

The dielectric properties of granular media saturated with DNAPL/water mixtures

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[1] We present the results of five experiments investigating the dielectric properties of granular materials partially saturated with trichloroethylene (TCE), a common dense non-aqueous contaminant. Previous research has investigated the radar signatures of similar solvents in controlled field experiments but no core-scale measurements have verified the appropriate petrophysical model. Broadband dielectric measurements were performed using a time domain reflectometry (TDR) system coupled to a solvent-compatible coaxial transmission line. Two synthetic samples and three natural aquifer samples were fully saturated with water and then subjected to an axial TCE injection until breakthrough was observed. The resulting dielectric measurements show good agreement with the empirical complex refractive index model (CRIM) allowing a reasonable prediction of the radar reflectivities and transmission velocities expected in field surveys targeting pools of similar non-aqueous contaminants. *INDEX TERMS*: 1831 Hydrology: Groundwater quality; 5109 Physical Properties of Rocks: Magnetic and electrical properties; 5194 Physical Properties of Rocks: Instruments and techniques. **Citation**: Ajo-Franklin, J. B., J. T. Geller, and J. M. Harris (2004), The dielectric properties of granular media saturated with DNAPL/water mixtures, *Geophys. Res. Lett.*, *31*, L17501, doi:10.1029/2004GL020672.

1. Introduction

[2] The field-scale detection and spatial delineation of toxic contaminants is a critical problem for environmental scientists charged with protecting our valuable water resources. Dense non-aqueous phase liquids or DNAPLs are a family of fluids which include some of the most problematic industrial contaminants such as the chlorinated solvents trichloroethylene (TCE) and tetrachloroethylene (PCE) [Pankow and Cherry, 1996]. A wide variety of geophysical techniques have been proposed for DNAPL detection in the shallow subsurface [Romig, 2000]. However, most methods lack the spatial resolution and/or sensitivity for characterization of small DNAPL lenses or pools. Ground-penetrating radar (GPR) possesses both desired properties in some geological scenarios when appropriate

source frequencies and source/receiver geometries are used. The Borden Project performed a series of controlled field-scale GPR experiments that succeeded in monitoring the downward migration of PCE in-situ through a series of pools at depth [Brewster and Annan, 1994]. No core-scale calibration experiments were performed and subsequent inversions of the Borden data set assumed the validity of existing volumetric mixing formulae.

[3] We present the results of five experiments investigating the dielectric properties of granular materials partially saturated with TCE. These measurements provide confirmation of the class of mixing laws used in previous modeling studies. Two synthetic samples and three natural aquifer samples of varying porosities were examined. All samples were initially water saturated before being subjected to an axial injection of TCE. TCE is a colorless fluid with a density of 1451 kg/m^3 , a dielectric constant of 3.35 [Nath, 1995], and a viscosity of 0.56×10^{-3} Poise [Mercer and Cohen, 1990]. TCE has a relatively low aqueous solubility ($1100 \text{ } \mu\text{g/L}$ [Montgomery, 1991]) but is also tightly regulated by the EPA with a maximum allowable concentration of $0.005 \text{ } \mu\text{g/L}$ in drinking water.

[4] Broadband dielectric measurements were performed during the TCE injection process using a time domain reflectometry (TDR) system coupled to a solvent-compatible coaxial transmission line. Since only water and TCE were used as saturating fluids, these results are most relevant to detection of DNAPLs in the saturated zone. The resulting dielectric measurements show good agreement with the empirical complex refractive index model (CRIM) allowing a reasonable prediction of the radar transmission velocities expected in field surveys targeting pools of similar non-aqueous contaminants.

1.1. Principles

[5] The key parameter for determining the radar signature of fluid saturation is the dielectric constant or relative dielectric permittivity. We will consider a simple conceptual model where the saturated subsurface is a three phase composite consisting of grain material, water, and non-aqueous contaminant. Because of the high dielectric constant of water (80) in comparison to non-magnetic soil minerals (4–8) [Nelson et al., 1989; von Hippel, 1954; Keller, 1987], electromagnetic (EM) properties are very sensitive to water saturation. Most chlorinated solvents are

non-polar with dielectric constants ranging from 2.2 to 11. The radar signature of DNAPLs is largely dependent upon the displacement of pore water. The complex frequency dependent dielectric constant (κ^*) can be written as the sum of a real dielectric constant (κ'), a high frequency loss term due to relaxation effects (κ''), and a DC conductivity term (σ_{dc})

$$\kappa^* = \kappa' + i \left[\kappa'' + \left(\frac{\sigma_{dc}}{2\pi f \epsilon_o} \right) \right] \quad (1)$$

where f is frequency, and ϵ_o is the permittivity of free space. For materials with low conductivity and a small κ'' loss term, $\kappa^* \sim \kappa'$ which allows the propagation velocity of electromagnetic waves through a homogeneous medium (V_{EM}) to be expressed as

$$V_{EM} = \frac{c}{\sqrt{\kappa'}} \quad (2)$$

where c is the velocity of light in a vacuum [Topp *et al.*, 1980]. For the range of frequencies used in subsurface radar, the dependence of κ' on f is weak and $\kappa'' \ll \kappa'$ [Davis and Annan, 1989]. In our case we assume σ_{dc} to also be negligible because of the low clay content in our samples and the use of DI water as the primary saturating fluid.

1.2. Previous Work

[6] Several experimental and theoretical works have examined the impact of NAPL saturation on bulk electromagnetic properties of rocks and soils. Endres and Redman [1993] investigate the consequences of using a modified differential effective medium theory to model the dielectric effects of saturating soils and rocks with various contaminants. Carcione *et al.* [2003] model the electromagnetic properties of NAPL saturated materials using the Hanai-Bruggeman relationship for dielectric properties. Santamarina and Fam [1997] measure the complex dielectric permittivity of soil/pollutant mixtures, using benzene, xylene, toluene, tetrachloroethylene, trichloroethylene, and chlorobenzene as organic pollutants. Kaolinite and bentonite clays were used as the porous background material. Although significant changes in dielectric properties were noted in both clays after injection of TCE, the relationship between complex permittivity and TCE saturation was not quantitatively determined. Persson and Berndtsson [2002] investigated the dielectric properties of synthetic soils partially saturated with sun-flower seed oil (SFSO) using the time domain reflectometry method. Their experiments yielded confirmation of a simple mixing model similar to CRIM.

1.3. A Simple Dielectric Model for 3-Phase Composites

[7] The Complex Refractive Index Model (CRIM) Roth *et al.* [1990] and Endres and Knight [1992] provide a useful form for estimation of the effective dielectric properties of multiphase materials. The model is only strictly valid for one dimensional layered composites in the ray theoretic limit, although in practice CRIM is often effective at modeling the properties of more complex composites. CRIM can be considered as a special instance of the more general Lichtnecker-Rother mixing equations with a fixed

γ exponent of $\frac{1}{2}$ [Mavko *et al.*, 1998; Gueguen and Palciauskas, 1994]. The effective dielectric constant, κ_{eff} , can be written in terms of the volumetric fractions f_i and dielectric values κ_i of the constitutive phases,

$$\kappa_{eff} = \left[\sum_{i=1}^N f_i \sqrt{\kappa_i} \right]^2 \quad (3)$$

[8] For the special case of a three phase mineral/water/NAPL mixture, the CRIM formula reduces to

$$\kappa_{eff} = [\phi(S_w \sqrt{\kappa_w} + S_n \sqrt{\kappa_n}) + (1 - \phi) \sqrt{\kappa_m}]^2 \quad (4)$$

where ϕ is the porosity of the solid matrix, S_w is the water saturation, S_n is the NAPL saturation, and κ_n , κ_w , κ_m are respectively the NAPL, water, and mineral dielectric constants.

2. Methods

[9] Techniques for the measurement of changes in soil dielectric properties due to fluid saturation have been extensively developed in the vadose zone science community. Time Domain Reflectometry (TDR) was first used for the assessment of cable integrity and spectroscopic measurements on fluids [Fellner-Feldegg, 1969] and was later adopted for water content measurements [Topp *et al.*, 1980]. The TDR method measures the 2-way reflection traveltime for a broadband EM pulse propagating within a sample-filled transmission line of known length. The reflection traveltimes are then converted into estimates of V_{EM} and κ using the transmission line length and a time calibration parameter extracted from measurements on two materials with known dielectric properties. Coaxial probes have uniform averaging properties in the direction of transmission but the sensitivity in lateral cross-sections is spatially variable due to the non-uniform electric field.

2.1. TDR Measurement System

[10] TCE's high reactivity with common plastics necessitated careful construction of a chemically compatible coaxial transmission line for the solvent injection measurements. The coaxial cell was based on a similar system described in Topp *et al.* [1980]. The cell, shown in Figure 1, was 33 cm long with a diameter of 4.76 cm and an inner conductor width of 0.64 cm. Flow ports were machined into the aluminum endcaps and poly-ether-ether-ketone (PEEK) fittings were chosen for solvent resistance and low electrical conductivity. Endcap seals were maintained using Viton O-rings. The TDR measurements were acquired using a Tektronix 1502C cable tester interfaced to a lab PC using the University Of Utah's WinTDR package.

[11] The TDR system's response was calibrated using the method of Heimovaara [1993] with distilled water and air used as the reference fluids. The sample holder's top and bottom reflections were identified by shorting both ends of the coaxial cylinder as suggested in Chan and Knight [2001]. Spectral analysis of the reflected arrival from one of our calibration traces indicated approximately 800 Mhz of usable bandwidth, somewhat less than the

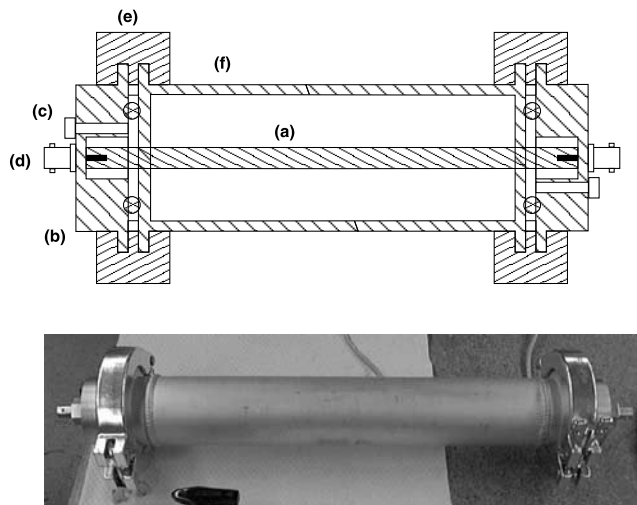


Figure 1. Schematic and photograph of the solvent-compatible coaxial transmission line used in the TCE flood experiments. (a) center conductor, (b) aluminum end-cap, (c) PEEK injection port, (d) BNC connector, (e) seal clamp, (f) aluminum cell casing. (Schematic not to scale). See color version of this figure in the HTML.

manufacturer specification (1.3 GHz) due to cable and connector losses.

2.2. Sample Acquisition and Preparation

[12] The natural aquifer samples were acquired in 4 inch diameter sleeves using a rotary sonic drilling system. The samples were initially wet sieved to remove shell and rock fragments larger than 1.5 mm. The resulting materials were oven dried for two days at 70 C before being homogenized and sequentially transferred to the sample holder. Samples were packed in an initially dry state by slowly saltating the material into the coaxial cell followed by tamping. Table 1 summarizes basic sample properties including porosity, sand/silt/clay fraction, and maximum TCE saturation before breakthrough. All three natural aquifer samples were sands with small amounts of silt and trace clay. The first synthetic sample was composed of glass beads (250–300 microns) and the second was a clean sub-angular quartz sand (150–212 microns).

2.3. Experimental Procedure

[13] After packing and mass measurements, the samples were slowly saturated (1 mL/min) at a fluid pressure of 200 KPa with de-aired DI water which had been previously

Table 1. Summary of Sample Characteristics

Sample	Porosity	Sand/Silt/Clay Fraction	Mean Grain Diameter ^a (μm)	Maximum TCE Saturation (%)
<i>Synthetic Granular Samples</i>				
Glass Beads	0.40	100/0/0	275	52.8
Clean Quartz Sand	0.38	100/0/0	181	53.6
<i>Natural Aquifer Samples</i>				
G20-N2-110-125	0.41	94/4/2	223	25.3
G20-N3-55-70	0.44	91/8/1	267	31.0
G20-N3-125-141	0.39	93/6/1	243	17.4

^aFor sand fraction.

equilibrated with glass beads. Three to four pore volumes of de-aired water were slowly passed through the sample after initial saturation to evacuate most of the remaining trapped air. Previous control experiments on similar soils indicated that this protocol typically leaves between 1% and 2.5% residual gas. TCE, dyed red (Oil Red O Dye, Sigma Aldrich) for visibility, was then injected at low fluid pressure (0.25 mL/min, ~50 KPa) using a precision syringe pump. Effluent mass was monitored to estimate the total injected TCE volume. TDR measurements were made at the initially water-saturated state and at 5 or 10 mL increments during the TCE injection process. TCE was injected until solvent breakthrough was observed in the effluent stream. Auxiliary sample properties measured include dry bulk density, grain density, sand/silt/clay fractions, and the mean grain diameter for the sand fraction. Porosities were estimated from dry bulk density and mean grain density measurements.

3. Results and Discussion

[14] Figures 2 and 3 show dielectric properties as a function of TCE saturation for the synthetic and natural soils respectively. Dielectric measurements correlated well with porosity and TCE saturation. Destructive excavation of the samples after TCE injection revealed preferred flow paths within the sample, visible as red zones within the soil fabric. In all cases the TCE distribution was concentrated in the lower half of the sample. Preferred flow paths were more apparent in the natural soil samples, probably due to larger variations in permeability.

[15] Literature values for grain dielectric properties were used for fitting the CRIM model. For the synthetic samples, grain dielectric values of 6.3 (Soda-Silica Glass [von Hippel, 1954]) and 4.27 (Quartz [Keller, 1987]) were used. The natural samples were assumed to be predominantly quartz with small amounts of feldspar (6.03 [Nelson et al., 1989]) and calcium carbonate (7.8 [Keller, 1987]) yielding an approximate grain dielectric constant of 5. The measurements for all five samples were compared to the CRIM model using the grain dielectric values noted above, a water dielectric constant of 80, a TCE dielectric constant of 3.35 [Nath and Dubey, 1980], and the measured sample porosity and saturation values. CRIM provided a reasonable fit for most of the dataset with minor departures at high and

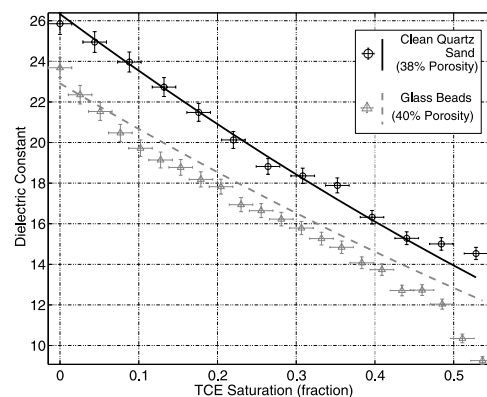


Figure 2. Dielectric constant measured as a function of TCE saturation for two synthetic samples with CRIM fits. See color version of this figure in the HTML.

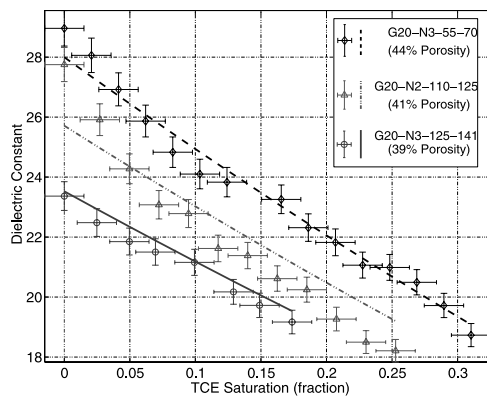


Figure 3. Dielectric constant measured as a function of TCE saturation for three natural sediment samples with CRIM fits. See color version of this figure in the HTML.

low water saturations. CRIM systematically underpredicted dielectric values for the G20-N3-55-70 sample. Some deviations from CRIM were expected since the TCE distribution in the samples was not a uniform layer. Better fits could be obtained by introducing an extra degree of freedom in the mixing equations as is done by *Persson and Berndtsson* [2002] or possibly through explicit inclusion of TCE patch geometry using differential effective medium theory [*Endres and Knight*, 1992]. The horizontal error bars in the data plots are generated from the 1 mL uncertainty in injected TCE volume and the 2% uncertainty in water saturation. The vertical error bars are calculated from a rough estimate of the uncertainty in picking the reflected arrival. Both synthetic samples exhibited higher peak TCE saturations, probably due to their relatively open pore structures.

[16] The dielectric properties we have measured provide a starting point for estimating the radar signature of TCE pools or monitoring the movement of dense contaminants in-situ. V_{EM} values calculated from our measurements allow investigation of the sensitivity of crosswell radar traveltimes tomography to TCE saturation. Currently, the primary limitation in using GPR methods for DNAPL detection is the inability to distinguish lithologic features from regions of contaminant saturation. This ambiguity might be alleviated through use of a second geophysical measurement (seismic e.g.) or through more complete use of the radar waveform to extract frequency dependent dielectric information.

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