6-1-2004

Effects of Microbial Processes on Electrolytic and Interfacial Electrical Properties of Unconsolidated Sediments

Gamal Z. Abdal Aal

Estella A. Atekwana
Missouri University of Science and Technology, atekwana@mst.edu

Lee D. Slater

Eliot A. Atekwana
Missouri University of Science and Technology

Effects of microbial processes on electrolytic and interfacial electrical properties of unconsolidated sediments

Gamal Z. Abdel Aal,[1] Estella A. Atekwana,[1] Lee D. Slater,[2] and Eliot A. Atekwana[1]

[1]   The effect of microbial processes on electrical properties of unconsolidated sediments was investigated in a laboratory experiment consisting of biotic and abiotic sand columns. The biotic column (nutrient, diesel and bacteria) showed (a) temporal increase in the real, imaginary, and surface conductivity, and (b) temporal decrease in the formation factor. The abiotic columns (nutrient; and nutrient and diesel) showed no significant changes. Increase in microbial population numbers, decrease in organic carbon source, nitrate, and sulfate and increase in dissolved inorganic carbon and fluid conductivity were indicative of microbial activity in the biotic column. We also measure relative increase in the interfacial electrical properties that exceed relative increase in the electrolytic conductivity. Thus changes in the real and imaginary conductivity were induced by microbial processes. These results suggest that interpretation of geoelectrical data from near surface environments should consider effects of microbial processes.   INDEX TERMS: 0614 Electromagnetics: Biological effects; 0925 Exploration Geophysics: Magnetic and electrical methods; 1831 Hydrology: Groundwater quality; 5109 Physical Properties of Rocks: Magnetic and electrical properties. **Citation:**   Abdel Aal, G. Z., E. A. Atekwana, L. D. Slater, and E. A. Atekwana (2004), Effects of microbial processes on electrolytic and interfacial electrical properties of unconsolidated sediments, *Geophys. Res. Lett.*, *31*, L12505, doi:10.1029/2004GL020030.

1.   Introduction

[2]   Replacement of water in sediments by hydrocarbon contaminants (resistivity $\sim 10^6$ ohm.m) results in a concurrent increase in the apparent resistivity of the sediments [*Lien and Enfield*, 1998]. However, some field studies show higher bulk electrical conductivity in unconsolidated aquifers impacted by hydrocarbon [e.g., *Werkema et al.*, 2003]. Over time, biotransformation of hydrocarbons by indigenous microorganisms induces changes in the physicochemical properties of the contaminated environment, potentially impacting their electrical response [*Atekwana et al.*, 2004]. Despite studies that show higher bulk electrical conductivity in hydrocarbon contaminated sediments, it is not entirely clear how the electrical properties of sediments are changed due to microbial processes. *Sauck* [2000] has suggested that increase in electrical conduction in hydrocarbon contaminated aquifers is due to increases in total dissolved solids in pore water resulting from interaction between by-products of hydrocarbon degradation and aquifer minerals. In addition to increase in electrolytic properties of aquifer pore fluids, microbial-mineral interactions may induce changes in surface chemistry at solid-fluid interfaces. Direct current (dc) resistivity methods are responsive to both electrolyte and solid-fluid interface chemistry. While diagnostic, dc resistivity does not differentiate between the relative contributions of electrolytic vs. interface conductivity to the enhanced conductivity observed for hydrocarbon contaminated sediments.

[3]   The induced polarization (IP) method is an extension of the dc-resistivity method. The sensitivity of IP to changes in surface chemical properties of rocks and soils [e.g., *Lesmes and Frye*, 2001] makes IP suitable for investigating effects of bio-physicochemical changes on electrical properties of sediments. The objective of this study was to investigate effects of microbial processes on low frequency electrical properties of unconsolidated sediments. Results from this study provide insights into how microbial activity impacts both electrolytic and interfacial conductivity of sediments.

2.   Materials and Methods

2.1.   Column Construction and Setup

[4]   The experimental columns were 50 cm long and constructed of 7.6 cm inner diameter polyvinyl chloride pipe (Figure 1). A fluid sampling port was installed in each column. Two coiled silver current injection electrodes were placed in each column 20 cm apart. Ag-AgCl potential electrodes were located between the current electrodes. Columns were filled with fine-grained (0.45–0.65 mm) sand collected from a field site in Michigan, USA. The sands were sterilized by autoclaving three times at $120°C$ for 30 minutes prior to use in the experiment. Dissolved diesel was used as an organic source and was prepared by adding 40 ml of diesel to 1 L of deionized (DI) water, shaken at room temperature ($\sim 23°C$) for 72 hours after which the undissolved diesel was decanted. The total hydrocarbon (benzene + toluene + ethylbenzene + xylene (BTEX)) dissolved in DI water was 0.29 mg/l. The nutrient used for the experiment consisted of 25% Bushnell Hass (BH) medium (Becton Dickinson, Detroit, MI). Two stock solutions of 25% BH medium were prepared using the DI water with dissolved diesel and another with sterilized DI water.

[5]   Three experimental columns were prepared with the following treatments: 1) a biotic column with 25% BH medium + diesel + bacteria, 2) an abiotic column with 25% BH medium (uncontaminated), and 3) an abiotic column with 25% BH medium + diesel (contaminated). Indigenous bacteria were cultured from diesel contaminated sediments from the same field site as the experimental sands. The bacteria was mixed with the BH + diesel solution and pumped into the biotic column. To ensure no microbial

---

[1]Department of Geological Sciences and Engineering, University of Missouri-Rolla, Rolla, Missouri, USA.

[2]Department of Earth and Environmental Sciences, Rutgers University, Newark, New Jersey, USA.
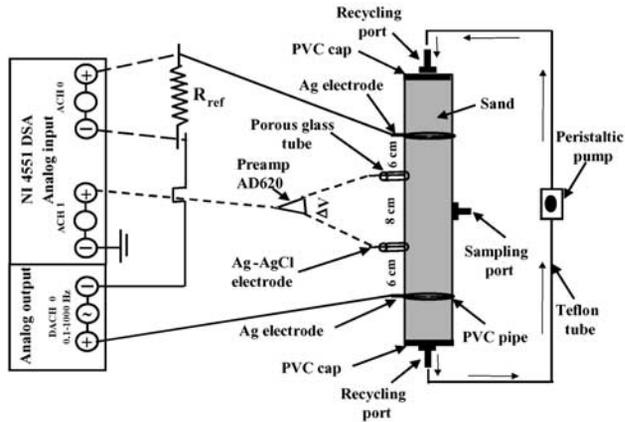
Figure 1. Schematic of column setup and instrumentation used in low frequency electrical measurements.

growth in the abiotic columns, HgCl was added to the stock solution of 25% BH medium and 25% BH medium + diesel. The columns were kept in a vented hood at 22 to 25°C. A peristaltic pump was used to circulate and homogenize fluids in the columns periodically, and prior to sampling and electrical measurements.

2.2. Sampling and Analyses

[6] Fluids (~45 ml) were periodically withdrawn from each column for biological and chemical analyses. After sampling, fluids from the appropriate stock solution were injected into the columns to maintain full saturation. Microbial population growth was measured from an aliquot of the fluid using the Most Probable Number (MPN) technique [*Salama et al.*, 1978]. Fluid conductivity and pH were measured by microelectrodes immediately after sampling. BTEX was measured by gas chromatography [*Loffe and Vitenberg*, 1984]. Nitrate, sulfate and calcium (Ca) were determined by ion chromatography. Dissolved inorganic carbon (DIC) was measured by the technique of *Atekwana and Krishnamurthy* [1998].

2.3. Low Frequency Electrical Measurements

[7] Induced polarization measurements were made using a National Instruments NI 4551 dynamic signal analyzer (Figure 1) with a current density below 0.1 A/m^2 [*Slater and Lesmes*, 2002]. Phase shift (φ) between current stimulus-voltage signal and conductivity magnitude ($|\sigma|$) were measured at forty frequencies and equal logarithmic intervals between 0.1 and 1000 Hz. Measurements were made biweekly for the first 20 weeks and monthly for the duration of the experiment. The real (σ') and imaginary (σ'') components of the complex surface conductivity were calculated as follows:

$$\sigma' = |\sigma| \cos \varphi \qquad (1)$$

$$\sigma'' = |\sigma| \sin \varphi \qquad (2)$$

[8] The real conductivity is an energy loss term that contains an electrolytic (σ_{el}) and interfacial (σ'_{surf}) component [e.g., *Lesmes and Frye*, 2001]

$$\sigma' = \sigma_{el} + \sigma'_{surf} = \frac{\sigma_w}{F} + \sigma'_{surf} \qquad (3)$$

where σ_w is the fluid conductivity and F is the sediment formation factor. The σ'_{surf} results from ion migration within the electrical double layer at grain-fluid interfaces and increases with increase in surface area, surface charge density, and surface ionic mobility [*Revil and Glover*, 1998]. The F for the sands was measured from σ' as a function of σ_w (0.02–0.32 S/m for NaCl solutions) at the beginning and end of the experiment. At high electrolyte concentrations, the contribution of σ'_{surf} to σ' is insignificant in the sands studied here, and F is derived from the gradient of σ' vs. σ_w (mean R^2 > 0.98).

[9] Imaginary conductivity is an energy storage or polarization term, which at low frequencies (<1000 Hz) is an interfacial phenomenon occurring at grain-fluid surfaces in saturated porous media [e.g., *Olhoeft*, 1985]. Imaginary conductivity is also sensitive to physicochemical properties at grain-fluid interfaces [*Slater and Lesmes*, 2002] and is linearly related to σ'_{surf} [e.g., *Schön*, 1996]. Consequently, σ'' shows an approximately linear dependence on surface area to pore volume ratio [e.g., *Slater and Glaser*, 2003] and sensitivity to surface chemistry that probably reflects the competing effects of surface charge density and surface ionic mobility [e.g., *Lesmes and Frye*, 2001].

3. Results

3.1. Microbial Population Growth and Pore Fluid Chemistry

[10] The initial biological, chemical, and electrical measurements are shown in Table 1. Temporal change in MPN, BTEX, nitrate, sulfate, DIC, pH, Ca, and σ_w are shown as percent change relative to values measured at the start of the experiment (Figure 2). The biotic column shows temporal increase in microbial population numbers, which was concurrent with decrease in BTEX, nitrate, and sulfate (Figure 2). No significant changes in the above parameters are observed in the abiotic columns. Further, the biotic column shows increase in DIC, decrease in pH, and increase in Ca and σ_w compared to minimal changes in the abiotic columns (Figure 2). Changes in biological and chemical parameters in the biotic column increase rapidly from the start of the experiment, becoming more asymptotic after 24 weeks. Periodic, low magnitude increases and decreases in nitrate, sulfate, and pH in the contaminated abiotic column (Figure 2) are probably experimental artifacts related to replacement of fluid in the column after sampling.

3.2. Low Frequency Electrical Measurements

[11] Temporal percent change in temperature corrected σ' and σ'' at 1 Hz are presented in Figure 3. We show data at 1 Hz here as it is close to the typical frequency used in field IP measurements. Similar trends are observed at all other measured frequencies. There is concurrent increase in σ' and σ'' in the biotic column and little change in the abiotic columns (Figure 3). The trend of the σ' response is similar to that observed in some biological and chemical parameters (e.g., MPN and Ca), showing rapid changes in the early stages (<20 weeks) of the experiment. This indicates sensitivity of σ' to the electrolyte composition. In contrast, σ'' shows small increases during the first 14 weeks, increasing more rapidly thereafter (Figure 3). Periodic small fluctuations in the σ' and σ'' are evident in the contaminated abiotic

Table 1. Results of Initial Biological, Chemical and Electrical Measurements (1Hz) for Biotic and Abiotic Sand Columns: MPN (Most Probable Number); BTEX (Benzene, Toluene, Ethylbenzene, Xylene); DIC (Dissolved Inorganic Carbon); σ_w (Fluid Conductivity); σ' (Real Conductivity); σ'' (Imaginary Conductivity); and σ'_{surf} (Surface Conductivity)

Measured Parameter	Biotic Column Contaminated	Abiotic Column Contaminated	Abiotic Column Uncontaminated
MPN/ml	220	30	10
BTEX (mg/l)	0.29	0.28	0
NO_3 (mg/l)	56.50	43.49	41.46
SO_4 (mg/l)	72.50	75.98	86.20
DIC (mg C/l)	17.04	15.96	5.56
pH	6.89	6.86	6.99
Ca (mg/l)	16.42	16.80	20.45
σ_w (S/m)	4.89×10^{-2}	1.05×10^{-1}	1.13×10^{-1}
σ' (S/m)	9.27×10^{-3}	1.13×10^{-2}	1.63×10^{-2}
σ'' (S/m)	7.45×10^{-6}	7.03×10^{-6}	1.24×10^{-5}
σ'_{surf} (S/m)	2.92×10^{-3}	1.69×10^{-3}	1.66×10^{-3}

Figure 2. Temporal percent change in microbial population numbers (MPN), benzene + toluene + ethylbenzene + xylene (BTEX), nitrate, sulfate, dissolved inorganic carbon (DIC), pH, calcium, and fluid conductivity from pore water from biotic and abiotic sand columns.
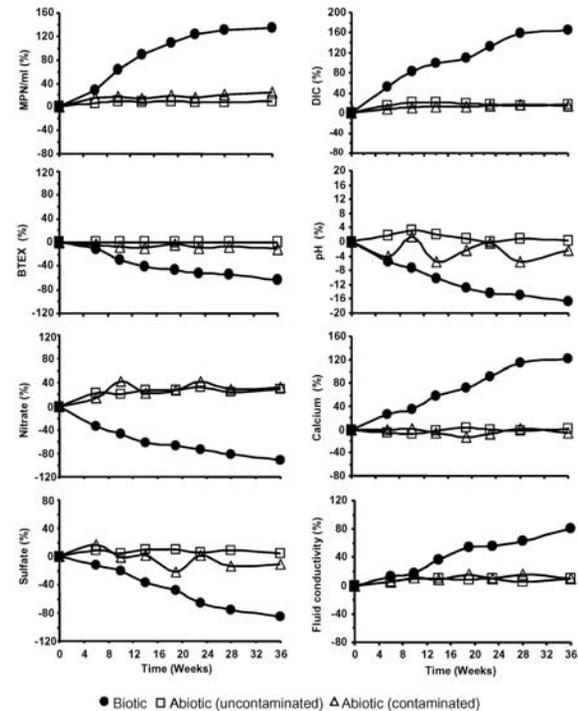
column and likely attributable to the removal/addition of fluid after sampling.

[12] The formation factor for the sands at the beginning of the experiment was 7.7 and decreased in all columns (biotic (4.5); abiotic contaminated (6.1); and abiotic uncontaminated (6.8)). Further, σ'_{surf} (based on equation (3)) for the biotic column increased to 7.68×10^{-3} S/m, while there was no significant change in the abiotic columns (Table 1).

4. Discussion and Conclusions

[13] The results of this study suggest that microbial processes alter the electrical properties of unconsolidated sediments rich in organic carbon. Lithologic variability between columns and variable water saturation are not responsible for the differences in temporal electrical changes observed between biotic and abiotic columns, since all columns were fully saturated and the sands were similar and of uniform size. We show temporal increase in σ' and σ'' in the biotic column (Figure 3), which we attribute to microbial processes. Concomitant increase in MPN, decrease in nitrate, sulfate, BTEX, and pH and increase in DIC, Ca and σ_w are consistent with microbial activity in the biotic column (Figure 2). In the biotic column, the relative increase in σ' (100%) exceeded the relative increase in σ_w (80%). This is consistent with the increase in σ'_{surf} for the sediments in the biotic column. The 120% relative increase in σ'', exceeding the 100% relative increase in σ', demonstrates that interfacial electrical properties are modified due to microbial activity.

[14] The formation factor is related to petrophysical properties (porosity, tortuosity, sample packing) and determines the electrolytic conductivity of sediments and rocks [*Archie*, 1942]. The larger decrease in F in the biotic column (58%) indicates either increase in porosity or decrease in tortuosity of electrolytic current flow path. During microbial mineralization of organic compounds, organic acids produced as metabolites and carbonic acids from degradation enhance mineral weathering [*Bennett et al.*, 1996]. Decrease in pH and increase in Ca (Figure 2) provide strong evidence for mineral weathering. It is possible that this enhanced mineral weathering resulted in an increase in porosity, causing the decrease in F for the biotic column. The electrolytic conduc-

tivity in the columns is determined by σ_w and F. Variation in σ_w is primarily responsible for the observed variation in the measured σ'. Enhanced mineral weathering will release ions into solution, increasing σ_w (Figure 2). Ca from mineral weathering is positively correlated to σ_w ($R^2 = 0.95$). The increase in σ' in large part derives from increase in σ_{el} associated with increasing σ_w during mineral weathering. Decrease in F, as observed in the biotic column also contribute to increase in σ_{el} and hence σ'.

[15] Interfacial electrical properties (σ'_{surf} and σ'') are determined by mineral grain surface area, surface charge density, ionic mobility, and interfacial tortuosity [*Börner et al.*, 1996]. The increase in interfacial conductivity and polarization observed in this experiment may be associated with the large surface area ($\sim 30-100$ m^2/g) of bacteria [*Van Der Wal et al.*, 1997a] and wall counterion charge density ($\sim 0.5-1.0$ Coulombs/m^2) of bacterial cells [*Van Der Wal et*
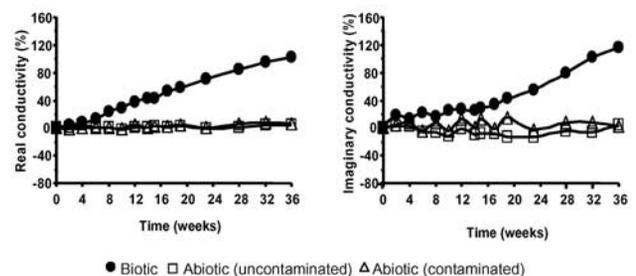
Figure 3. Temporal percent change in real and imaginary conductivity in biotic and abiotic sand columns.

al., 1997b]. Surface area exerts a primary control on interfacial electrical properties [e.g., *Revil and Glover*, 1998], with surface charge density and surface ionic mobility being second order effects [e.g., *Lesmes and Frye*, 2001]. The large surface area of clays is responsible for enhanced IP effect observed in clay containing materials [e.g., *Garrouch and Sharma*, 1994]. Bacterial surface areas are estimated to equal or exceed those of kaolinite (10–22 m^2/g) [*Bickmore et al.*, 2002]. Therefore, we speculate that the increase in surface area due to microbial growth (Figure 2) and attachment to mineral surfaces contributed to and enhanced the surface area of mineral grains. This, coupled with increases in surface charge density at the mineral grain-electrolyte interface (due to enhanced mineral weathering), enhanced electrical double layer polarization and caused temporal increase in σ'_{surf} and σ''. Increasing the ionic strength of the bulk solution increases the likelihood of bacteria attachment to mineral surfaces [*Newby et al.*, 2000]. Thus the time lag (0–14 weeks) observed in the σ'' response (Figure 2) may perhaps relate to the time required for microbial colonization of mineral surfaces, such that the interfacial conductivity measured with IP is impacted. It is conceivable that the IP response due to microbial activity is not impacted until sufficient biofilms form on mineral surfaces.

[16] An alternative mechanism for the observed σ'' behavior might relate to redox chemistry associated with microbial activity. Induced polarization is enhanced when metals are present in a soil; this polarization enhancement is generally attributed to migration of redox active ions to and from mineral surfaces, where electron transfer accompanies the transition from electrolytic to electronic conduction (see *Olhoeft* [1985] for review). *Naudet et al.* [2003] suggest the possibility of redox-driven energy transfer between electrolytic current flow and electronic conduction in biofilms. Such a process could conceivably generate an IP response. We are unable to quantify the direct relationship between different redox process in our experiment and electrical properties in this dataset. Further studies are required to quantify how microbial induced redox processes may contribute to changes in electrical properties.

[17] The results presented in this study are consistent with results of low frequency electrical measurements made on sediments from a hydrocarbon contaminated site undergoing intrinsic bioremediation [*Abdel Aal et al.*, 2003]. In the *Abdel Aal et al.* [2003] study, contaminated samples showed higher σ'' magnitudes relative to uncontaminated samples, with the highest σ'' magnitudes measured for samples within zones where peak microbial populations and activity are known to occur [*Atekwana et al.*, 2004]. We conclude that microbial processes play a significant role in altering both electrolytic and interfacial geoelectrical properties.

References

Abdel Aal, G. Z., E. A. Atekwana, L. D. Slater, and C. Ulrich (2003), Induced polarization (IP) measurements of soils from an aged hydrocarbon contaminated site, paper presented at Symposium on the Application of Geophysics to Engineering and Environmental Problems, Environ. and Eng. Geophys. Soc., San Antonio, Tex., April 6–10, 190–202.

Archie, G. E. (1942), The electrical resistivity log as an aid in determining some reservoir characteristics, *T. Am. Inst. Min. Metall. Pet. Eng.*, 146, 54–62.

Atekwana, E. A., and R. V. Krishnamurthy (1998), Seasonal variations of dissolved inorganic carbon and $\delta^{13}C$ of surface waters: Application of a modified gas evolution technique, *J. Hydrol.*, 205, 265–278.

Atekwana, E. A., D. D. Werkema, J. W. Duris, S. Rossbach, E. A. Atekwana, W. A. Sauck, D. P. Cassidy, J. Means, and F. D. Legall (2004), In-situ apparent conductivity measurements and microbial population distribution at a hydrocarbon contaminated site, *Geophysics*, 69, 56–63.

Bennett, P. C., F. K. Hiebert, and W. J. Choi (1996), Microbial colonization and weathering of silicates in a petroleum-contaminated groundwater, *Chem. Geol.*, 132, 45–53.

Bickmore, B. R., K. L. Nagy, P. E. Sandlin, and T. S. Crater (2002), Quantifying surface areas of clays by atomic force microscopy, *Am. Mineral.*, 87, 780–783.

Börner, F. D., J. R. Schopper, and A. Weller (1996), Evaluation of transport and storage properties in the soil and groundwater zone from induced polarization measurements, *Geophys. Prospect.*, 44, 583–601.

Garrouch, A. A., and M. M. Sharma (1994), The influence of clay content, salinity, stress and wettability on the dielectric properties of brine-saturated rocks: 10 Hz to 10 MHz, *Geophysics*, 59, 909–917.

Lesmes, D. P., and K. M. Frye (2001), Influence of pore fluid chemistry on the complex conductivity and induced polarization responses of Berea sandstone, *J. Geophys. Res.*, 106, 4079–4090.

Lien, B. K., and C. G. Enfield (1998), Delineation of subsurface hydrocarbon contaminated distribution using a direct push resistivity method, *J. Environ. Eng. Geophys.*, 2, 173–179.

Ioffe, B. V., and A. G. Vitenberg (1984), *Headspace Analysis and Related Methods in Gas Chromatography*, 304 pp., John Wiley, Hoboken, N. J.

Naudet, V., A. Revil, J. Y. Bottero, and P. Begassat (2003), Relationship between self-potential (SP) signals and redox conditions in contaminated groundwater, *Geophys. Res. Lett.*, 30(21), 2091, doi:10.1029/2003GL018096.

Newby, D. T., I. L. Pepper, and R. M. Maier (2000), Microbial transport, in *Enironmental Microbiology*, edited by R. M. Maier et al., 585 pp., Academic, San Diego, Calif.

Olhoeft, G. R. (1985), Low frequency electrical properties, *Geophysics*, 50, 2492–2503.

Revil, A., and P. W. J. Glover (1998), Nature of surface electrical conductivity in natural sands, sandstones and clays, *Geophys. Res. Lett.*, 25, 691–694.

Salama, I. A., G. G. Koch, and H. D. Tolley (1978), On the estimation of the most probable number in a serial dilution technique, *Commun. Stat.-Theorm.*, 1267–1281.

Sauck, W. A. (2000), A conceptual model for the geoelectrical response of LNAPL plumes in granular sediments, *J. Appl. Geophys.*, 44, 151–165.

Schön, J. H. (1996), *Physical Properties of Rocks—Fundamentals and Principles of Petrophysics, Handbook of Geophysical Exploration: Seismic Exploration*, vol. 18, 583 pp., Oxford, UK; Tarrytown, N. Y., Pergamon.

Slater, L., and D. Glaser (2003), Controls on induced polarization in sandy unconsolidated sediments and application to aquifer characterization, *Geophysics*, 68, 1547–1558.

Slater, L., and D. P. Lesmes (2002), IP interpretation in environmental investigations, *Geophysics*, 67, 77–88.

Van Der Wal, A., M. Minor, W. Norde, A. J. B. Zehnder, and J. Lyklema (1997a), Conductivity and dielectric dispersion of gram-positive bacterial cells, *J. Colloid. Interface Sci.*, 186, 71–79.

Van Der Wal, A., W. Norde, A. J. B. Zehdner, and J. Lylkema (1997b), Determination of the total charge in the cell walls of Gram-positive bacteria, *Colloid. Surface. B.*, 9, 81–100.

Werkema, D. D., E. A. Atekwana, A. Endres, W. A. Sauck, and D. P. Cassidy (2003), Investigating the geoelectrical response of hydrocarbon contamination undergoing biodegradation, *Geophys. Res. Lett.*, 30(12), 1647, doi:10.1029/2003GL017346.

———————————

G. Z. Abdel Aal, E. A. Atekwana, and E. A. Atekwana, Department of Geological Sciences and Engineering, University of Missouri-Rolla, 125 McNutt Hall, 1870 Minor Circle, Rolla, MO 65409, USA. (atekwana@umr.edu)

L. D. Slater, Department of Earth and Environmental Sciences, Rutgers University, 195 College Ave., New Brunswick, NJ 07102, USA.