



# BROADBAND GEOELECTRICAL SIGNATURES OF WATER-ETHANOL SOLUTIONS IN OTTAWA SAND

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## ABSTRACT

Ethanol has fast become the most widely used and distributed biofuel since its introduction as a fuel oxygenate to replace MTBE in gasoline and the emergence of "Flex Fuel" vehicles (Figure 1). Where ethanol is included in gasoline as a fuel oxygenate, subsurface releases have resulted in increased solubility and the transport of harmful BTEX compounds. In the case of "neat ethanol" (pure or slightly denatured) spills, large quantities of ethanol may initially reduce microbial populations, exacerbate pre-existing subsurface contamination in soil and groundwater, and potentially form explosive conditions through methanogenesis. There is a growing need for rapid assessment of subsurface releases to allow for quick remedial action following such releases. Surface and borehole geophysical measurements could provide rapid results to assess the extent of a release; however, little work has been done to understand the signature of ethanol in the subsurface. We measure the broadband geoelectrical signature of various ethanol-water mixtures in a matrix of Ottawa sand to determine select geoelectrical parameters which may be applied in field scale studies. In the lower frequency range (Hz to kHz), resistivity and induced polarization parameters were measured and compared to the well known Cole-Cole model. At high frequencies (MHz to GHz), the dielectric constant of several ethanol-water solutions was measured. We use the empirical complex refractive index model (CRIM) to compare measured and predicted values of the dielectric constant. The low frequency electrical resistivity ranged from approximately 570 ohm-m (water in sand) to approximately 2300 ohm-m (pure ethanol in sand). The dielectric constant ranged from approximately 17.8 (water in sand) to 9.2 (pure ethanol in sand). These initial results suggest that geoelectrical field measurements would be useful to delineate an ethanol release in the environment soon after a spill under suitable site conditions. Based on the propensity of ethanol for biodegradation more work is needed to assess the temporal evolution of an ethanol spill in geologically complex environments.

## OBJECTIVE

The goal is to investigate the broadband geoelectrical signatures of ethanol-water solutions in a sand matrix to determine whether geophysical techniques can be used to observe the distribution of ethanol in the subsurface.

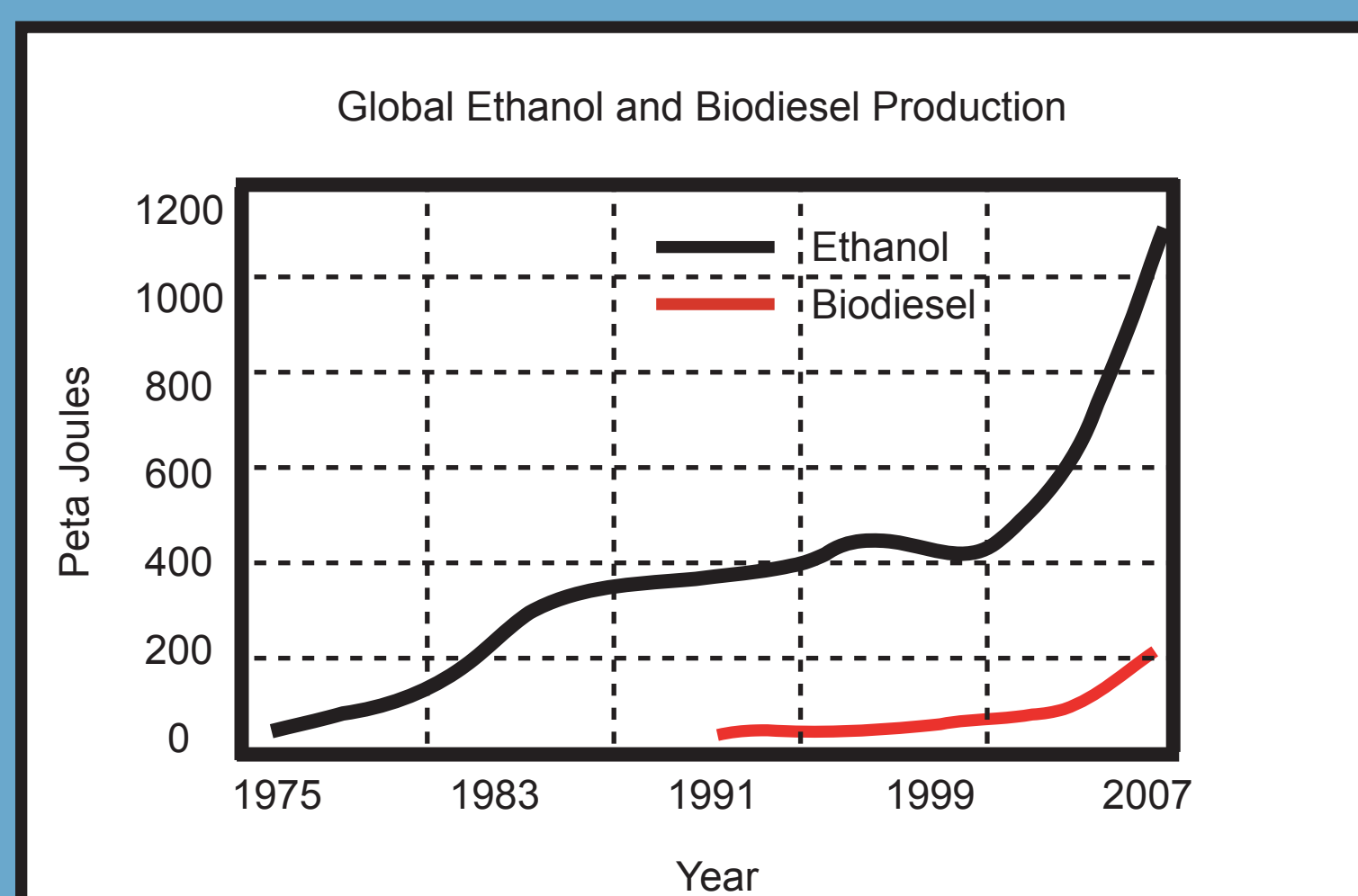


Figure 1: Ethanol production has increased substantially in the last 35 years.

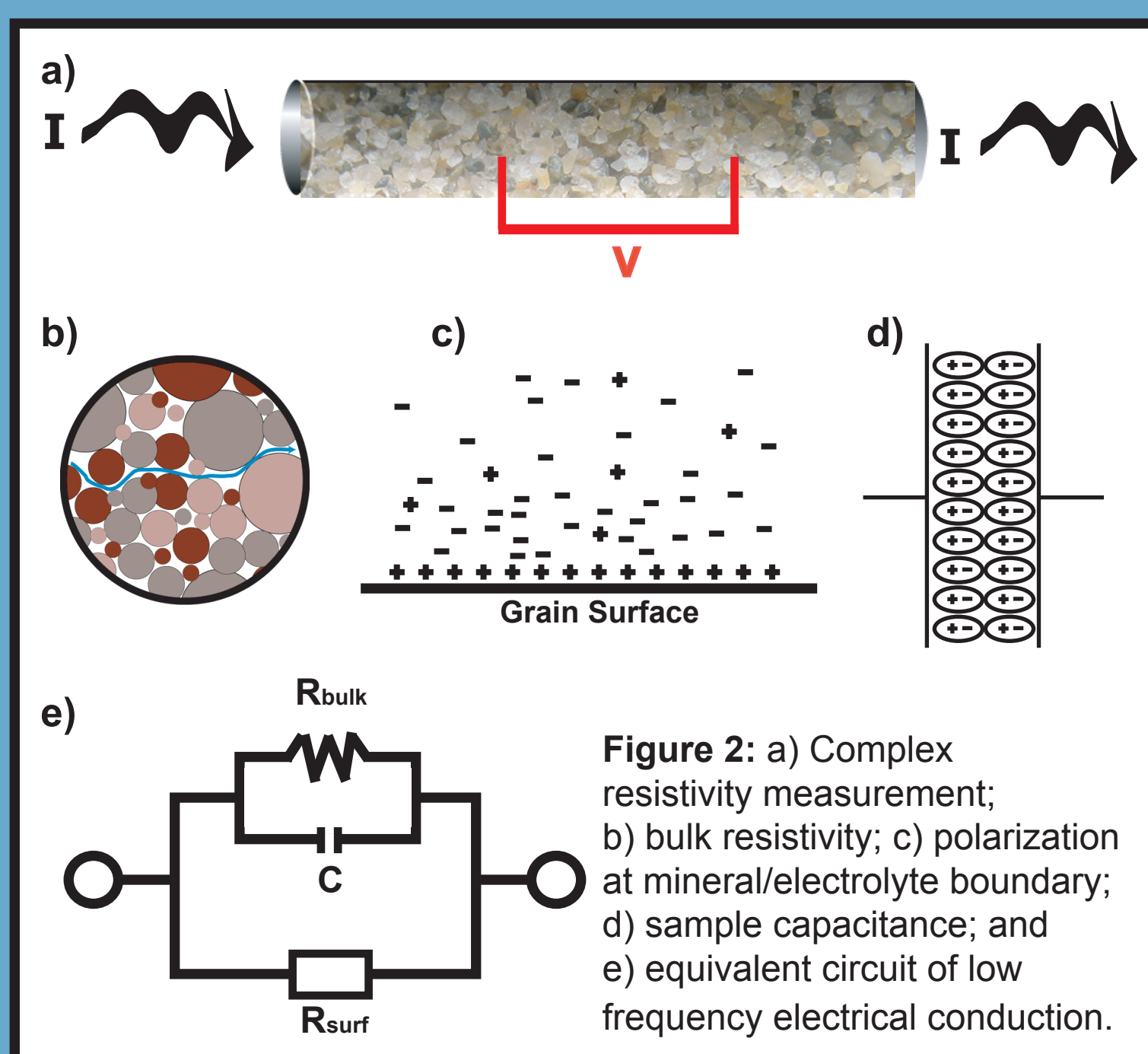


Figure 2: a) Complex resistivity measurement; b) bulk resistivity; c) polarization at mineral/electrolyte boundary; d) sample capacitance; and e) equivalent circuit of low frequency electrical conduction.

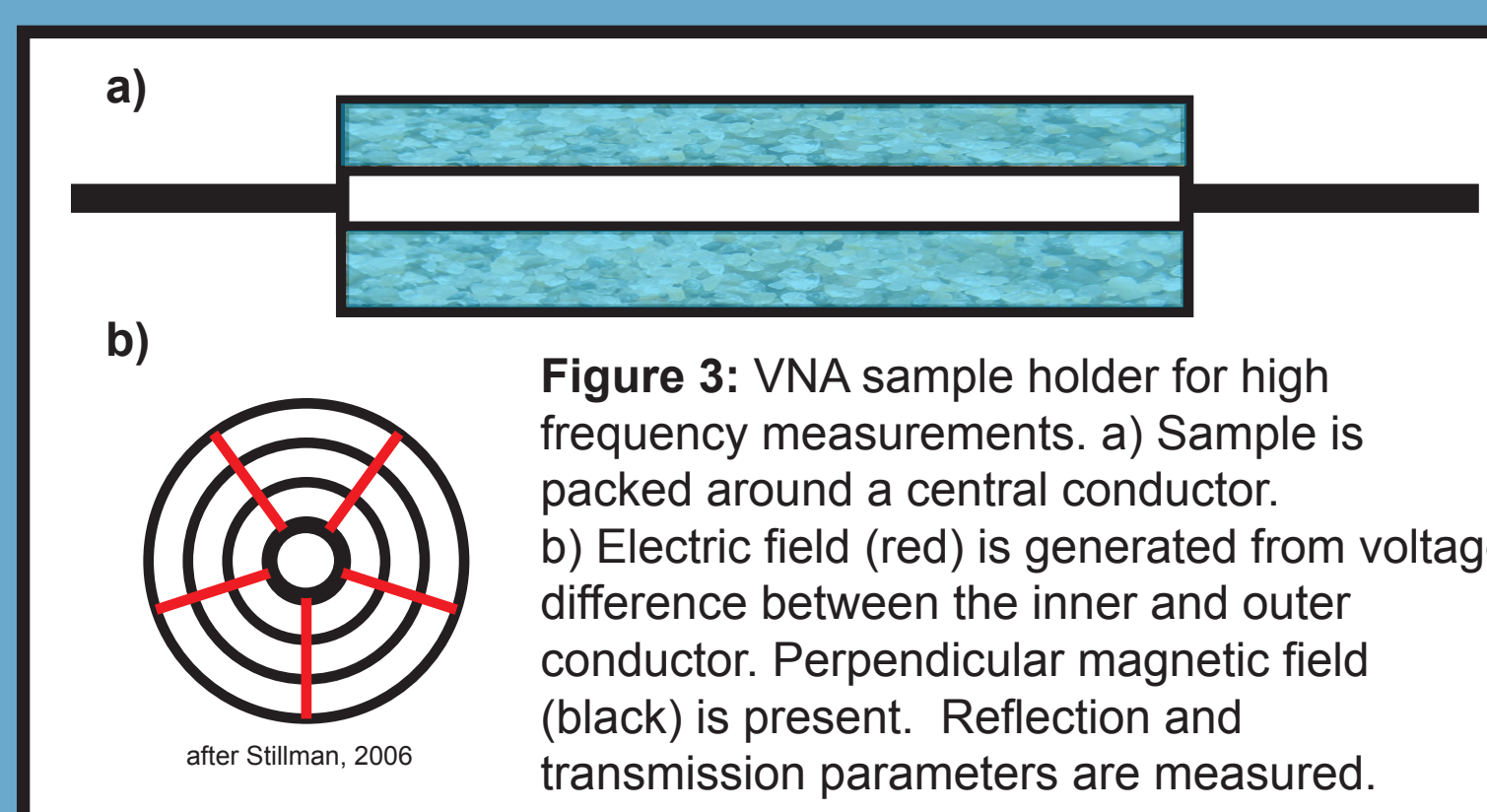


Figure 3: VNA sample holder for high frequency measurements. a) Sample is packed around a central conductor. b) Electric field (red) is generated from voltage difference between the inner and outer conductor. Perpendicular magnetic field (black) is present. Reflection and transmission parameters are measured.

## INTRODUCTION

- Ethanol:**
  - Replaces methyl tertiary-butyl ether (MTBE) as a fuel oxygenate in reformulated gasoline (up to 10 percent by volume in gasoline).
- "Flex Fuel" vehicles use E85 (85 percent ethanol, 15 percent gasoline).
- It is not considered to be harmful to human health, but it has secondary environmental effects.
- Many studies focus on groundwater impact.
- Decreases the natural attenuation of benzene, toluene, and xylenes (BTEX) because it is preferentially biodegraded.
- Cosolvency effects on existing non-aqueous phase liquids (NAPL) allows for increased transport and partitioning of harmful and otherwise immobile chemicals at the water table (Stafford et al., 2009).
- Potentially explosive conditions due to methanogenesis in the absence of aerobic microbial degradation.
- Assessment techniques are needed to determine the extent of subsurface release since ethanol exacerbates existing environmental conditions.

## METHODS

### Complex Resistivity (CR) - low frequency range

- Instrument: HP3325A
- At varying frequencies, electrical resistivity is measured and phase is measured.
- The real portion represents the bulk resistivity, which includes electrolytic conduction (or resistance) mechanisms.
- The imaginary component represents conduction along the solid surfaces and electronic double layer (Kemna, 2005), (Figure 2).
- Here, we measure the magnitude and phase of the conductivity response, which is real and imaginary components in polar form (Figure 4).

### CR(mHz-kHz)

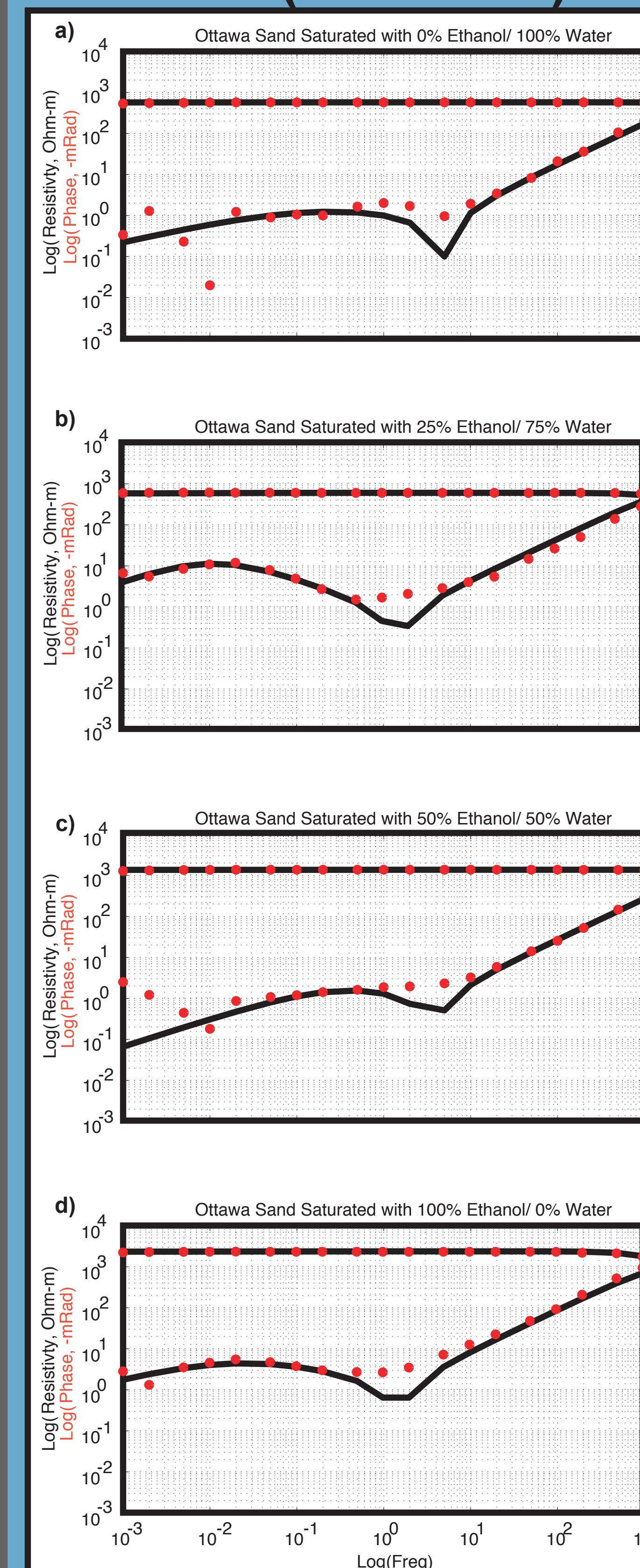


Figure 4: Experimentally measured resistivity and phase (red) plotted with empirical Cole-Cole model with two dispersions (black).

### Dielectric displacement - high frequency range

- Instrument: HP8753E Vector Network Analyzer
- Current is propagated by electric displacement mechanisms in poor conductors at high frequencies.
- Propagation occurs when a time varying electric field is applied and polarizes a material through induced magnetic fields and resultant secondary electric fields (Annan, 2005) (Figure 3).
- Resultant measurement is the dielectric constant and the loss tangent (measure of dissipation in electromagnetic wave propagation) (Figure 5).

### VNA(MHz-GHz)

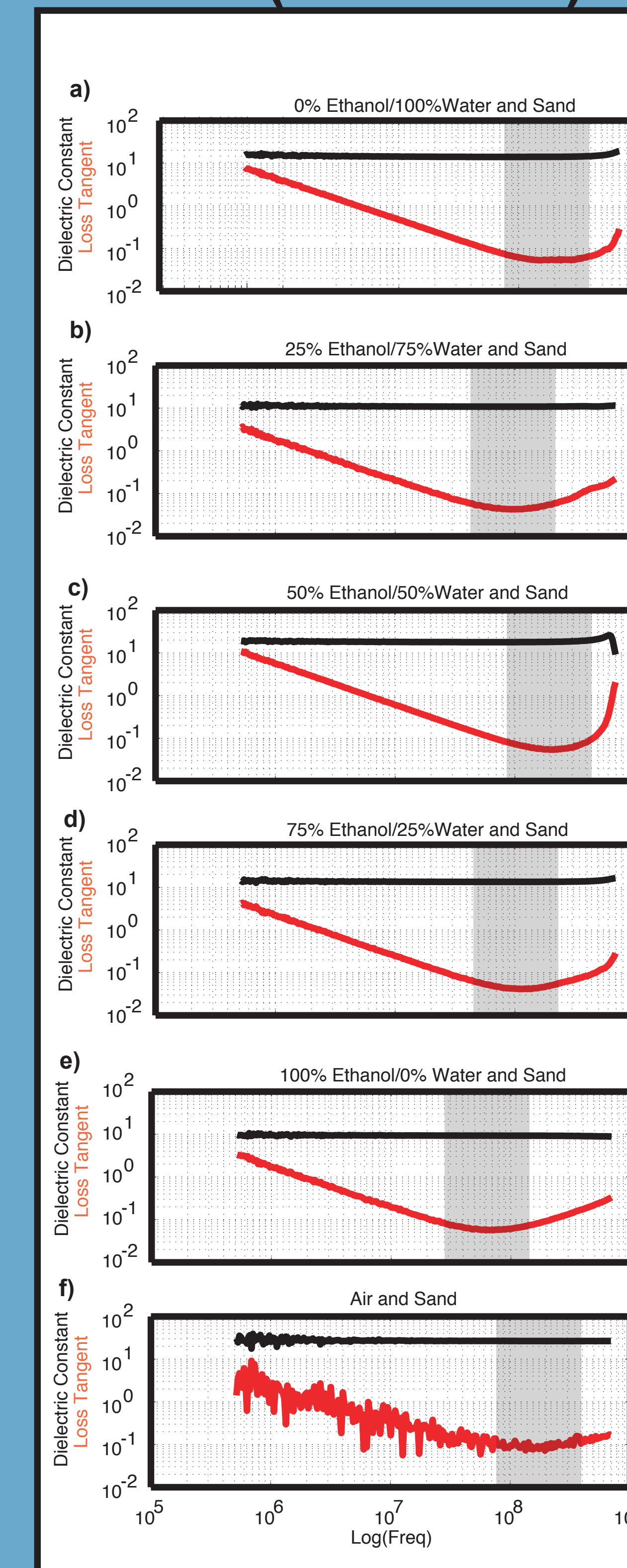


Figure 5: Dielectric constant (black) and loss tangent (red) as a function of frequency. Gray area indicates region where dielectric constant was chosen for further comparison (low loss).

### Modeling - to interpret the empirical data

- Low frequency range: the Cole-Cole model**
  - Induced polarization parameters calculated by effectively treating the sample as an equivalent circuit consisting of a resistor in parallel with a capacitor (Lesmes and Frye, 2001).
  - USGS Cole-Cole Code (Campbell and Horton, 2000) for two dispersions (Figure 4, Table 1).

### High frequency range: the Complex Refractive Index Model (CRIM)

- A simple mixing model is used to determine equivalent dielectric constant of a sample by relating its constituent parts (Figure 6).

### Forward Modeling - to determine the field scale applicability

- DC Electrical Resistivity (Figure 9):
  - Surface survey: 48 electrodes, spaced at 0.5 m
  - Borehole survey: 3 boreholes, 15 electrodes each, 0.5 m spacing
  - 5% Gaussian noise added to measurements prior to inversion
  - Inversion with R2 (Binley and Kemna, 2005)
- GPR modeling (Figure 8):
  - Surface reflection survey with 50 MHz EM wave
  - 2D FDTD GPR code (Irving and Knight, 2005)

## CRIM Model

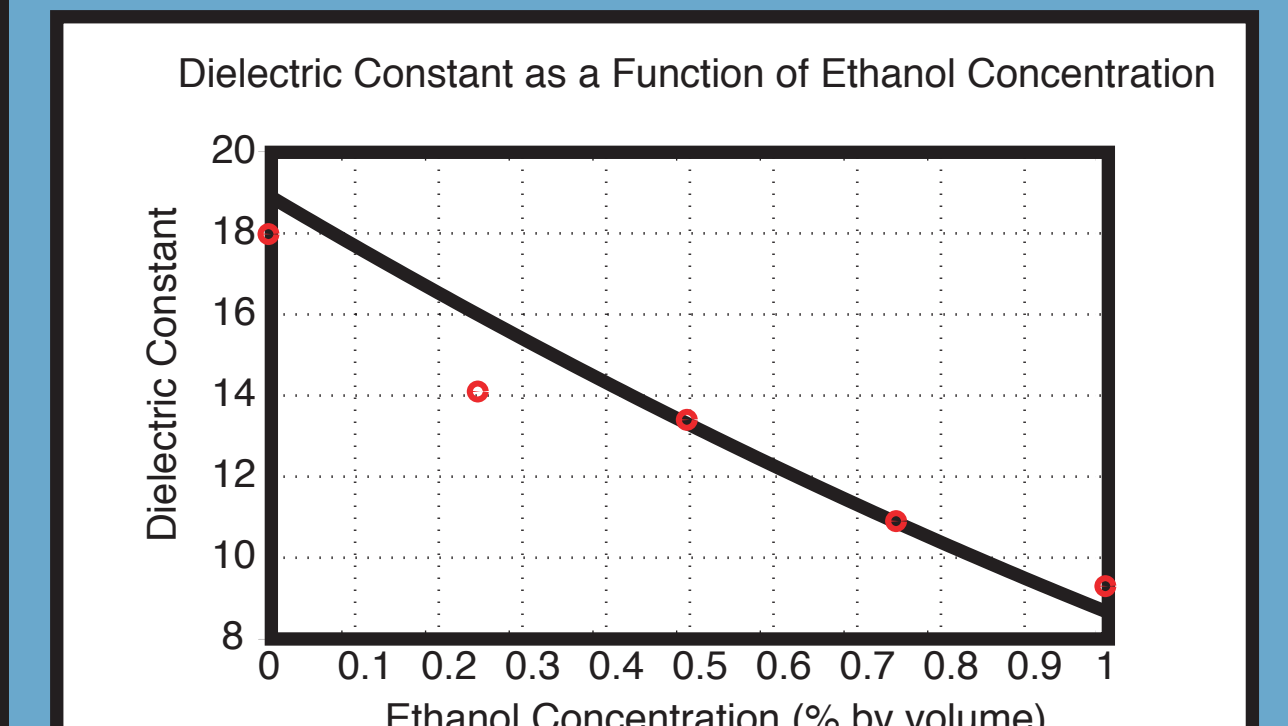


Figure 6: CRIM model (black) compared to experimental data (red).

## EM Wave Velocity

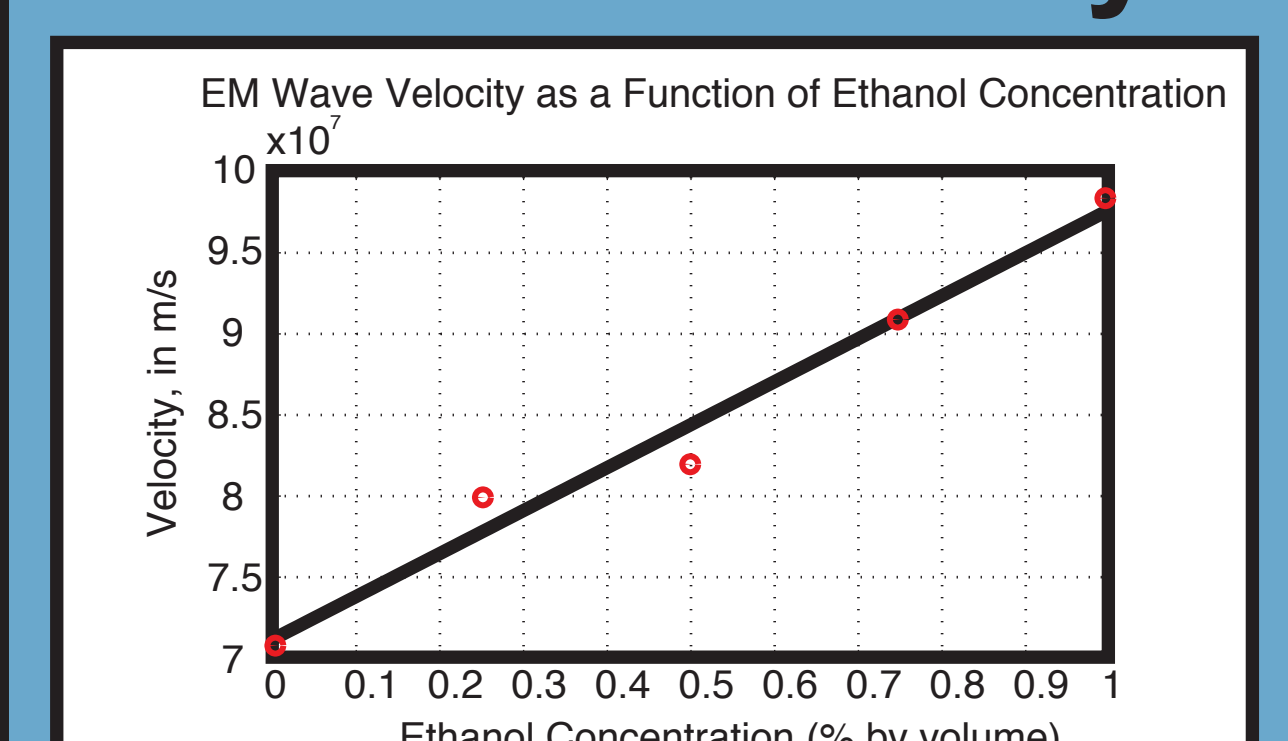


Figure 7: EM wave velocity (black) as a function of ethanol concentration compared to experimental data.

## IP Parameters

Table 1:

Cole-Cole Parameters	0% Ethanol	25% Ethanol	50% Ethanol	100% Ethanol
Rdc	571	565	1261	2268
m1	1.247	0.770	2.084	1.355
c1	2.26e5	8.71e5	1.94e5	1.35e5
c2	1	1	1	1
m2	0.0002	0.031	0.0053	0.018
c3	4.90e1	0.310	0.310	0.310
c4	0.504	0.788	0.688	0.583

1 and 2 indicate the dispersion term number  
 - Rdc is static (DC) resistivity  
 - m is chargeability  
 - c is the relaxation time  
 - c is the frequency effect

## GPR Forward Modeling

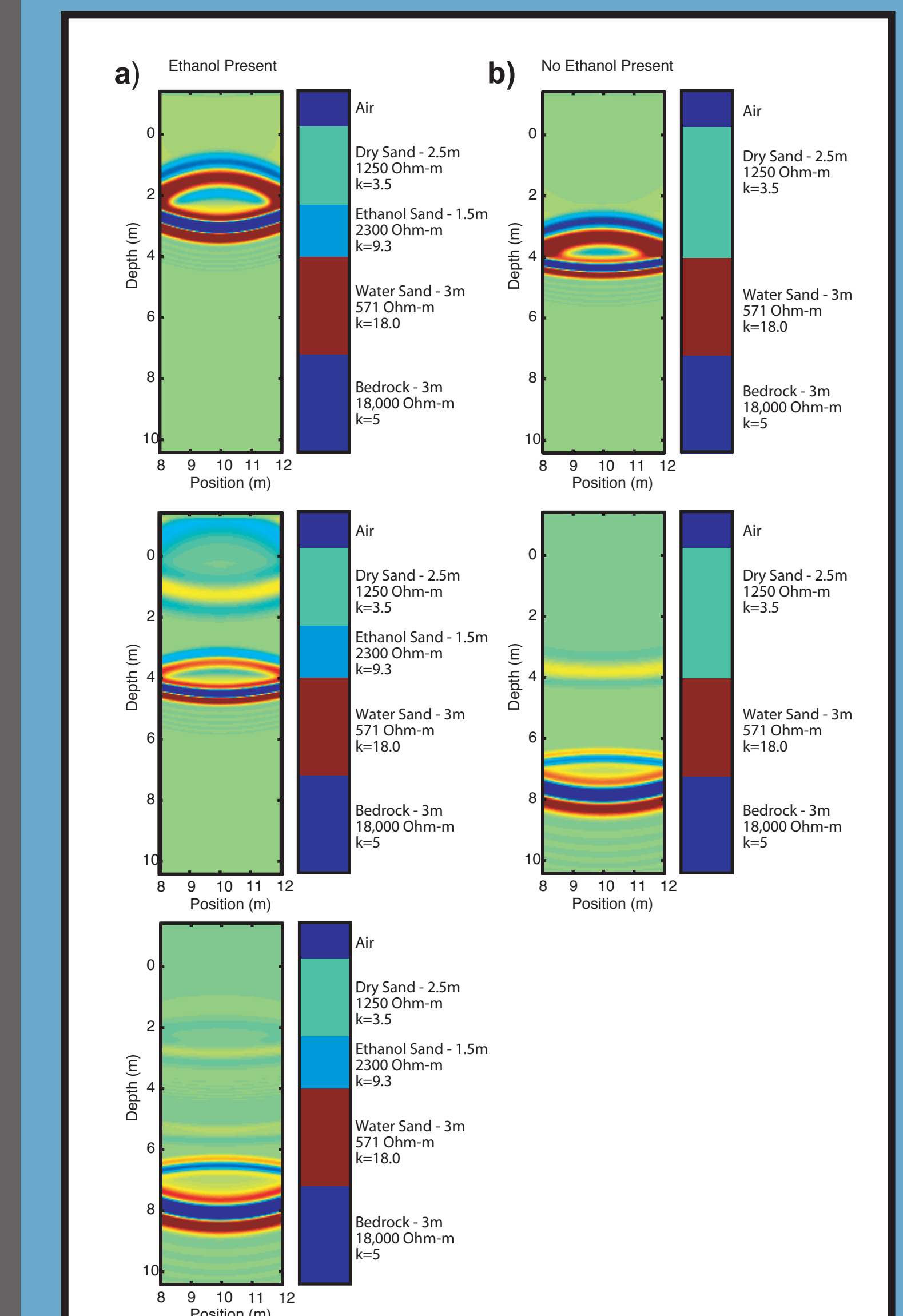


Figure 8: a) Modeling of GPR response to ethanol layer present above the water table. Three reflections coincide with three defined interfaces in the subsurface. b) Two reflections coincide with two defined interfaces (no ethanol present).

## Resistivity Forward Modeling

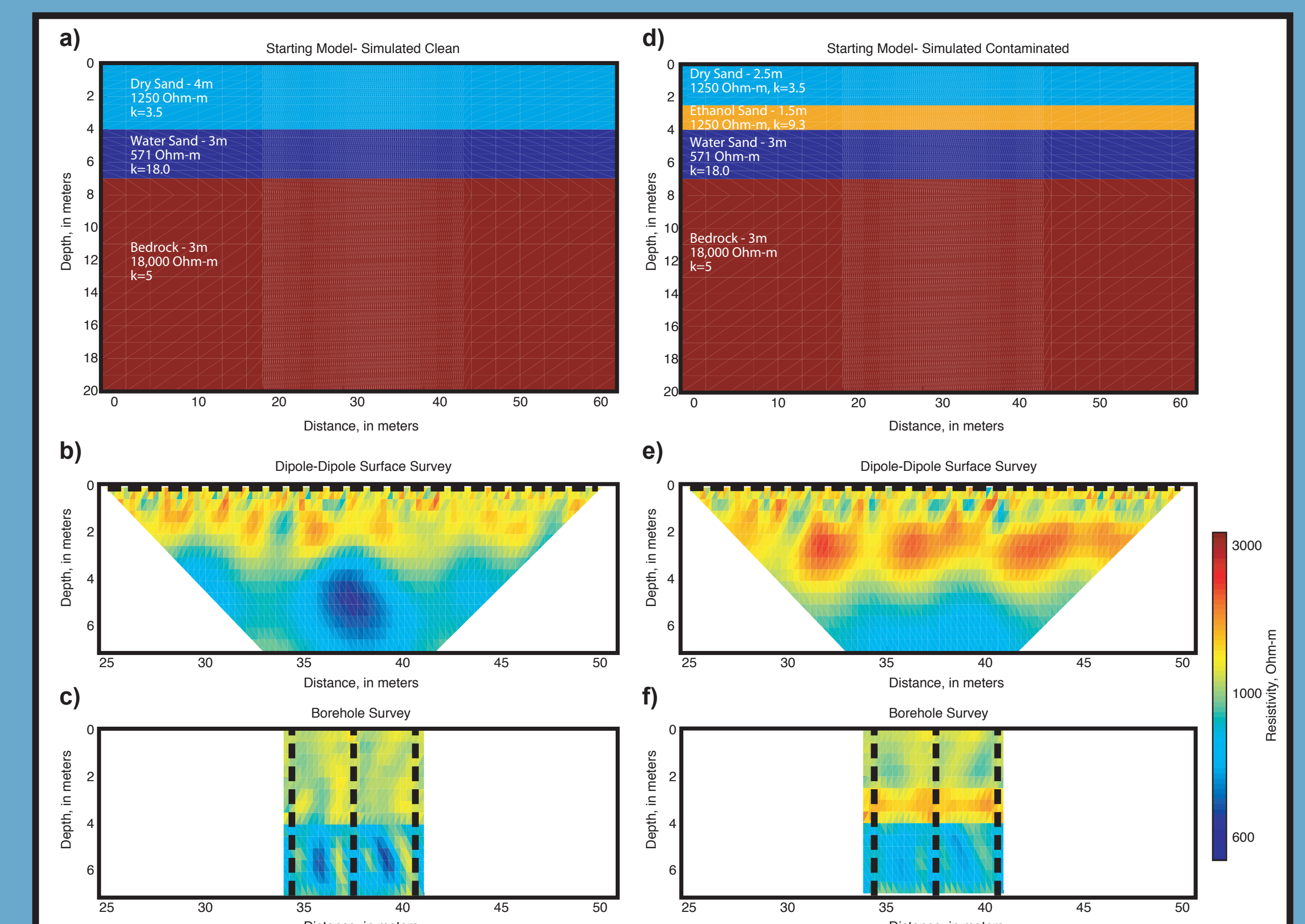


Figure 9: a) Subsurface resistivity distribution- no ethanol b) surface electrical resistivity model results- no ethanol c) borehole resistivity model results- ethanol present d) subsurface resistivity distribution- ethanol present e) surface electrical resistivity model results- ethanol present f) borehole resistivity model results- ethanol present. Black dashes indicate location of electrodes.

## DISCUSSION

- Laboratory investigations of ethanol contaminated sands are useful in determining field scale parameters. Useful parameters are electrical resistivity and dielectric constant, for which DC resistivity surveys and GPR methods can be used (as demonstrated by the forward modeling exercise).
- The Cole-Cole model is capable of fitting the experimental data. Two dispersions are apparent from the data and model, one at low frequencies (<1Hz) and one in the higher frequency range (>1Hz). The CRIM model is useful for simple, 2- or 3- component mixtures. It may be used to help determine ethanol concentration. Electromagnetic wave velocity appears to be predictably dependent on ethanol concentration.
- While the Cole-Cole model may be useful to fit individual experimental results, the parameters do not appear to be correlated with %ethanol concentration (e.g. chargeability does not appear to be a function of ethanol concentration).

## FUTURE WORK

- Time lapse column measurements incorporating TDR, resistivity, and temperature.
- Tank scale GPR measurements with a simulated ethanol spill.
- Field scale study of ethanol contaminated site.

## ACKNOWLEDGMENTS

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