage (5–55%) of the heterotrophic microbial community at depths coincident with the higher conductivity compared to ~5% at the uncontaminated location. The coincidence of a higher percentage of oil-degrading microbial populations in zones of higher bulk conductivity suggests that the higher conductivity in these zones may result from increased fluid conductivity related to microbial degradation of LNAPL, consistent with geochemical studies that suggest that intrinsic biodegradation is occurring at the site. The findings from this study point to the fact that biogeochemical processes accompanying biodegradation of contaminants can potentially alter geoelectrical properties of the subsurface impacted media.

INTRODUCTION

Light nonaqueous-phase liquid (LNAPL) contamination of soils remains a major problem of global environmental concern. The task of locating and quantifying the amount of LNAPL present and its subsequent degradation in soils has presented significant challenges to scientists and engineers involved in soil cleanup and remediation. The partitioning of hydrocarbons in the subsurface into various phases (vapor, residual, free, and dissolved) and their spatial and temporal nature are difficult to characterize, compounding the problem of soil remediation (Davis et al., 1993).

Geophysical techniques hold great promise as inexpensive and minimally invasive sensors of subsurface LNAPL contam-

ination. As such, geophysical techniques, including ground-penetrating radar (GPR), electromagnetic induction, and electrical resistivity, have been widely used to detect hydrocarbon-impacted zones in the subsurface (e.g., Mazáč et al., 1990; Benson and Stubben, 1995; Grumman and Daniels, 1995; Endres and Greenhouse, 1996; Atekwana et al., 2000). The theoretical basis for using geoelectrical methods to detect LNAPL contaminants in the subsurface depends on the contrasting electrical properties of the LNAPLs versus the pore and groundwater displaced by the LNAPL. According to Archie's law (Archie, 1942), the conductivity of porous geologic material (in the absence of clays) can be described by

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

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where σ_b is the bulk conductivity of the porous medium, σ_w is the electrical conductivity of the pore fluids (fluid conductivity), ϕ is the porosity, m is the cementation factor, a is a constant related to rock or sediment type, S_w is the water saturation or fraction of pores containing water, and n is an empirical factor.

With LNAPL contamination, both S_w and σ_w are lowered as a result of the partial replacement of pore waters with lower conductivity LNAPL, resulting in a decrease in σ_b of the impacted media. This scenario forms the basis for the insulating layer model supported by short-term laboratory and controlled hydrocarbon spill experiments (DeRyck et al., 1993) as well as petrophysical modeling (Endres and Redman, 1996). On the basis of the above model, geoelectrical data have been interpreted from many hydrocarbon-contaminated sites.

Effects of biodegradation on electrical properties

LNAPL-impacted sites investigated are rarely fresh spills, as depicted by the insulating layer model and the controlled spill studies. Ample evidence in the geochemical and microbiological literature suggests physical and chemical alteration of hydrocarbons in contaminated sediments by indigenous microorganisms (e.g., Cozzarelli et al., 1990, 1994, 2001). For example, geochemical investigations at hydrocarbon-contaminated sites suggest that major metabolic products of hydrocarbon biodegradation are carbonic and volatile organic acids (e.g., Cozzarelli et al., 1990, 1994). These organic electrolytes—especially organic acids—enhance the dissolution of silicate minerals such as feldspars and quartz (McMahon et al., 1995). In one study, in-situ microcosm experiments in a hydrocarbon-contaminated aquifer showed that minerals were colonized by indigenous bacteria and chemically weathered at rates faster than theoretically predicted (Hiebert and Bennett, 1992). We suggest that increases in dissolved ion concentrations in pore water accompanying enhanced mineral dissolution should increase the electrical conductivity of the impacted media (Sauck, 2000). Recent geoelectrical investigations at aged (i.e., altered) hydrocarbon spill sites have documented higher bulk conductivities coincident with the zones of hydrocarbon impact (Sauck et al., 1998; Atekwana et al., 2000, 2002; Shevnin et al., 2003; Werkema et al., 2003). Further, other studies have documented attenuated GPR reflections, most likely from increased bulk conductivity in regions with subsurface hydrocarbon contamination (Maxwell and Schmok, 1995; Bermejo et al., 1997; Sauck et al., 1998; Bradford, 2003).

Despite the apparent connection between microbial degradation of hydrocarbon and possible changes in the geoelectrical properties of soils, relatively few or no studies have been conducted to document this relationship. In this study, we simultaneously measured bulk conductivity variations, the heterotrophic and oil-degrading microbial population distribution, and water quality parameters indicative of pore-fluid conductivity changes at an aged LNAPL-impacted site to investigate this relationship. This study is part of a larger multidisciplinary research effort to investigate the effects of biodegradation processes on the geoelectrical properties of hydrocarbon-contaminated sites.

SITE DESCRIPTION

This study was conducted in a city park directly south of the former Crystal Refinery in Carson City, Michigan (Figure 1).

Detailed descriptions of the study site are in Atekwana et al. (2000). Continuous hydrocarbon releases (mostly JP4 jet fuel and diesel) from storage facilities and pipelines resulted in petroleum hydrocarbons seeping into the subsurface, impacting soils and groundwater for more than 50 years. The contaminated aquifer has variable thickness (approximately 4.6–6.1 m thick) and is composed of glacial outwash. Fine- to medium-grained sands characterize the unsaturated zone, while the saturated zone consists of medium-sized sands and gravels underlain by a clay unit. The topography at the site is undulating, causing the depths to the water table from the ground surface to vary from 0.6 to 0.9 m in the western portion of the study area and from 4.6 to 5.8 m in the eastern portion.

The groundwater table varies up to 0.9 m annually at the site (Werkema, 2002), resulting in a hydrocarbon smear zone of variable thickness across the contaminated locations. Contours showing the hydrocarbon-phase distribution at the study site are shown in Figure 1. Recent geochemical studies at the site suggest that intrinsic biodegradation is occurring in the contaminated groundwater. Methanogenesis is the dominant redox process within the core of the plume, while denitrification and sulfate, iron, and manganese reduction occur at the fringes of the plume (Legall, 2002). Byproducts of biodegradation such as biosurfactants and high carbon dioxide concentrations have been measured in contaminated groundwater and soils at this site (Cassidy et al., 2002; Legall, 2002).

FIELD INVESTIGATIONS

In this study, we determined the distribution of LNAPL, sediment grain-size distribution, bulk conductivity, heterotrophic and oil-degrading microbial populations, volatile organic acids, and groundwater specific conductance in contaminated and uncontaminated locations at the study area. Each monitoring location consisted of an instrument cluster that included a vertical resistivity probe (VRP), multilevel lysimeters, and multilevel piezometers (Figure 1).

Subsurface LNAPL distribution

Subsurface LNAPL distribution was determined from sediment cores. The cores were collected using 5.0-cm-diameter, 122-cm-long acetate liners for direct push coring on a Geoprobe™ drill rig. The sediment cores were characterized for vertical distribution of hydrocarbon by observing staining of the sediments (residual LNAPL) and the presence of free-phase hydrocarbon compared to a core from an uncontaminated location at the study site.

Sediment grain-size distribution

Sediment grain-size distribution was determined from the same core used for LNAPL characterization. The percent gravel (>4.8 mm), sand (4.8–0.06 mm), and silt/clay (<0.06 mm) were determined for selected depth intervals by sieve analysis after drying the sediments to a constant weight at 105°C. Sieved sediment sampling intervals were either 15 or 30 cm.

In-situ conductivity measurements

Apparent conductivity data were collected using in-situ vertical resistivity probes (VRPs) installed in contaminated and

uncontaminated portions of the study site. The VRPs consisted of 3.8-cm inner diameter (ID) PVC dry wells with 1.3-cm-long stainless steel screws installed at 2.5-cm intervals. The screwheads on the outside of the dry PVC wells served as the electrode contact with the geologic formation, and the threaded ends inside the wells enabled apparent resistivity measurements. Installation of the VRPs included a small bentonite slurry annulus, which facilitated installation below the saturated zone and decreased the contact resistance with the surrounding geologic formation in the unsaturated zone. After bentonite equilibration, apparent resistivity measurements were collected for a 5.0-cm Wenner array using a Syscal R2 resistivity meter with an automated/semiautomated switching system for switching between the electrodes (Werkema et al., 1998, 2000). The VRP profiles were generated by incrementing the Wenner array every 5.0 cm with depth. The profiles are presented as conductivity (the reciprocal of resistivity) in Figures 2–4.

Microbial sampling and cell extraction

The total heterotrophic and oil-degrading microbial populations were enumerated for sediment collected about 1 m

adjacent to each VRP. Soil cores were obtained using a 2.5-cm-diameter by 61-cm-long acetate liner for direct push coring (using a hand-operated Geoprobe™ system). Prior to sediment sampling, the acetate liners and liner caps were disinfected in the laboratory with an 80% ethanol solution and dried in a laminar flow hood. In the field, the cores were aseptically collected, capped, and placed on ice and out of direct sunlight. The samples were subsequently transported to the laboratory and stored at 4°C until analysis to minimize further bacteria growth. The holding time prior to microbial enumeration did not exceed 10 days.

Sub sampling of the sediment for microbial enumeration was conducted at ~15-cm intervals. Prior to sampling the core, the outside of the sleeve was disinfected with 80% ethanol. A sterilized razor blade was used to cut a 2 × 2-cm portion of the core sleeve, exposing the soil. The outer portion of soil was aseptically removed, and about 1 g of soil was collected and placed in sterile 15-ml polypropylene tubes for extraction of microbial cells and subsequent enumeration of microbes.

The total heterotrophic and oil-degrading microorganisms were determined using a modification of the procedure described by vanElsas and Smalla (1997); 9.5 ml of 0.1% sodium pyrophosphate was added to 1 g of soil, shaken for 30 minutes,

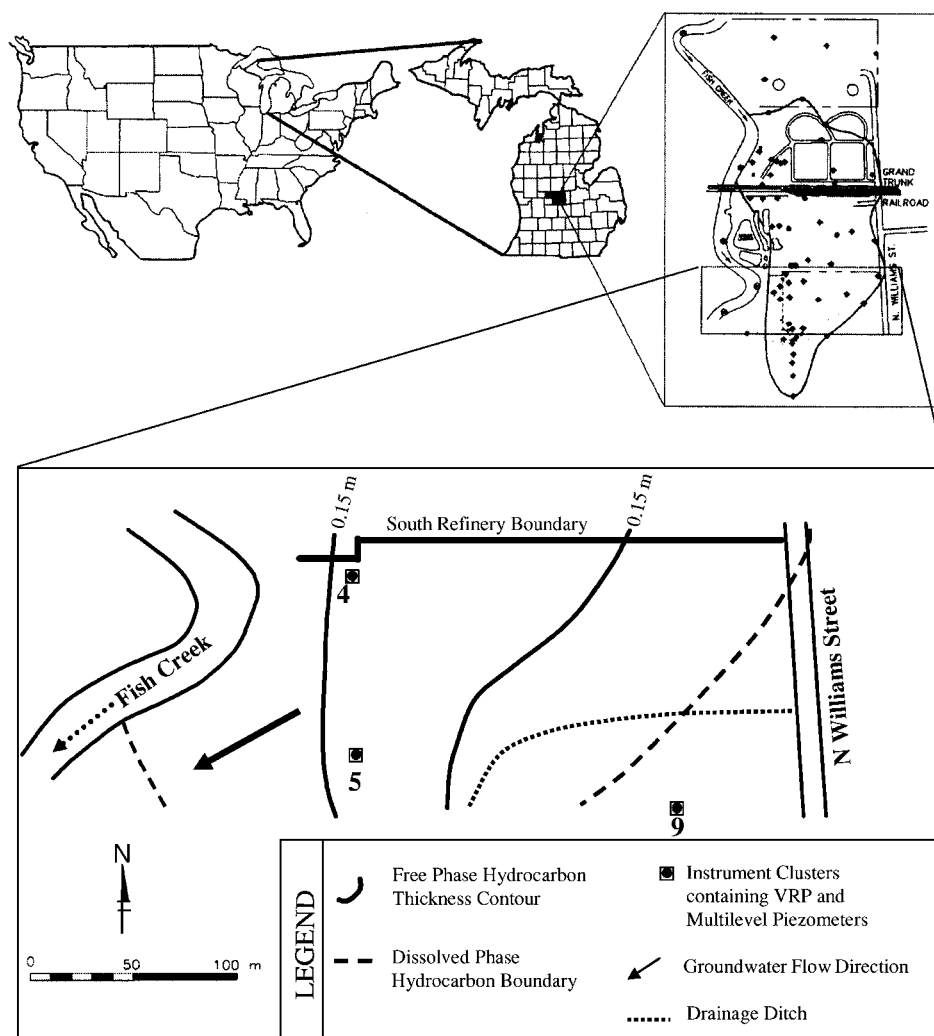


FIG. 1. Former Crystal Refinery, Carson City, Michigan. Vertical resistivity probe and instrument clusters locations.

and centrifuged at ~ 900 g for 10 minutes. The most probable number of bacteria (MPN/g of soil) was determined from aliquots of the supernatant using the 96-well plate method with 10% trypticase soy broth (TSB) medium to enumerate the total heterotrophic microorganisms. This low-nutrient medium simulated the natural soil environment. It was not selective and enabled all heterotrophic bacteria to grow. Growth in 96-well plates was scored by using a microplate reader (EL800, BioTek Instruments), determining the optical density at 600 nm. A minimal Bushnell-Haas (BH) medium (Becton Dickinson, Detroit, Michigan) was supplemented with NaCl, with *n*-hexadecane as the sole carbon source. This selective medium was used to enumerate the hydrocarbon-degrading microorganisms as described by Wrenn and Venosa (1996) and Haines et al. (1996). Growth was identified using iodonitrotriazolium violet (INT), which forms an insoluble red precipitate in wells containing bacteria that can use hexadecane as a sole carbon source.

After each plate from the 96-well plate had been scored, the number of positive wells at each serial dilution was entered into a computer program to determine the most probable number of bacteria per gram of soil and the 95% confidence limits at each sample point (Klee, 1993). The computer program provided MPN numbers that were corrected for positive bias in published MPN charts (Salama et al., 1978).

Pore-water and groundwater specific conductance and volatile organic acids

Pore-water and groundwater specific conductance was measured with a HydroLabTM multiparameter probe. Pore water was collected using suction lysimeters, and groundwater was sampled at 30-cm depth intervals from 0.64-cm PVC tubing fitted with 10-cm nylon screens. The pore water from lysimeters was evacuated using standard techniques. Groundwater from the multilevel piezometers was pumped to the surface using a peristaltic pump. Volatile organic acids were determined using ion chromatography, and values were reported as acetic acid in milligrams per liter.

RESULTS

Results of the grain-size analyses, distribution of LNAPL, bulk conductivity, and microbial population are summarized graphically in Figures 2–4. All depths reported in this study are in elevations above sea level. We present the results from three monitoring locations: two from the core of the plume (VRP4 and VRP5) and one from a background site (VRP9) with no detectable hydrocarbons but comparable soil characteristics (see Figure 1 for VRP locations).

Background location (VRP9)

Results from the background location (VRP9) are presented in Figure 2. Lower bulk conductivity (<5 mS/m) characterizes the unsaturated zone, but apparent conductivity increases gradually through the capillary fringe into the saturated zone. Below the water table (~ 225 m), the bulk conductivity remains relatively constant (~ 15 mS/m) to the base of the aquifer. This location shows a uniform grain-size distribution (sands) until approximately 224.2 m elevation (Figure 2a) with no direct relationship to the bulk conductivity profile.

The heterotrophic microbes and microbes capable of degrading hydrocarbon (oil degraders) in soils at this location ranged from 10^2 to 10^6 and from 10^2 to 10^5 MPN/g of soil, respectively. The microbial numbers decreased slightly with depth for both the total heterotrophic and oil-degrading microbial populations (Figure 2c). This is expected, since (1) our enumeration method will only count aerobic bacteria and (2) oxygen concentrations are expected to decrease with depth. In general, the oil-degrading microbial population represented on average less than 5% of the total heterotrophic microbial community.

Specific conductance of groundwater (fluid conductivity) from the multilevel piezometers ranged from 8 to 39 mS/m in the capillary fringe and upper portions of the saturated zone, whereas higher values (76–88 mS/m) occurred at the base of the aquifer. Volatile organic acids were below detectable levels at this location. There was no recovery of water from the lysimeters at VRP9.

Contaminated locations (VRP4 and VRP5)

The distribution of LNAPL at the contaminated locations is shown in Figures 3b and 4b. Evidence of the presence of hydrocarbon was noticeable above the water table as a dark gray to light gray stain on the sediments. The staining was the result of LNAPL coating sediments under unsaturated conditions. Thus, the stained zone, which was of variable thickness (up to 2 m thick), resulted from LNAPL smeared on the sediments and defined the maximum and minimum fluctuations in the water table across the study site. With a rising water table, the free LNAPL was nested within the smear zone. The free LNAPL observed at contaminated locations ranged from ~ 15 cm to ~ 61 cm. Results from LNAPL-impacted soils at the study site were represented by instrument locations VRP5 and VRP4 (see Figure 1 for location).

VRP5.—Figure 3 presents the results from VRP5. The bulk conductivity of the vadose zone was low and ranged from 0.1

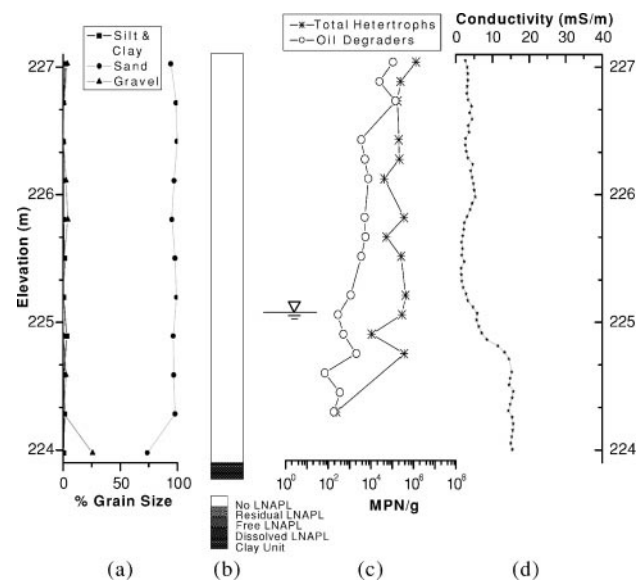


FIG. 2. VRP9 background. (a) Grain-size distribution location. (b) LNAPL distribution. (c) Microbial population distribution. (d) In-situ conductivity variation.

to 0.7 mS/m to an elevation of 226 m. At this elevation and coincident with the top of the contaminated zone (residual LNAPL), the bulk conductivity increased from approximately 0.3 to 2 mS/m (Figure 3d). At lower elevations, the bulk conductivity progressively increased within the residual LNAPL zone, reaching approximately 22 mS/m at 225 m. An alternating polarity conductivity high of 49 mS/m, coincident with the free-phase LNAPL–water interface, occurred at 225 to 224.8 m. The alternating polarity response was typical of the Wenner array across a sharp geoelectric boundary (Telford et al., 1990). Note that the highest bulk conductivity values coincided with the free LNAPL and the upper part of the saturated zone. Below the upper part of the saturated zone to the base of the aquifer, bulk conductivity gradually decreased to an average value of 18 mS/m to the maximum depth of the VRP at an elevation of 223.5 m. Thus, we observed a zone of enhanced conductivity approximately 2 m thick, extending from 224 to 226 m. The lithologic data in Figure 3a shows predominantly sands in the upper parts of the aquifer, with a change from predominantly sand to sand and gravel at 224.5 m.

Heterotrophic microorganisms from soil samples near VRP5 ranged from 10^2 to 10^7 MPN/g of soil, and oil-degrading microorganisms ranged from 10^1 to 10^4 MPN/g of soil. In samples above 227 m elevation, the oil-degrading bacteria made up 99.9% and 12% of the total heterotrophic community, respectively. The microbial community in the near-surface zone, where leaf litter and other organic carbon predominated, probably adapted to degrading humus and other organic carbon compounds, including alkanes—the carbon source present in our BH test medium. At depths between 227 and 226 m, with no LNAPL contamination, the population of oil degraders averaged 0.3% of the total heterotrophic microbial community. At 226 to 225 m at the transition between residual and free LNAPL, the oil degraders represented on average 5% of the total microbial community. Below 225 m, where dissolved and free LNAPL were present, the oil degraders made up an average of 30% of the total microbial community. Thus, except for

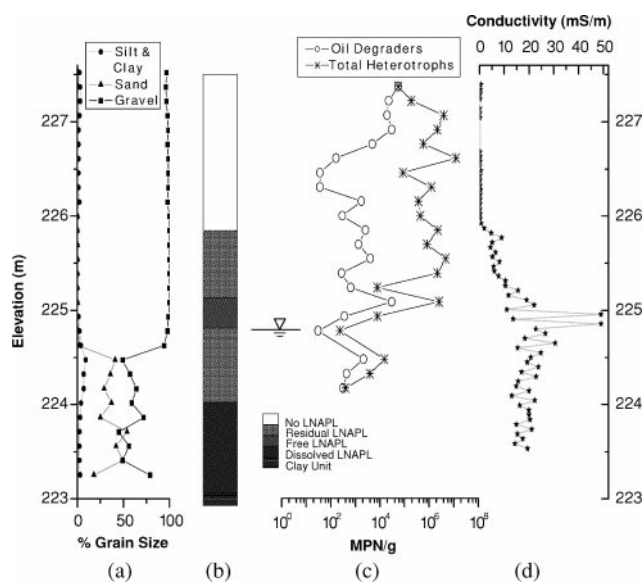


FIG. 3. VRP5, an LNAPL-contaminated location. (a) Grain-size distribution. (b) LNAPL distribution. (c) Microbial population distribution. (d) In-situ conductivity variation.

the A horizon, the largest fraction of oil degraders was found in the free and dissolved LNAPL, coinciding with higher bulk conductivity.

Fluid conductivity from the upper parts of the aquifer was higher (84 mS/m) at VRP5 compared to similar depths in the saturated zone (8 mS/m) at VRP9, the background location. In the lower parts of the saturated zone, the fluid conductivity was 90 mS/m. Fluid conductivity obtained from a lysimeter within the residual LNAPL zone (225.5 m) at VRP5 was 52 mS/m. Also, volatile organic acids measured in groundwater from this location ranged from 12.9 to 16.2 mg/l.

VRP4.—The bulk conductivity profile from VRP4 is shown in Figure 4d. Lower bulk conductivity (0.3 mS/m) characterized the vadose zone to an elevation of 225.8 m. At this elevation, the bulk conductivity progressively increased through the residual LNAPL zone, reaching a maximum of approximately 37 mS/m at 224.9 m below the saturated zone (coincident with the submerged smear zone). Below this conductivity maximum, the profile decreased to an average value of 20 mS/m through the saturated zone that was contaminated with dissolved LNAPL. Again, the zone of enhanced conductivity was approximately 2 m thick, equivalent to the LNAPL smear zone, and extended from 224 to 225.8 m. The lithologic logs (Figure 4a) showed a change in grain size from predominantly sand to sand and gravel at 224.5 m elevation. This grain size change occurred 0.5 m below the zone of maximum conductivity, suggesting the conductivity profile was not significantly affected by variations in lithology. Rather, the variations in the conductivity profile appeared to be coincident with the presence of LNAPL contamination (LNAPL smear zone).

The heterotrophic microorganisms ranged from approximately 10^3 to 10^6 MPN/g soil, and the oil degrading microorganisms ranged from 10^2 to 10^5 MPN/g soil. Again, there was a higher percentage of alkane degraders in the near-surface zone at 226.7 m (26%). Within the vadose zone with no visible

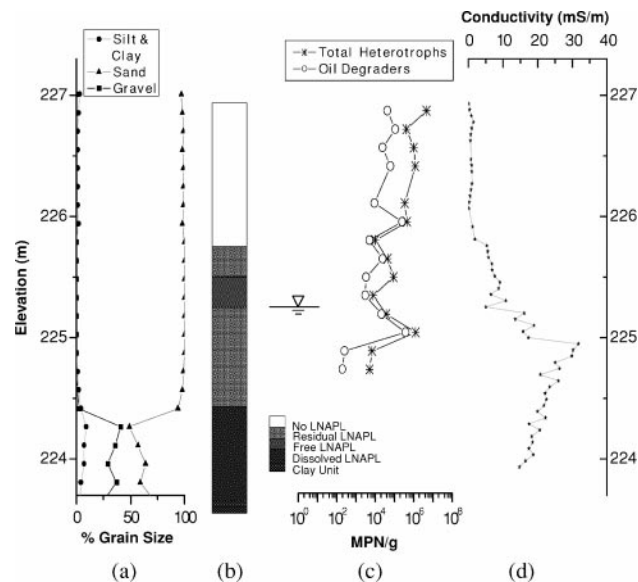


FIG. 4. VRP5, an LNAPL-contaminated location. (a) Grain-size distribution. (b) LNAPL distribution. (c) Microbial population distribution. (d) In-situ conductivity variation.

LNAPL contamination (between 226.7 and 225.8 m), the oil degraders represented on average only 3% of the total heterotrophic microbial community. Below 225.8 m elevation, where residual, free, and dissolved LNAPL were present, the oil degraders accounted for 55% of the total heterotrophic microbial community. Thus, a higher percentage of oil degraders were concomitant with the presence of LNAPL and higher bulk conductivity (Figure 4).

The fluid conductivity at this location (~100 mS/m) was higher compared to fluid conductivities at VRP5 and VRP9. Pore-water samples obtained from a lysimeter within the unsaturated zone (226.5 m) at this location had a fluid conductivity of 71 mS/m. No data were available for volatile organic acids at VRP4.

DISCUSSION AND CONCLUSION

Results of in-situ bulk conductivity measurements at the study site showed higher conductivities at the contaminated locations (VRP4 and VRP5) compared to background (VRP9). A conductive zone ~2 m thick was observed to be coincident with the zone of contamination (smear zone), in direct contradiction to the insulating layer model which predicts low bulk conductivity for hydrocarbon-contaminated sediments. The data revealed three zones where higher bulk conductivity measurements were observed: (1) in the unsaturated zone with residual LNAPL, (2) in zones with free LNAPL, and (3) in the upper parts of the saturated zone contaminated with dissolved LNAPL.

The higher bulk conductivity observed at the contaminated locations could result from several factors, which include geologic heterogeneity (especially in the presence of clays), increase in water saturation, and increase in the fluid conductivity resulting from dissolution of minerals resulting from biodegradation of the contaminant mass [equation (1)]. Grain-size analyses showed that the sediments in the unsaturated zone consisted of fine to medium sands (with relatively minor clays). The lithology below the saturated zone was typically medium to coarse sand with gravel. Although the variability in the bulk conductivity profiles could simply be related to variations in lithology, observed changes occurred at elevations not coincident with changes in lithology. For example, at VRP4 the increase in conductivity from 0.3 to 10 mS/m occurred at an elevation of 225.6 to 225.9 m, coincident with the boundary between the residual LNAPL (below) and the clean sediment (LNAPL free) above. We observed, a further increase in bulk conductivity to a maximum of 37 mS/m at 224.9 m. The change in lithology from sands to sands and gravel occurred at 224.5 m, below the elevations where the bulk conductivity changes were observed.

Because elevations where changes in lithology and bulk conductivity were observed are not coincident, the higher bulk conductivity observed at contaminated locations cannot be explained entirely by geologic heterogeneity (increase in silt, clay, gravel, or sand content). Bulk-conductivity variations in the unsaturated zone at both the uncontaminated and contaminated locations may be attributed to saturation effects. Increased saturation from infiltration will increase the bulk conductivity of the sediments. However, within the impacted vadose zone (at the contaminated locations), the bulk conductivity is expected to be lower, since partial replacement of water by LNAPL will

lower the water saturation and hence its conductivity (i.e., insulating layer model).

Instead, we observed the opposite effect: the bulk conductivity within the LNAPL-impacted vadose zone was higher than the bulk conductivity of the uncontaminated vadose zone. Further, within the saturated zone, the maximum bulk conductivity at VRP9 was approximately 15 mS/m, compared to 37 mS/m for the contaminated locations (e.g., VRP4). Hence, the contaminated-zone conductivities were approximately twice that of the uncontaminated location. Again, this was inconsistent with the expected decrease in conductivity attributable to the presence of the more resistive LNAPL at the contaminated locations [equation (1) and per the resistive or insulating layer model]. Thus, we hypothesize that the higher bulk conductivities at the contaminated location are associated with microbial activity stimulated by the presence of petroleum hydrocarbons.

Corroborating evidence was provided by the microbial population data. The numbers of oil-degrading microorganisms were estimated by growing the bacteria in a selective medium (BH) with hexadecane as the sole carbon source. The total heterotrophic bacterial community was assessed by growing them in a diluted medium suitable for growing soil bacteria (1/10 TSA). These methods represented a traditional culture-based approach to bacterial enumeration. By using molecular methods, however, microorganisms which can be cultured under laboratory conditions often represent only a small fraction of the total microbial community present at diverse natural habitats (MacNaughton et al., 1999).

Nevertheless, despite these limitations, the assessment of microbial numbers by culturing is still a valid method for comparative purposes, as here in the enumeration of alkane degraders and the total heterotrophic bacteria. Although our data points represent four independent samplings from the same depth, some of the resulting microbial numbers seem to fluctuate, especially in the saturated zone at VRP4 and VRP5. This probably represents the considerable spatial heterogeneity of the soil habitat, which is enormous from the microbial perspective (in the micrometer range). In addition, samples were taken every 15 cm, which is on a finer scale than previously reported from other aquifers contaminated by crude oil, e.g., at the Bemidji site in Minnesota (every 50–100 cm; Bekins et al., 1999).

Thus, except in the upper soil zone, where a higher percentage of aerobic hydrocarbon degraders is likely to be found because of their adaptation to leaf litter and humus and more oxygenated conditions, it is significant that, at the uncontaminated location (VRP9), on average only 5% of the total heterotrophic microbial population are oil degraders, whereas at VRP4 and VRP5, at the depths where LNAPLs are present, the oil degraders represent on average 5–55% of the heterotrophic microbial community. Although microbial numbers are not a direct measure of bioremediation activity, they provide a measure of the biodegradation potential of this particular sediment (Bossert and Kosson, 1997). Therefore, the presence of the larger fraction of microorganisms able to degrade hydrocarbons indicates a potential for intrinsic bioremediation at this site. Geochemical studies from this site suggest that methanogenesis is the dominant redox process occurring at VRP4 and VRP5 (Legall, 2002). Further, the Legall (2002) study shows the depletion of terminal electron acceptors (nitrate, sulfate, manganese IV, and iron III) and higher concentrations of CO₂,

suggesting that intrinsic biodegradation is occurring at the contaminated locations. The geochemistry results also suggest anaerobic conditions within the contaminated portions of the aquifer. Our enumeration of oil-degrading microbial populations at VRP4 and VRP5 estimates only the aerobic and facultative anaerobic fractions of the microbial community, whereas the geochemistry results suggest the presence of anaerobes. Thus, our estimates of oil-degrading microbial populations at the contaminated locations are probably low. Therefore, we expect that by using anaerobic culturing techniques and molecular analysis in the future, a more accurate and detailed understanding will be gained of the relation between microbial community structure and geochemical/concurrent geophysical changes.

Measurements of fluid conductivity from the upper parts of the saturated zone (dissolved phase) at contaminated locations (VRP4 and VRP5) show higher values (84–99 mS/m) than VRP9, the background site (8–38 mS/m). Although at all VRP locations the fluid conductivity increased with depth to the base of the aquifer, values from contaminated locations were still higher than values from the background location (VRP9). We suggest that the higher fluid conductivity for the contaminated groundwater indicate higher total dissolved solids (TDS) resulting from enhanced mineral weathering at the contaminated locations. Higher TDS at the contaminated locations compared to the background location have been observed at the study site (Atekwana et al., 2003). The higher TDS value results from higher concentrations of calcium, magnesium, sodium, silica, and bicarbonate ions observed in contaminated groundwater at this site (Legall, 2002) and is consistent with the weathering of minerals in the aquifer.

Our observations are consistent with studies from other hydrocarbon-contaminated aquifers that show positive correlation between higher organic acid concentrations and higher dissolved silica concentrations (McMahon et al., 1995). The McMahon et al. (1995) study point to the fact that microbial enhanced mineral dissolution can account for high fluid conductivity at hydrocarbon-contaminated aquifers. Hence, the occurrence of intrinsic bioremediation, the presence of organic acids, and elevated percentages of oil-degrading microbial populations at contaminated locations in our study provide circumstantial evidence linking the higher bulk conductivities to higher TDS resulting from enhanced mineral weathering because of acids produced during biodegradation of the LNAPL in both the saturated and unsaturated zones.

Also, we observed no significant decrease in bulk conductivity associated with the free LNAPL zone. This finding is significant because intuitively, this zone is expected to have the lowest conductivities, since oil is an insulator and we expect significant oil saturation within this zone. A recent study at this site (Cassidy et al., 2002) showed in-situ rhamnolipid biosurfactant production by indigenous microbes at the contaminated locations. This finding was consistent with laboratory studies that reported the production of biosurfactants under both aerobic and anaerobic conditions, resulting in significant emulsification of diesel fuel (Cassidy et al., 2001). We suggest that the emulsion of LNAPL as a result of in-situ biosurfactant production during biodegradation would break up the initial continuous LNAPL layer, providing conductive leachate pathways for the electrical current flow. This phenomenon offers a reasonable explanation why sediments contaminated with

residual and free-phase hydrocarbons are conductive and not resistive. Hence, our model states that the increase in bulk conductivity observed at many aged LNAPL-impacted sites may be the combined effect of increases in dissolved ion concentrations (from enhanced mineral dissolution by acids) and apparent emulsification of LNAPLs (accompanying biosurfactant production) during biodegradation. Thus, we infer from this study that hydrocarbon-degrading environments are complex. Those methods that combine physical, biological, geochemical, and hydrologic information may provide further insights and greater understanding of hydrocarbon degradation in natural field settings.

Microbial processes may play an important role in altering geophysical properties of contaminated sediments. Hence, the influence of biological activity on in-situ physical properties can no longer be ignored in the geophysical investigations of contaminated sites. Conductive zones as depicted by the VRPs may represent areas of active biodegradation and demonstrate the potential for geoelectrical techniques to be used in conjunction with traditional techniques in investigating intrinsic microbial mineralization of hydrocarbons at contaminated sites. However, fundamental geophysical research at both the lab and field scale is needed to understand how microbial mediated processes of LNAPL-impacted sediments alter their geoelectrical properties.

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