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Field evidence for geophysical detection of subsurface zones of enhanced microbial activity

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[1] Geochemical data from closely spaced vertical intervals in a hydrocarbon-impacted aquifer were used to assess the relationship between bulk conductivity and zones of enhanced microbial activity. The bulk conductivity was measured using in situ vertical resistivity probes. Microbial activity was verified using terminal electron acceptors (nitrate, sulfate, iron, and manganese), dissolved inorganic carbon (DIC), and major ion chemistry. Peaks in bulk conductivity in the aquifer overlapped with zones where nitrates and sulfates were depleted, total petroleum hydrocarbon, iron, manganese, dissolved ions, and DIC were elevated, suggesting a link between higher electrical conductivity and zones of enhanced microbial activity stimulated by the presence of hydrocarbon. Thus the subsurface expression of microbial activity is apparently recorded in the bulk conductivity measurements. Our results argue for combining geophysics with biogeochemistry studies to delineate subsurface zones of enhanced microbial activity. **INDEX TERMS:** 0915 Exploration Geophysics: Downhole methods; 0925 Exploration Geophysics: Magnetic and electrical methods; 1831 Hydrology: Groundwater quality; 5109 Physical Properties of Rocks: Magnetic and electrical properties. **Citation:** Atekwana, E. A., E. Atekwana, F. D. Legall, and R. V. Krishnamurthy (2004), Field evidence for geophysical detection of subsurface zones of enhanced microbial activity, *Geophys. Res. Lett.*, *31*, L23603, doi:10.1029/2004GL021576.

1. Introduction

[2] Microorganisms are involved in a wide variety of geologic processes and play an important role in altering the chemical and physical properties of their environments [Bennett *et al.*, 1996; Chapelle and Bradley, 1997], and may have significant ramification for near surface geophysical investigations conducted at depths where microbial communities are abundant and biological processes are most active. There is interest in investigating biological interactions with geologic media and the accompanying changes in geophysical properties [e.g., Meju, 2000; Naudet *et al.*, 2003; Werkema *et al.*, 2003; Atekwana *et al.*, 2004a, 2004b]. Possible links between geophysics and microbial processes come from recent laboratory experiments. Abdel Aal *et al.* [2004] showed in a laboratory column contaminated with diesel and amended with bacteria that temporal

increases in real and imaginary conductivity were concurrent with temporal increase in microbial population numbers and major ions, and decrease in diesel and terminal electron acceptors (TEAs). In a mesoscale experiment designed to mimic field conditions, Atekwana *et al.* [2003] show that dissolved ions in pore waters were higher in diesel contaminated columns compared to uncontaminated columns, and that zones of higher bulk conductivity were concomitant with zones of higher populations of alkane-degrading microbes. Ntarlagiannis *et al.* [2004] show that when bacteria were stimulated with fluids enriched in lactate and sulfate in the presence of iron and zinc, intense microbial growth and activity was accompanied by sulfide and zinc precipitation and changes in the interfacial properties (imaginary conductivity). The above cited laboratory experiments underscore the fact that geomicrobial activity can be detected by geophysical methodologies.

[3] While previous work by Naudet *et al.* [2003] has demonstrated a relationship between self potential and redox potential, currently, little work exists assessing the relationship between redox processes and geophysical signatures at field settings. Here, we investigated the relationship between TEAs (nitrate, sulfate, iron, and manganese) and geophysical properties at a hydrocarbon-contaminated aquifer. Hydrocarbon-contaminated sites are model laboratories to investigate microbial-geophysical relationships because the excess organic substrate stimulates microbial activity, hence microbial impact on geophysical properties may be more readily assessed. We show that higher bulk conductivity overlapped with discrete zones of TEAs, suggestive of higher microbial activity. Thus geophysical methodologies may play an important role in delineating zones of enhanced microbial activity.

2. Site Description

[4] The study site has been used for multidisciplinary research since 1998. Atekwana *et al.* [2000], Cassidy *et al.* [2002], Werkema *et al.* [2003], and Atekwana *et al.* [2004a, 2004b] provide details on the study site and describe ongoing geophysical, microbiological, and geochemical investigations at the site. Continuous hydrocarbon releases (mostly crude oil, JP4 jet fuel, and diesel) from storage facilities and pipelines resulted in seepage of petroleum hydrocarbons into the subsurface, impacting sediments and groundwater for more than 50 years. Contamination in this aquifer occurs in the residual, free, and dissolved phases. The aquifer is glacially derived unconsolidated fine to

Table 1. Multi Level Piezometer (MLP) Location, Bulk Conductivity, Total Petroleum Hydrocarbon, Temperature, Specific Conductance, NO₃⁻, SO₄²⁻, Fe(II) and Mn(II), DIC, Ca²⁺, and Mg²⁺ From Hydrocarbon Contaminated and Uncontaminated Groundwater^a

Well ID	Elevation (m)	Bulk Conductivity (mS/M)	Total Petroleum Hydrocarbons (mg/l)	Temperature (°C)	pH	Specific Conductance (μS/cm)	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	Fe (μg/l)	Mn (μg/l)	DIC (mg C/l)	Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)
MLP-9	225.00	3.6	ND	13.5	7.1	470	5.6	18.9	20	5	29.9	62.2	15.3
	224.55	18.4	ND	12.4	7.3	772	5.8	40.5	18	5	71.2	106.9	29.2
	224.07	16.1	ND	11.7	7.1	852	2.0	44.4	18	161	84.7	129.3	39.5
	223.78	-	ND	13.7	7.0	875	2.0	45.4	17	42	87.3	131.6	41.2
MLP-3	225.58	10.4	0.30	16.4	6.3	256	0.1	23.5	1571	212	30.1	7.4	1.7
	225.13	23.6	12.22	15.3	6.4	948	0.8	46.8	14539	1466	170.6	189.9	19.5
	224.68	25.4	14.78	14.4	6.5	1064	0.1	5.4	11904	1031	206.3	258.1	32.6
	224.23	21.3	0.78	14.2	6.7	1030	ND	ND	4222	333	153.3	191.0	37.5
	223.77	21.2	0.14	13.1	6.8	920	ND	36.8	3382	226	107.7	154.5	35.3
	223.30	22.2	0.01	13.7	6.5	910	21.0	83.3	164	79	86.7	149.5	48.1
MLP-5	224.96	15.2	19.30	19.1	6.1	185	33.1	ND	4077	328	45.0	20.2	2.4
	224.51	23.2	481.00	-	6.4	318	0.1	1.6	9639	601	89.9	103.9	7.1
	224.06	18.2	3.61	15.9	6.4	931	1.1	ND	8539	145	165.4	189.7	23.2
	223.61	17.7	0.92	17.1	6.7	891	0.9	ND	7298	90	126.2	153.1	32.5
	223.13	-	0.76	17.0	7.1	885	ND	2.0	7491	97	130.0	151.5	32.4

^aBulk conductivity data is from the saturated zone. - = No data, ND = below detection limits.

medium grained sands with some gravel overlying a clay aquitard.

3. Methods

[5] In this study, we investigated locations in the aquifer where the source of dissolved hydrocarbon contamination in groundwater is from residual (VRP3/MLP3) and free phase (VRP5/MLP5) hydrocarbon. We compare the contaminated locations to a background location (VRP9/MLP9). The locations investigated are instrumented with vertical resistivity probes (VRPs) for measuring bulk conductivity and multi-level piezometers (MLP's) for sampling groundwater.

[6] *Werkema* [2002] and *Atekwana et al.* [2004a] provide details of the VRP installation. Briefly, the VRPs consist of 3.8 cm inner diameter PVC dry wells with 1.3 cm long stainless steel screws installed at 2.5 cm intervals. The screw heads on the outside of the dry PVC wells serve as electrode contact with the geologic formation and the threaded ends inside the wells enable apparent resistivity measurements. Vertical resistivity profiles at each location were generated by incrementing the Wenner array every 5.0 cm with depth providing a resolution of 5 cm.

[7] The MLPs were constructed of 6.4 mm PVC tubing fitted with a 15 cm screen, and were installed approximately 30 cm apart from the base of the aquifer into the vadose zone using a Geoprobe[®] drill rig. Groundwater from each MLP was pumped to the surface using a peristaltic pump and passed through a flow cell into which a HydroLab[™] down hole Minisonde was immersed. Water temperature, pH, and specific conductance were monitored. After stabilization the readings were recorded and water samples were collected for chemical analyses. Water samples analyzed for total petroleum hydrocarbons (benzene+toluene+ethyl benzene+xylenes) were collected without headspace in pre-acidified 40 ml glass vials fitted with teflon-lined screw caps, cooled to 4°C on ice, and transported to a commercial laboratory for analysis using EPA Method 2020. Water for major anions and cations analyses were filtered in the field using a 0.45 μm pore size in-line filters (Gelman Sciences, Inc.) prior to collection. Water was collected in 250 ml

polyethylene bottles (pre-acidified for cations), cooled to 4°C on ice, and transported to the laboratory. Nitrate, sulfate, calcium, and magnesium were analyzed by ion chromatography. Total iron (Fe(II)) and manganese (Mn(II)) were measured by Inductively Coupled Plasma-Atomic Emission Spectrometer. Water for dissolved inorganic carbon (DIC) determination was collected and analyzed using the technique described by *Atekwana and Krishnamurthy* [1998].

4. Results and Discussions

4.1. Bulk Conductivity Distribution in Contaminated and Uncontaminated Locations

[8] In situ resistivity measurements are presented as conductivity (the inverse of resistivity) to allow for direct comparison with geochemical data. The bulk conductivity values presented in Table 1 are averaged values measured over an interval of 15 cm corresponding to that sampled for groundwater at each MLP, while the bulk conductivity plotted on Figure 1 are the actual values measured at 5 cm resolution. The bulk conductivity was generally greater (10–49 mS/m) at the contaminated locations at VRP3 and VRP5 compared to background values of 4–18 mS/m at VRP9 (Figure 1). Within the contaminated aquifer, peak conductivity values occur about 50 cm below the water table, within a zone 50–100 cm thick (area enclosed in dashed lines; Figure 1). The bulk conductivity is controlled by variations in lithology (grain size), mineralogy of the aquifer, percent water saturation, and the electrolytic properties of the pore fluids. The grain size data (Figure 1) shows vertical variation in grain size. However, the zones of enhanced bulk conductivity for contaminated locations are not entirely related to lithologic variations, especially increase in silt+clay. The positive conductivity bulge at VRP3 begins (~225.3 m) before silt+clay content in the sediments increase, and does not remain constant despite nearly constant values for the silt+clay with depth. Also, at VRP5, the highest bulk conductivity values occur at depths (~224.5 m) with higher sand content compared to lower depths with higher silt + clay (Figure 1).

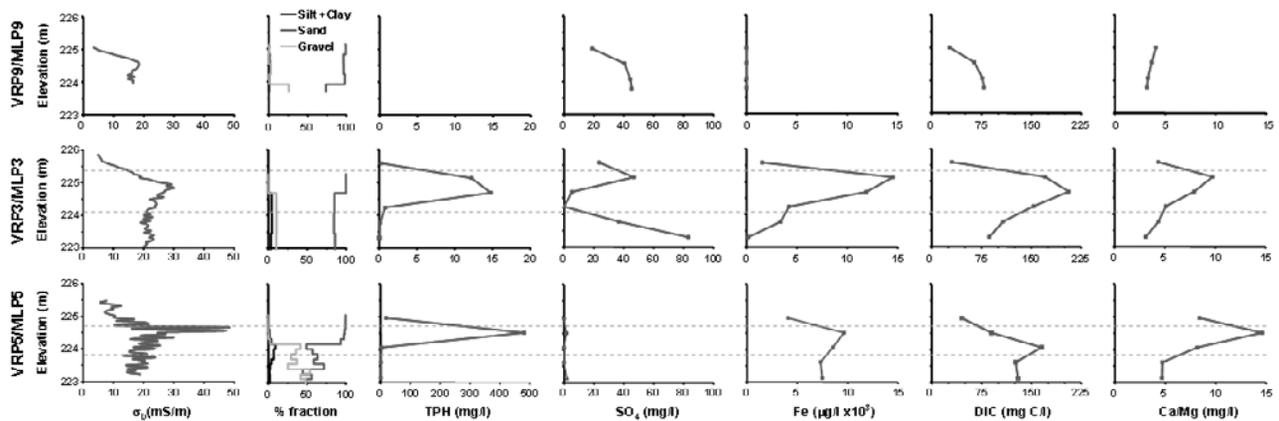


Figure 1. Vertical profiles of bulk conductivity (σ_b) measured at 5 cm intervals, % fraction of silt + clay, sand, and gravel, total petroleum hydrocarbon (TPH), SO_4^{2-} , Fe(II), DIC, and Ca/Mg ratios in groundwater for uncontaminated location (VRP9/MLP9) and contaminated locations (VRP3/MLP3; VRP5/MLP5).

[9] The bulk conductivity values reported are from the saturated zone, thus saturation is not expected to be an important factor. The mineralogy of the aquifer is predominantly quartz with minor carbonates, gypsum, and sodium and calcium plagioclase. Although the true vertical distribution of the mineralogy at sub-cm scale is not known, it is unlikely that this controls the bulk conductivity as evidence for hydrocarbon degradation and enhanced mineral weathering will later show. We believe that the vertical conductivity distribution is due to higher microbial activity stimulated by the presence of hydrocarbon contamination and the accompanying biogeochemical changes resulting from microbial degradation.

4.2. Relationship Between Bulk Conductivity and Enhanced Microbial Activity

4.2.1. Microbial Activity, Terminal Electron Acceptors (TEAs) and CO_2 Production

[10] Enhanced microbial activity in the subsurface requires a carbon source and TEAs that are utilized by microbes to mineralize carbon. Microbes capable of degrading hydrocarbon have been isolated from sediments and groundwater in the study aquifer [Cassidy *et al.*, 2002; Atekwana *et al.*, 2004a]. For carbon source and distribution of TEAs, our results show that maximum concentrations of total petroleum hydrocarbons (TPH) at VRP3 and VRP5 often occurred at depth intervals coincident with peaks in bulk conductivity (Figure 1). Depth intervals with higher TPH show depletion of NO_3^- (Table 1) and SO_4^{2-} (e.g., MLP3; Figure 1). At MLP5 both NO_3^- and SO_4^{2-} were depleted from the aquifer. Zones of lower NO_3^- and SO_4^{2-} result from their utilization during microbial mineralization of the hydrocarbon [e.g., Vroblesky and Chapelle, 1994]. TPH at the base of the aquifer was low and may have limited consumption of NO_3^- and SO_4^{2-} , hence the higher values at the base of the aquifer at MLP3. Since SO_4^{2-} concentrations observed at the base of the aquifer at MLP3 were higher than at the background location (MLP9), this may suggest additional SO_4^{2-} input from the weathering of gypsum.

[11] Fe(II) (Figure 1) and Mn(II) (Table 1) are elevated in contaminated locations compared to the background

location at MLP9 and indicates that both are being released to groundwater through the reduction of Fe(III) and Mn(IV) coating mineral grains in the aquifer [e.g., Jensen *et al.*, 1998]. The zones with higher Fe(II) and Mn(II) are coincident with zones of elevated TPH, depleted NO_3^- and SO_4^{2-} , and higher bulk conductivity (Figure 1). This suggests to us that the bulk conductivity magnitude in contaminated locations is higher due to effects of the redox processes accompanying microbial carbon mineralization.

[12] During microbial mineralization of hydrocarbon the CO_2 produced increases the DIC concentration in groundwater [e.g., Aggarwal and Hinchee, 1991]. DIC was higher in the contaminated groundwater (30–206 mg C/l) compared to background (30–87 mg C/l) and zones with peak concentrations of DIC are the same zones with peak concentrations of TPH and higher bulk conductivity (Figure 1). The increased DIC in the contaminated locations is reflected in pH values that range between 7.1–6.1 compared to 7.3–7.0 for uncontaminated groundwater (Table 1). Thus the presence of an organic source, consumption of NO_3^- and SO_4^{2-} , reduction of Fe(III) and Mn(IV), and the production of CO_2 in the contaminated aquifer suggest higher microbial activity in zones of hydrocarbon contamination.

4.2.2. Evidence for Microbe-Mineral/Rock Interaction Via Mineral Weathering

[13] Higher microbial activity is related to bulk conductivity of sediments through enhanced mineral weathering [Sauck, 2000]. Bacterial mineralization of hydrocarbons augments CO_2 in the aquifer and produces organic acids that increase mineral weathering [e.g., Hiebert and Bennett, 1992]. Based on the aquifer mineralogy, we expect enrichment of Si, Ca, Mg, and Na resulting from enhanced weathering by aggressive CO_2 -rich and organic acids-rich groundwater at contaminated locations [Stumm and Morgan, 1995]. Ionic ratios provide a reasonable approach to evaluate enhanced mineral weathering, rather than the total ion concentrations because water-rock interactions that govern uptake or release of ions in aquifers are not strictly controlled by mineral solubility [Stumm and Morgan, 1995]. The Ca/Mg ratio in the groundwater in the contaminated portions of the aquifer ranged between 3.1–14.6 compared to uncontaminated portions with values of 3.2–4.1

(Figure 1). The higher Ca/Mg ratios in the contaminated groundwater are indicative of higher production of Ca relative to background, and consistent with weathering of feldspars. Depth intervals of higher Ca/Mg ratios are coincident with zones of elevated TPH, Fe(II), Mn(II), and higher bulk conductivity, the same intervals where depletion of NO_3^- and SO_4^{2-} was occurring. Hence, compared to uncontaminated locations, groundwater in contaminated portions of the aquifer show evidence of enhanced mineral weathering related to microbial hydrocarbon mineralization.

4.3. Microbe Induced Mineral Weathering and Implications for Bulk Conductivity

[14] The overall picture of microbial processes presented in this study is similar to results from other hydrocarbon contaminated aquifers [e.g., Cozzarelli *et al.*, 2001; Smith *et al.*, 1991]. Observations of the vertical distribution of bulk conductivity, TPH, NO_3^- , SO_4^{2-} , Fe(II), Mn(II), and the production of CO_2 (DIC) are significant because together they provide evidence for the various redox processes operative in the contaminated aquifer and suggest that redox zones are reflected in the bulk conductivity signature.

[15] The ionic content of groundwater is related to the fluid conductivity because most dissolved solutes in natural waters are ionic and conduct electricity [Stumm and Morgan, 1995]. The specific conductance of groundwater in the uncontaminated aquifer at MLP9 increases continuously with depth. In contrast, the groundwater specific conductance in contaminated locations shows peak values in the same zones as the bulk conductivity (Table 1). Given that groundwater specific conductance is a bulk measurement of the fluid property, its enhancement due to microbial induced mineral weathering can serve as an indirect link between the bulk electrical properties of the sediment and microbial activity.

[16] From the results of this study, we suggest that microbial activity alters the physical environment directly as seen in higher groundwater temperatures in the contaminated locations relative to uncontaminated locations (Table 1). Indirectly, microbial activity enhances mineral weathering which increases the ionic content of groundwater. Thus, the bulk conductivity is an intrinsic property of the sediment media and is ideally suited for discerning changes in bulk water chemistry and physical changes imported to the aquifer from microbial processes.

5. Summary and Conclusions

[17] In-situ high resolution bulk conductivity and geochemical data from closely spaced vertical sampling intervals in a hydrocarbon-contaminated aquifer were used to investigate the relationship between bulk conductivity and microbial activity. We provide the first field evidence linking geophysical parameters to specific redox processes. Major negative and positive peaks in geochemical parameters (e.g., redox sensitive parameters, DIC, and ionic ratios) in contaminated locations are coincident with positive peaks in the vertical profiles of bulk conductivity. No such relationship between bulk conductivity and geochemical parameters was observed at the uncontaminated location. Thus bulk conductivity measurements record an integrated summary of process-driven biogeochemical

changes reflected in the changing pattern of redox zonation. We conclude that zones of higher bulk conductivity in contaminated aquifers are indicative of higher microbial activity stimulated by the presence of excess organic carbon source and available TEAs. Accordingly, zones of higher conductivity may be used to guide sediment and water sampling for microbiological and geochemical investigations such that microbial processes may be more effectively studied.

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