SCATTERING RESPONSE OF HIGH FREQUENCY GROUND PENETRATING RADAR FOR DNAPL SITE CHARACTERIZATION

by

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ABSTRACT

A 1,400 MHz cross borehole radar system was used to detect and quantify dense non-aqueous phase liquid (DNAPL) saturation changes during a controlled spill of tetrachloroethylene (PCE). The frequency of the radar system developed for the experiment is approximately 500 MHz higher than has previously been used. The combination of experimental parameters and data analysis methods has allowed three significant contributions toward solving the problems of locating and quantifying DNAPL contaminants. This is the first ground penetrating radar (GPR) investigation to map frequency, polarization, and angular scattering responses, all of which show evidence of scattering processes. Second, the analysis of prespill and postspill scattering indicates changes in pore scale heterogeneity and aggregate behavior due to the presence of DNAPL. Third, the high frequency and traveltime inversion enabled the highest resolution imaging (cm scale) ever obtained with a GPR study of DNAPL contamination.

The Environmental Protection Agency (EPA) sponsored two similar spill experiments at the Richmond Field Station in California. PCE was spilled into a 2.4 m diameter by 2.0 m deep tank, filled with sand-clay media saturated with water. A layer of kaolinite clay was placed one meter below the surface to mimic the function of a clay aquitard, confining the PCE within the saturated sand. The implications of a high frequency radar system are: higher spatial resolution, increased scattering, shorter wavelength, and its concomitant decreased depth of penetration. To partially compensate for the shallower depth of penetration and investigation the radar measurements were acquired between boreholes. The use of boreholes allows the improved DNAPL site characterization methods demonstrated here to be projected to DNAPL contamination problems at depth. The two vertical boreholes penetrating all the layers in the tank were diametrically positioned approximately 0.75 meters apart. Zero offset (ZOG) and common source gather (CSG) data were acquired between the two boreholes before, during, and after the spill. The times of the direct arrivals of the ZOGs were converted to velocity and permittivity. The Bruggeman Hanai-Sen (BHS) mixing formula was applied recursively to obtain values for the vertical distribution of porosity followed by PCE saturation. The traveltimes from the CSGs were inverted to obtain slowness tomograms.
The slowness values were used to calculate forward waveform models, which were compared to the observed radar traces. Scattering and electromagnetic loss tangent models were developed to explain the amplitude losses exhibited in the observed radar traces as the spill progressed. The scattering losses indicated changes in heterogeneity occurring at the pore and fluid movement scales from the displacement of pore water by PCE.
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ACKNOWLEDGMENTS

This research was supported by the United States Geological Survey (USGS), Mineral Resources Program, and the U.S. Environmental Protection Agency (EPA) under Interagency Agreement DW14937586-01-0. The experiments were conducted under the direction of Aldo Mazzella (EPA).

Members of the USGS Crustal Imaging and Characterization Team assisted me in numerous ways: designing and providing hardware, helping to acquire data, supplying processing software, and providing ideas to improve my methods and results, I’d especially like to thank, Bob Horton and Karl Ellefsen, also Craig Moulton, Dave Wright, Mike Powers, Phil Brown, Ray Hutton, Larry Sne, and Vic Labson. Special thanks are also due to my committee members from Colorado School of Mines: Tissa Illangasekare, Tom Boyd, Misac Nabighian, and Stephen Liu, as well as Maryla Deszcz-Pan and Mike Friedel from the USGS. John Creighton read every word of this thesis. I am grateful for his detailed feedback and encouragement.

The Colorado School of Mines, Department of Geophysics provided a teaching assistantship to help fund my first two years of Graduate School. I was also supported by the Devon Energy Scholarship Program. My Advisor, Gary Olhoeft, as well as being a boundless source of knowledge about ground penetrating radar and electromagnetic properties, provided critique, ideas, guidance and support throughout my graduate studies. For that I am sincerely thankful.
Arthur Kevin Wallin
11th of February, 1955 – 10th of May, 2004

With love and gratitude... for the sacrifices you made for Sarah and I
... and the joy that you brought to our lives

“Do, or do not. There is no try.”
INTRODUCTION

In May 2004 and September 2005, the Environmental Protection Agency (EPA) sponsored two experiments whose purpose was to bring together several prototype geophysical instruments, use them to monitor a time lapse spill of tetrachloroethylene (PCE), and evaluate their effectiveness at resolving and tracking the movement of the PCE. The two experiments differed primarily in that during the latter less PCE was spilled over a longer duration. This thesis focuses on a time lapse study of both spills using 1.4 GHz cross borehole ground penetrating radar (GPR). The radar system was designed with the objective of increasing the resolution limits previously obtained with lower frequency ground penetrating radar. Seldom, if ever, has borehole radar with such a high frequency been utilized for any purpose. Its application to a controlled spill provides new techniques that improve the ability to locate and quantify PCE contamination. Other authors (Sneddon 2003, Sneddon et al. 2000, and Sander 1994) have developed methods to calculate PCE saturations from surface radar data. This is the first time that PCE saturations have been obtained from inversion of two-dimensional crosswell GPR traveltime data. Although traveltime inversion and attenuation analysis have been used previously to analyze lower frequency GPR (Olhoeft (1992), Binley et al. (2001), Majer et al. (2002), Alumbaugh et al. (2002), Kowalsky et al. (2004), Day-Lewis et al. (2002), Rucker and Ferre (2004)), this is the first instance, in the context of DNAPLs, of utilizing traveltime inversion to obtain slowness tomograms from crosswell radar with this high of a frequency range, and using them to construct forward waveform models, and models of scattering and electromagnetic loss mechanisms.

This thesis includes six chapters which encompass the pertinent aspects of using a high frequency radar to monitor such a spill, namely, electromagnetic and fluid flow theory, experimental parameters, porosity and PCE saturation estimation from one and two dimensional crosswell radar data, traveltime inversion, waveform modeling, and analysis of loss mechanisms. In addressing the role of electrical, magnetic and geometric properties on the performance of GPR (Olhoeft 1998) several assumptions are made.
Electrical properties including conductivity, permittivity, and the presence of clay, water and PCE and their influence on those properties are important to determining velocity and direct current conduction and dielectric relaxation losses. Scattering of wavelength scale heterogeneities is important. Magnetic properties and geometric properties such as orientation, polarization, waveguides and multipathing are not considered significant in this study and are not addressed.

Chapter 1 begins by describing some of the work that has already been done regarding GPR and PCE detection, followed by an introduction to the electromagnetic theory important to GPR, including a discussion on loss and attenuation necessary for understanding and interpreting the data acquired during the experimental PCE spills. This first chapter also includes a discussion of fluid flow and contaminant transport geared toward geophysicists who work on environmental contamination problems. The Chapter also includes some of the expressions that govern contaminant transport and shows the basic laws from which they are derived.

The first part of Chapter 2 describes the design of the PCE spill experiment including the tank and spill parameters along with a description of the instrumentation that was developed to acquire high frequency cross borehole GPR. This is followed by results of independent laboratory measurements of the electrical properties of the sand, clay, and fluids used in the experiment.

In Chapter 3 the zero offset gather results of the data acquired in both experiments are presented, along with their associated one-dimensional permittivity models. The permittivity profiles are used with the Bruggeman-Hanai-Sen (BHS) formula to calculate porosity and PCE saturations versus depth following the method presented by Sanders (1994) and Sneddon et al. (2000). However, their method has been extended so that PCE saturation can be calculated for all porosity values within the tank and is not limited to an average. Finally, the saturations are used with Fresnel volumes to estimate the volume of PCE which is then compared to the actual amount of PCE spilled. Chapter 3 also contains an analysis and quantification of error encountered in the experiment.

A nonlinear regularized traveltime inversion of the common source gather data from the 2004 experiment is presented in Chapter 4. The forward model and inversion routine were provided by Karl Ellefsen, U.S. Geological Survey (Ellefsen 1998). The
results include slowness tomograms for different values of regularization parameters. A method for determining the ideal balance between over-fitting and under-fitting the travelttime data thereby justifying a particular model choice is also presented. The slowness values for each cell of the chosen models were used to calculate two-dimensional PCE saturations using the BHS mixing formula presented in Chapter 3.

The theory discussed in Chapter 1 is used in Chapter 5 to explore the causes of wavelet dispersion seen in the sequential radar data sets. A Ricker wavelet is propagated through a homogeneous isotropic medium using a range of conductivity and permittivity values to demonstrate their influence on amplitude and velocity. Two-dimensional slowness models obtained from travelttime inversions of the 2004 common source gather data (Chapter 4) are used as inputs to the forward modeling program Waveform2d (Ellefsen 2006). The modeled waveforms are compared with radar traces from the pre-spill and post-spill data. To further explore the mechanisms responsible for attenuation, Chapter 5 also includes modeling of scattering and electromagnetic losses for the different electrical properties representative of the pre and post spill conditions. The scattering losses are not limited to a linear Rayleigh regime, but include Mie and optical scattering. They indicate that heterogeneities too small to be detected by GPR imaging may still be resolved at scales similar to what has been obtained with complex resistivity (Grimm et al. 2005).

The final chapter summarizes the main findings of this study, discussing the positive results as well as some of the pitfalls. It also provides recommendations of what future work is needed to build upon what has already been accomplished. Appendix A describes a straight-ray-path forward model written by the author, and shows results from a non-regularized inversion of the same data that were inverted in Chapter 4, using a least squares minimization routine written by Per Christian Hansen (1998). Appendix B includes names and descriptions of the different Matlab routines that were developed specifically for this thesis, and an index of the other CD-ROM files. The data, matlab codes, and a copy of the thesis can all be found on the accompanying CD-ROM.
CHAPTER 1

GEOPHYSICS AND DNAPL

Tetrachlorethylene (PCE), a solvent often used for dry cleaning, falls into a class of contaminants known as dense non-aqueous phase liquids (DNAPLs). These contaminants have densities greater than that of water, and are immiscible in water. In the past, improper disposal of PCE was common. Unfortunately, due to the physical characteristics of DNAPLs (immiscibility and toxicity) small quantities have the potential to contaminate large volumes of ground water. GPR is ideal for investigation of DNAPL spills because the relatively high resolution, as compared with other geophysical methods, provides the capability to track the movement and to delineate small fingers and pools of the chemical. PCE spills have been examined in the past with lower frequency commercial systems (160 MHz to 500 MHz) in natural and controlled artificial environments (Brewster and Annan 1994, Annan et al. 1991, Greenhouse et al. 1993, Sander 1994, and Sneddon et al. 2000). The controlled tank spill of PCE described in this thesis, the high frequency (1.4 GHz) of the radar system used and the density of the data acquired allows enough resolution to detect the variations in traveltime and signal strength associated with changes in PCE saturation of just a few percent.

Stricter regulations and penalties for illicit discharge of DNAPLs have resulted in a decline in the number of these types of occurrences. However, small spills can go undetected until there is a problem with ground water contamination. In many cases governmental agencies have been left with the responsibility for remediating the environmental damage. Many spill sites have already been located and are subject to ongoing remediation and or monitoring. Even a small pool left behind or put into motion by remediation activity has the potential to pollute ground water supplies. The subsurface movement of this class of contaminant is difficult to predict. It is driven by gravity and capillary forces into pools, fingers and blobs leaving behind large residual saturations.
High frequency GPR can be used to quantify some of the parameters used in the characterization of DNAPL spills, including spatial variation of saturation and porosity. Surface GPR can discriminate targets that are on the order of 1/3 of the radar wavelength. Crosswell radar tomography also shares this resolution ability with vertical resolution being somewhat better than lateral resolution. Schuster (1996) shows that the lateral resolution limits of tomography are dependent upon the length of the boreholes, their separation and wavelength. The 1.4 GHz radar pulse used in this experiment is perhaps the highest frequency used in such an application, resulting in better resolution than has previously been achieved.

1.1 Geophysical Investigation of DNAPL Contamination

DNAPL contamination has been investigated by numerous geophysical techniques, including nonlinear complex resistivity, electrical resistivity tomography, seismic profiling and tomography, dielectric logging, and surface and borehole GPR. Sites discussed frequently in the literature, where these methods were tested or used are Savannah River Site (McKinley 2003), Canadian Forces Base Borden (Brewster and Annan 1994, Annan et al. 1991, Greenhouse et al. 1993, Sander 1994, and Sneddon et al. 2000), Hanford Disposal Site (Last and Horton 2000) and Hill AFB (ITRC 2000). All of these techniques were used to study contamination at the Savannah River Site (McKinley 2003, Grimm et al. 2005). Electrical resistivity tomography, along with surface and borehole GPR, were used to study DNAPL contaminants at Canadian Forces Base Borden in Ontario (Brewster and Annan 1994, Annan et al. 1991, Greenhouse et al. 1993, Sander 1994, and Sneddon et al. 2000) and the Hanford disposal Site (Last and Horton 2000). Lane et al. (2004), reports on using borehole GPR for monitoring a vegetable oil injection experiment that simulates remediation. Yang (2002), used resistivity profiling to locate and monitor the DNAPL plume at a Taiwanese site contaminated with dichloromethane and chlorobenzene.

Borehole GPR was demonstrated at the Savannah River Site where it successfully detected high concentrations of DNAPL in the saturated zone, but did not provide enough
information to quantify those concentrations (ITRC 2000). A three dimensional 160 MHz borehole radar survey was acquired at Canadian Forces Base Borden during a PCE injection experiment (Olhoeft 1992). Sander et al. (1992), reported results of 500 MHz surface radar monitoring of the PCE injection in Cell 4 at Canadian Forces Base Borden and found that the borehole radar successfully tracked the vertical and horizontal migration of the contaminant. Brewster and Annan (1994), describe the 200MHz surface GPR monitoring of the spill, and Kueper et al. (1993) report on the excavation of the spill zone and spatial distribution of the DNAPL. Sneddon (2000) used 500 MHz surface radar data acquired during the 1991 spill, and the framework established by Sander (1994), to model DNAPL saturation values and calibrate three-dimensional fluid flow models. Numerous borehole radar investigations have been reported that characterize the general hydrology of different sites. Borehole radar tomography studies of the vadose zone have been conducted by Binley et al. (2001) Majer et al. (2001), and Alumbaugh et al. (2002). Results of hydrologic characterization using borehole GPR have been published by Kowalsky et al. (2004), Day-Lewis et al. (2002), and Rucker and Ferre (2004). The results of studies such as these and those presented in this thesis can be applied in investigations of contaminated sites to detect and monitor DNAPL contaminants.

The performance of a GPR system in the field is largely determined by the electrical properties of the subsurface and the frequency of the radar system used. In the case of electrically conductive soils the radar signal may be attenuated to the extent that the received signal is too small to make reliable interpretations. Lower frequency radar will have less resolution capability than a higher frequency system with shorter wavelengths, but higher frequency electromagnetic waves will be more quickly dissipated in the subsurface by scattering losses. Other considerations include the geometry used in a crosswell radar survey. For example, the distance between wells plays an important role in received signal strength. The angular coverage by raypaths will impact the amount of lateral resolution.

In general, the direct detection of DNAPL is a difficult problem and a perfect solution remains elusive. Without prior knowledge of the existence or location of DNAPL pools is it possible to detect them? DNAPL typically has a low dielectric
permittivity, and in the vadose zone the lack of electrical property contrast makes direct detection unlikely. However, given suitable conditions, monitoring the migration of a DNAPL plume might be possible. In the case of DNAPL in the saturated zone there are electrical property contrasts which GPR is ideally suited to detect. The velocity of an electromagnetic wave depends, for the most part, on dielectric permittivity. Water saturated sandstone has a relative dielectric permittivity (RDP) of 20 while DNAPL has an RDP of less than 3. GPR is sensitive to the resulting velocity contrasts. The water saturated sand or sandstone has a higher conductivity than DNAPL saturated sandstone by orders of magnitude. Conductive regions tend to decrease the radar signal strength. There might be high velocity zones and strong signal amplitudes through DNAPL saturated areas that may be used as an indication of the contaminant. GPR may also be used to locate impermeable clay barriers that would cause entrapment of the DNAPL into pools. A DNAPL pool in the saturated zone above a clay aquitard would generally yield a high velocity signal with less attenuation of signal strength relative to the signal above and below. The higher velocity is due to decreasing RDP in the DNAPL saturated region. While larger amplitudes result from an increase in resistivity. However, scattering losses due to heterogeneities formed by DNAPL may decrease the received signals. Likewise, conductivity increases have been observed in the case of PCE contamination possibly due to the washing of conductive salts from soil particles into pore water (Olhoeft 2007, pers. comm.). The travel times and waveforms of radar data give information that can be used to estimate dielectric permittivity ($\varepsilon$) and electrical conductivity ($\sigma$). $\varepsilon$ and $\sigma$, in turn, can be used to estimate porosity and fluid saturations.

When applying geophysical methods such as GPR for the detection and location of DNAPL contamination, the best results are obtained using a multidisciplinary approach. This may include a combination of statistical analysis, data and interpretations from partitioning tracer tests, mass flux models, geologic investigations, well log evaluations, and geophysical models.
1.2 Influence of Electromagnetic Properties on GPR

Some of the parameters of primary importance for this experiment and analysis are the physical and electrical properties of the soil medium (sands and clays), and fluids (pore water and PCE) and how they effect the velocity and shape of radar pulse as it travels between the transmitting and receiving antennas. In this application the magnetic permeability is assumed to be that of free space, $4\pi \times 10^{-7}$ H/m [Henrys/meter], and the medium is homogeneous and isotropic. The velocity and phase of the radar wave are strongly affected by the electrical properties of the medium through the relationships established by Maxwell’s equations. In the case of iron bearing or magnetic soils it is necessary to use a complex magnetic permeability (Olhoeft 1998).

1.2.1 Electrical conductivity and dielectric permittivity

Electrical properties include the electrical conductivity and frequency dependent complex dielectric permittivity. Electrical conductivity is a measure of the ability to transport charge. Soils with electrical conductivities greater than about 30 mS/m [milliSiemens/meter] are usually impenetrable to GPR (Powers 1995). With increased conductivity there is greater attenuation of the radar signal as energy is dissipated through charge motion and associated heat generation. Depending upon the conductivity of the contaminated soil, the high electrical resistivity of PCE ($1 \times 10^5$ MΩm [mega-Ohm meters], Lucius et al.1992) makes GPR an exceptional geophysical tool to apply to the DNAPL contaminant problem.

Dielectric permittivity is a measure of polarizability, the ability of the charges in a material to separate and align with an externally applied electric field. It is a complex and frequency dependent quantity described by the Cole-Cole distribution (Cole and Cole, 1941),

$$
\varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}}.
$$ (1.1)
$\tau$ is the relaxation time constant, and $1-\alpha$ is the distribution breadth parameter. $\varepsilon_0$ and $\varepsilon_\infty$ are the zero and infinite frequency permittivity values. $\omega = 2\pi f$ is the angular frequency. $f$ is frequency in hertz. The real and imaginary terms on the left hand side describe energy storage and loss respectively (discussed in section 1.2.2). In free space permittivity is $8.854 \times 10^{-12}$ F/m [Farads/meter]. Relative dielectric permittivity (RDP) is simply the ratio of the permittivity of a material to that of free space, $\varepsilon_r = \varepsilon / \varepsilon_0$, forming a dimensionless quantity. PCE has a permittivity of 2.3 (Lucius et al. 1992). Values of relative permittivity range between 1 for free space and 81 for fresh water. The RDP of dry quartz is 4.5. When it is in the form of sand the air content must be considered, and the RDP will decrease. The RDP of water saturated sand is greater and depends on moisture content. There are also interactions between materials that can increase or decrease permittivity values. In the case of salt water, the permittivity is decreased due to the interaction between salt ions and water molecules. The water molecules that hydrate the salt ions are fixed to the ions by the ion-dipole attraction. They are no longer available to rotate freely under an applied electric field. Since some of the water molecules now have more resistance to rotation or polarization, the permittivity is decreased relative to the value for deionized water (Horton 2007, pers. comm.). In the case of clays, the electric double layer (EDL) is compressed with increased salinity, which increases conductivity. As the EDL gets thinner, there is less room for charges to separate, yielding a reduced polarizability and hence, lower permittivity. Conversely, with lower salinity the clay exhibits less compression of the EDL resulting in a higher permittivity. The electrical properties, $\varepsilon$ and $\sigma$, are also a function of temperature with values increasing as temperature increases. The experiment described herein was performed at room temperature. Thus, the influence of temperature on $\varepsilon$ and $\sigma$ was considered negligible.

There are five major frequency dependent mechanisms that describe charge separation, listed here in order from high to low: electronic polarization, molecular polarization, ionic polarization, orientational polarization, and interfacial polarization. Electronic polarization ($10^{14}$ Hz) refers to the distortion of the electron cloud of an atom in the presence of an applied electric field. Molecular polarization ($10^{12}$ Hz) describes
the distortion of the molecules influenced by an electric field. In both of these phenomena constituents of the respective particles become distorted into an asymmetric configuration resulting in charge separation. In Ionic polarization ($10^{12}$ Hz) the ions segregate into positive and negative groups in alignment with the external electric field. Rotation of polar molecules without distortion is described as orientational polarization. This phenomenon, in combination with ionic polarization occurs at frequencies less than $10^{10}$ Hz (Olhoeft 1981). Interfacial polarization occurs below $10^8$ Hz, when charges align at interfaces in opposition to an applied electric field, an internal field forms, and the two cancel one another out (Kutrubes 1986).

1.2.2 Loss and attenuation mechanisms

Effective use of GPR for geophysical investigations is dependent upon conditions which result in an acceptable level of signal attenuation or other losses, in other words signals that are within the dynamic range of the system. Only a fraction of the transmitted energy is actually returned to the receiving antenna. The amount of energy received will be dependent upon how much power was transmitted in the direction of the target, the amount of power that contacts a target and is reflected in the direction of the receiver and the amount of that reflected power that is intercepted by the receiving antenna. Losses important to GPR can be categorized into two main types, those that are unrelated to the medium under investigation and those that are dependent upon the properties within the subsurface where, in the case of GPR, the signal is being transmitted. In the first category are losses caused by antenna properties and geometry, including angular and frequency dependent gain functions, antenna ground coupling normalization and geometric spreading. The other types of loss fall under the category of attenuation. These include dielectric, conductive, and magnetic relaxation losses, and scattering.

The power of the signal at the receiving antenna is partially described by the radar equation (Powers 1995 and Burton 2004),
\[ P_r = P_0 G_t \left[ \frac{1}{(P^r \cdot P^{r})^2} \prod_{j=1}^{n-1} e^{-2\alpha_j r_j} K_j^2 \right] G_r \left( \frac{\lambda^2}{4\pi} \right) \]  

(1.2)

It contains terms that are relevant to the geometry and physical antenna properties,

- \( P_r \) is the power received [W],
- \( P_0 \) is the power transmitted [W],
- \( G_t \) and \( G_r \) are angular and frequency dependent gain functions for the transmitting and receiving antennas, respectively,
- \( \frac{1}{(P^r \cdot P^{r})^2} \) is the geometrical spreading term.

The terms that are inherent to the materials between the antennas and the electromagnetic wave being propagated are,

\[ \prod_{j=1}^{n-1} e^{-2\alpha_j r_j} K_j^2 \text{ [m}^2\text{]}, \]

- \( K_j \) is the complex reflection or transmission coefficient,
- \( \alpha_j \) is the attenuation constant [Np/m],
- \( r_j \) is the radius of the propagating wavefront [m],
- \( j \) is the index number of the ray segment being calculated,
- \( n \) is the number of layers between the transmitting and receiving antennas,
- and \( \lambda \) is the wavelength of the received energy[m].

In addition to the parameters of the radar equation, polarization, target shape and size, and scattering will influence the power received. Radiation patterns can be used to describe the angular dependence or directivity of a transmitting and receiving antenna. The received power will depend upon the angle between the two antennas, and the electrical and geometric properties of the medium between them. Patterns were calculated from common source gather from the 2005 experiment and are presented in Chapter 3.

Frequency dependent dispersion and scattering are the mechanisms that are primarily responsible for the change in wavelet shape due to the materials between the transmitting and receiving antennas. A propagating pulse has a center frequency, as well
as other attendant frequencies, each one propagating with a different phase velocity and
attenuating at different rates. This results in dispersion of the wavelet shape. The
foregoing is described as frequency dependent dispersion. Scattering can occur at a
surface or be due to a volume, and comprises the reflection, refraction, or diffraction of
the propagating wave. In GPR it is caused by a contrast in electrical and/or magnetic
properties. Scattering can be either beneficial allowing the radar to detect a target, or it
can be appear as noise and not allow the discrimination of targets. Waveguides, cutoff
frequencies and modes, can also influence the wavelet shape, but in this case it is due to
constructive and destructive interference and not material properties.

The real and imaginary terms of permittivity (Equation 1.1) describe energy
storage and loss. The following discussion, relating the product of charge separation
distance and cycle time to energy loss, is summarized in Table 1.1.

<table>
<thead>
<tr>
<th>FREQUENCY AND CYCLE LENGTH</th>
<th>DISTANCE OF CHARGE SEPARATION ACHIEVED AND ENERGY STORAGE</th>
<th>TIME SPENT IN MOTION</th>
<th>ENERGY LOSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOW FREQUENCY ⇒</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LONG CYCLE TIME &gt; NECESSARY FOR FULL CHARGE SEPARATION DISTANCE</td>
<td>MAXIMUM</td>
<td>MINIMUM</td>
<td>LOW PER CYCLE</td>
</tr>
<tr>
<td>RELAXATION FREQUENCY (ω=1/τ) ⇒ CYCLE TIME = NECESSARY FOR FULL CHARGE SEPARATION DISTANCE</td>
<td>MEAN</td>
<td>MAXIMUM</td>
<td>MAX PER CYCLE</td>
</tr>
<tr>
<td>HIGH FREQUENCY ⇒</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SHORT CYCLE TIME &lt; NECESSARY FOR FULL CHARGE SEPARATION DISTANCE</td>
<td>MINIMUM</td>
<td>MAXIMUM</td>
<td>LOW PER CYCLE</td>
</tr>
</tbody>
</table>

During polarization charges will separate until the internal field between the
charges comes into balance with the applied electric field. If the velocity of the charge
motion is high enough, they will maintain an equilibrium until the oscillating field
reverses, at which time they will move again. During motion energy will be lost to heat
in proportion to the distance moved. Energy will be stored in proportion to the distance
of charge separation. At low frequency the distance traveled is maximized creating maximal storage, and the amount of time spent in motion is minimal relative to the cycle time, so that there is low loss per cycle. At highest frequency charges separate, but never completely balance with the applied field. Since the charges only move a small distance there is small loss and small storage, which is still proportional to the total separation achieved. At the relaxation frequency charge separation is maximized with no rest before the reversal of the field. This causes maximum loss overall as the charges are in constant motion over maximum distance. The storage in this case is the average of the high and low frequency limits. This frequency is given by, \( \omega = 1/\tau \) (Olhoeft 1998). In a study by Ohoeft and Capron (1994), interfacial polarization losses, which occur in water wet porous media, were reported to be dominant below 300 MHz. At frequencies above a gigahertz, dry sand will have scattering losses related to the scale of heterogeneity relative to the radar wavelength. There is a small band, between water interfacial losses and particle size scattering losses where frequency dependent dispersion is at a minimum (Olhoeft 1994). At the frequencies of this experiment, \( 10^8 \) to \( 10^9 \) Hz, the orientational polarization of the water molecule is the dominating mechanism of charge separation. Hence, it can be shown that the most significant attenuation will be due to scattering not to dielectric relaxation and conduction losses.

1.3 Electromagnetic Theory and GPR

The theory of electromagnetic wave propagation and GPR are treated extensively by numerous authors including, Ward and Hohmann (1987), Balanis (1989), Wait (1970), Daniels (1989), Powers (1995), thus it is not discussed in detail in this thesis. What follows is a brief summary of Maxwell’s equations, the relevant constitutive equations, an abbreviated derivation of the Helmholtz equation and statement of its solutions, at the end of the section are expressions important to GPR, namely velocity, wavenumber, phase and attenuation parameters, and loss tangents.

Maxwell’s equations in the frequency domain relate electric and magnetic fields to their sources,
The constitutive equations are, $J = \sigma E$ (Ohm’s Law), $D = \varepsilon E$ and $B = \mu H$ where, $E$ is the electric field strength [volts/m], $B$ is magnetic flux density [teslas] or [webers/m²]. $H$ is the magnetic field strength [amperes/m]. $J$ is the current density [amperes/m²]. $D$ is the dielectric displacement current or electric flux density in [coulombs/m²]. $\rho$ is charge density in [coulombs/m²].

The vector wave equation in the frequency domain (Helmholtz equation) for the electric field (Equation 1.9) is obtained by taking the curl of Maxwell’s second equation (Faraday’s induction law) for the electric field,

$$\nabla \times \nabla \times E = -\mu \frac{\partial}{\partial t} (\nabla \times H).$$

Applying the identity $\nabla \times \nabla \times A = \nabla (\nabla \cdot A) - \nabla^2 A$ after substituting 1.3(a) and applying the constitutive equations yields,

$$\nabla (\nabla \cdot E) - \nabla^2 E = -\mu \frac{\partial}{\partial t} \left( \sigma E + \varepsilon \frac{\partial E}{\partial t} \right).$$

The first term on the left hand side is the gradient of a scalar leaving,

$$\nabla^2 E = \mu \sigma \frac{\partial E}{\partial t} + \mu \varepsilon \frac{\partial^2 E}{\partial t^2}.$$  

The electric field has an $e^{i\omega t}$ time dependence, and its first and second derivatives are,

$$\frac{\partial E}{\partial t} = i\omega \varepsilon E e^{i\omega t} \text{ and } \frac{\partial^2 E}{\partial t^2} = -\omega^2 E e^{i\omega t}.$$  

Ignoring the time dependence and writing the wavenumber $k$ as,

$$k^2 = \omega^2 \mu \varepsilon - i\omega \mu \sigma.$$

Equation 1.6 is simplified giving the homogeneous Helmholtz equation for the electric field,
\[ \nabla^2 E + k^2 E = 0 \quad (1.9) \]

The homogeneous Helmholtz equation for the magnetic field is derived in a similar fashion and is given by,

\[ \nabla^2 H + k^2 H = 0 \quad (1.10) \]

The electromagnetic properties including conductivity, permittivity, and magnetic permeability are combined in the wavenumber, \( k \). \( k \) can be also be written as the difference between the real phase parameter, \( \beta [\) radians/m\(] \), and the imaginary attenuation constant, \( \alpha [\) nepers/m\(]) \).

\[ k(\omega) = \beta(\omega) - i \alpha(\omega) \quad (1.11) \]

\( \beta \) and \( \alpha \) are frequency dependent and are given by,

\[ \beta = \left(\frac{\omega}{c}\right) \sqrt{\frac{\sqrt{A^2 + B^2} + A}{2}} \quad (1.12) \]

\[ \alpha = \left(\frac{\omega}{c}\right) \sqrt{\frac{\sqrt{A^2 + B^2} - A}{2}} \quad (1.13) \]

Where,

\[ A = \mu_i \epsilon_r - \mu_r \left( \epsilon_r' + \frac{\sigma_s}{\omega \epsilon_o} \right) \quad (1.14) \]

And,

\[ B = \mu_i \epsilon_r' + \mu_r \left( \epsilon_r'' + \frac{\sigma_s}{\omega \epsilon_o} \right) \quad (1.15) \]

The wave equation solution for the electric field of a plane wave propagating at the speed of light, \((c = 3 \times 10^8 \) m/s\)) in direction \( x_i \) is

\[ E(x_i) = \hat{n}_{\perp x_i} E_0 \cos \left[ \omega \left( t - \frac{x_i}{c} \right) \right] \quad (1.16) \]

When the conductive and dielectric relaxation losses are taken into account the wave no longer propagates at \( c \), and the attenuation and phase parameters are incorporated. The wave equation solution becomes (Powers 1995),
\[ E(x_i) = \hat{n}_{\perp i} E_0 e^{-\alpha x_i} \cos(\omega t \pm \beta x_i). \]  

(1.17)

\( n \) is a unit vector perpendicular to the direction of propagation. The phase velocity and wavelength are related to frequency and the phase parameter,

\[ v = \frac{\omega}{\beta(\omega)} \]  

(1.18)

\[ \lambda = \frac{2\pi}{\beta(\omega)} \]  

(1.19)

When \( \frac{\sigma}{\omega \varepsilon_0} \leq 1 \), then the phase parameter can be approximated by,

\[ \beta(\omega) \approx \frac{\omega}{c} \sqrt{\varepsilon_r}. \]  

(1.20)

Substituting 1.20 into 1.18 and rearranging, the velocity [m/s] is simplified to,

\[ v = \frac{c}{\sqrt{\varepsilon_r}}. \]  

(1.21)

The loss tangent is a measure of phase shift between the electric and magnetic fields that occurs as an electromagnetic field propagates. It is equal to the cotangent of the phase angle between the displacement currents, \( \mathbf{D} \), and electric field, \( \mathbf{E} \), for the case of dielectric relaxation losses. In the case of magnetic and conductive losses it is the cotangent of the phase angle between the \( \mathbf{J} \) and \( \mathbf{E} \) and \( \mathbf{B} \) and \( \mathbf{H} \) fields. Conductive losses occur primarily as electromagnetic energy is converted to heat. Each loss tangent can be written for each type of loss independently (Powers 1995) or written together. At all frequency and conductivities the total electric loss tangent (including dielectric and conductive losses) is given by,

\[ \tan \delta = \frac{\varepsilon' + \frac{\sigma}{\omega \varepsilon_0}}{\varepsilon'}. \]  

(1.22)

Incorporating the magnetic loss tangent (\( \mu''/\mu' \)), the total loss tangent is written as,

\[ \tan \delta = \frac{\alpha}{\beta}. \]  

(1.23)

The loss tangent represents the loss per cycle in nepers/radian. It is used in Chapter 5 as an aid to analyzing the attenuation exhibited in the radar traces.
1.4 DNAPL in Public and Environmental Health

Non-aqueous phase liquids (NAPLs) are a class of volatile organic compounds (VOCs) that are immiscible with water. Examples include dry cleaning fluid (tetrachloroethylene or PCE), oil, oil based paint, solvent and fuel. When the density of these liquids is greater than that of water, they are categorized as DNAPLs (dense non-aqueous phase liquids). PCE is often found with other VOCs that are byproducts of the PCE degradation process (microbial degradation resulting in the loss of chlorine atoms), including TCE (trichloroethylene), dichloroethylene, carbon tetrachloride and vinyl chlorides (EPA 816-R-99-006, 1999). A PCE molecule contains two carbon and 4 chlorine atoms. Hence there are numerous synonyms including: perchloroethylene, PERC and tetrachloroethene (Lucius et al. 1992). The chemical used in this spill experiment was laundry grade PCE, and will be referred to from hereon as PCE.

An internet search for “PCE contamination” will generate over half a million results. Contaminated sites exist throughout the United States and encompass everything from local dry cleaners that have improperly disposed of small amounts of contaminated wastewater and chemicals to industrial and military sites where large scale contamination has occurred. PCE is used in some illicit methamphetamine production creating a new source of small scale contamination. PCE is one of 21 VOCs whose maximum concentration limit (MCL) is determined and regulated by the EPA under the Safe Drinking Water Act (SDWA). An EPA study published in 1999 found that PCE has been detected at concentrations greater than the allowed MCL (5 µg/L), in more than 1% of the U.S. surface waters and is one of five contaminants to exceed the MCL in more than 1% of U.S. ground water supplies (EPA 816-R-99-006, 1999). It is the second most commonly found contaminant in the industrialized world following TCE. PCE has a high toxicity and, based on animal testing, is likely a carcinogen (Lucius et al. 1992).

Negative effects of exposure to PCE, either with the chemically directly or its vapors, range from temporary physical symptoms like nausea and dizziness to permanent liver and nervous system damage.

The density of PCE allows it to sink into ground and surface waters limiting its volatilization. The low solubility of PCE (1500 mg/L in contrast with NaCl at 350,000
mg/L) provides the potential for long term contamination. The large number of contaminated sites creates the potential for widespread risk to drinking water supplies. As an illustration the amount of PCE necessary for contamination above the MCL in a volume of water equal to an Olympic sized (25 m x 50 m x 2 m deep) swimming pool is a mere 12.5 grams, less than 8 cm³. In saturated sand, with water filled porosity of 20%, that same 8 cm³ of PCE would contaminate a volume equal to five Olympic sized swimming pools, or 10 acres of ground 1 foot deep. The foregoing scenarios presume that the PCE is evenly distributed and mixed with the water. Due to the limited solubility, a more likely condition is a small entrapped pool of PCE, contaminating the ground water flowing across its surface for decades or perhaps centuries.

1.4.1 Theory of fluid flow in porous media

For a thorough understanding of the application of geophysics to environmental contamination problems it is helpful to have a basic understanding of fluid flow in the subsurface. Detailed explanations of hydrology and contaminant transport can be found in numerous texts including, Freeze and Cherry (1979), Fetter (2001), and Stephens (1995). A brief summary of the governing theory of fluid flow and contaminant transport is given in Illangasekare and Saenton (2004), with the most important relationships repeated here. Porous media are characterized by porosity and hydraulic conductivity. Porosity (ϕ) is the ratio of void volume to total volume,

\[ \phi = \frac{V_{\text{void}}}{V_{\text{total}}} \]  \hspace{1cm} (1.24)

Hydraulic conductivity (K) depends on the intrinsic permeability (k) of the medium, fluid density (ρ), dynamic viscosity (μ) and the gravitational constant (g).

\[ K = \frac{k\rho g}{\mu} \]  \hspace{1cm} (1.25)

Darcy’s equation relates fluid flux, q, to the gradient of the hydraulic head, h, via the hydraulic conductivity,
\[ q = -K \frac{dh}{dx}. \] (1.26)

Utilizing the expression for hydraulic conductivity Darcy’s equation can be written for a multiphase (\( \alpha \)) system as,

\[ q_\alpha = -\frac{k_{r,\alpha} k_{ij}}{\mu_\alpha} (\nabla p_\alpha - \rho_\alpha g \nabla z) \] (1.27)

\( k_r \) is relative permeability, \( z \) is elevation, \( p_\alpha \) is pressure of phase \( \alpha \) and \( k_{ij} \) is the permeability tensor. Darcy’s law can be used to calculate the pore velocity to give,

\[ \vec{v}_i = -K_{ij} \frac{\nabla h}{\phi}. \] (1.28)

The continuity equation for a multiphase system is,

\[ -\nabla \cdot (\rho_\alpha q_\alpha) + Q_\alpha = \frac{\partial}{\partial t} (\phi p_\alpha S_\alpha). \] (1.29)

Where, \( \alpha \) represents the phase in the multiphase system, and is typically wetting (water), non-wetting (NAPL) or vapor. \( Q_\alpha \) is the source-sink term, \( S_\alpha \) is the saturation for the \( \alpha \) phase (\( V_{sat}/V_{total} \)). \( \phi \) is porosity of the media, \( \rho_\alpha \) is the density of the \( \alpha \) phase fluid.

Combining the continuity equation and Darcy’s equation yields the generalized multiphase fluid flow equation,

\[ \nabla \cdot \left[ \frac{k_{r,\alpha} k_{ij}}{\mu_\alpha} \left( \nabla p_\alpha - \rho_\alpha g \nabla z \right) \right] + Q_\alpha = \frac{\partial}{\partial t} (\phi S_\alpha). \] (1.30)

The contaminant will move through the groundwater by advection, dispersion and a combination of other less significant reactive processes such as adsorption and biodegradation. Advection is the transport of the contaminant due to groundwater flow. Dispersion as discussed in this section is the mechanical mixing and molecular diffusion of the contaminant with the groundwater, it shouldn’t be confused with dispersion of an electromagnetic wave discussed in section 1.2.2. These processes form the advection-dispersion-reaction equation (Illangasekare, 2004),

\[ \frac{\partial (\phi c)}{\partial t} = \nabla \cdot (D_{ij} \nabla c - \phi \nabla \bar{c}) + \sum R_n, \] (1.31)

which describes the fate and transport of dissolved contaminants in groundwater. \( D_{ij} \) is the dispersion coefficient tensor, which describes dispersion of the solute in the
transverse and longitudinal directions. \( c \) is the solute concentration, and \( \Sigma R_n \) is the sum over the different reactive processes.

### 1.4.2 Behavior of DNAPL in unconsolidated sediments

The flow of a fluid in sediments is a function of the properties of the fluid, the properties of the solid, and their interaction. Fluid properties for the PCE include density, interfacial tension, viscosity, and solubility. Values for these are given in Table 1.2.

**Table 1.2 Physical Properties of Tetrachloroethylene (C\(_2\)Cl\(_4\))**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density 20°C</td>
<td>1.62 [g/cm(^3)]</td>
</tr>
<tr>
<td>Specific Gravity 15°C</td>
<td>1.6311</td>
</tr>
<tr>
<td>Absolute Viscosity 15°C</td>
<td>1.932</td>
</tr>
<tr>
<td>Interfacial Liquid Tension 25°C</td>
<td>44.4 [dyn/cm]</td>
</tr>
<tr>
<td>Surface Tension 20°C</td>
<td>32.86 [dyn/cm]</td>
</tr>
<tr>
<td>Water Solubility</td>
<td>1.5×10(^2) [mg/L]</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>178 [mm Hg]</td>
</tr>
<tr>
<td>Henry’s Law Constant</td>
<td>2.59×10(^{-2}) [atm·m(^3)/mol]</td>
</tr>
<tr>
<td>Organic Carbon Partitioning Coefficient</td>
<td>3.64×10(^2) [ml/g]</td>
</tr>
<tr>
<td>Octanol Water Partitioning Coefficient</td>
<td>3.98×10(^2) [ml/g]</td>
</tr>
<tr>
<td>Contact Angle PCE, clay substrate, aqueous phase liquid</td>
<td>23-48°</td>
</tr>
<tr>
<td>Contact Angle PCE, clay substrate, air</td>
<td>153-168°</td>
</tr>
</tbody>
</table>

(Lucius et al., 1992)

The physical properties of the media in the spill experiment are the chemical properties of the sands, clays and water, porosity, hydraulic conductivity, grain size and saturation. These are described in Chapter 2. Figure 1.1 is a sketch of the different states of a DNAPL in the subsurface. A spilled DNAPL migrates downward through the vadose zone and encounters the capillary fringe, the water table and then the saturated zone.
With a density of 1.6 g/cm³ PCE tends to migrate vertically through the saturated zone until it encounters less permeable boundaries, where it may pool or flow along the boundary until it can overcome the local entry pressure and breakthrough. In addition variations in spatial wettabiity, and physical and chemical heterogeneities will effect PCE entrapment and migration (Illangasekare et al. 1995, Kueper and Frind 1991). Therefore, although it is primarily gravity driven, PCE migration tends to be unpredictable, with pools, fingering into isolated ganglion and blobs, the norm. As a result, the flow is not always down-dip along boundaries and not always predicted by geology.

The average grain sizes within the layers in the tank will change due to the different clay-sand mixes. As a result the pore radius is largest in the clean sand layers and gets smaller as clay percentages increase. Consequently, the capillary pressure, $P_c$, which is inversely proportional to pore radius will vary according to the following relationship,

$$P_c = \frac{2\sigma \cos \theta}{r}.$$  \hspace{1cm} (1.32)
\( \theta \) is the contact angle, and \( \sigma \) is the surface tension of the fluid. Figure 1.2 is the capillary pressure curve showing the hysteresis between the displacement of water by non-wetting fluid followed by the drainage of non-wetting fluid and the imbibition of water. The upper curve represents the drainage of water (wetting fluid) as it is displaced by DNAPL (non-wetting fluid). At the beginning the sand is fully saturated with wetting fluid \( (S_{w}=1) \), the nonwetting fluid overcomes the displacement pressure \( (P_d) \), reaches the entry pressure \( (P_e) \) and begins to displace the water, continuing until the water is trapped in small pore spaces and can no longer be displaced, leaving a residual wetting

Figure 1.2 Capillary pressure \((P_c)\) curve for drainage showing displacement pressure \((P_d)\), pore entry pressure \((P_e)\), change in saturation with wetting fluid \((S_w)\) and residual saturation \((S_{wr})\) for the displacement of water with NAPL.
phase saturation (Swr). The lower curve is the drainage of the DNAPL. When the non-wetting fluid is draining and being displaced by water some of it will become trapped in the pore space leaving residual saturations that can occupy up to half of the pore volume. For smaller pore radii the drainage curves will shift up and to the right.

Within the sand tank, the less permeable boundaries occur at the clay layer interfaces where pore entry pressure increases due to the decrease in grain size and pore radius. The DNAPL flows along these boundaries until capillary pressure reaches entry pressure allowing it to breakthrough and continue its downward migration.

1.4.3 Environmental Science Investigations to quantify DNAPL volume

A DNAPL spill will leave a source zone in the subsurface that continues to generate mass flux. Monitoring a spill via dissolved concentrations present in screened wells provides little, if any, information about the entrapment architecture of the DNAPL source (Saenton and Illangasekare 2004). Saenton and Illangesekare (2004) hypothesize that the mass flux from the entrapment zone is controlled by the vertical distribution of mass flux. The method they propose to model the source zone may be less costly than currently used methods to quantify DNAPL saturations which typically employ partitioning tracer tests.

In a partitioning tracer test reactive and non-reactive tracers are injected into a contaminated area. The breakthrough of the reactive partitioning tracer is compared to the breakthrough of the non-reactive (conservative) tracer. The lag in breakthrough correlates to the saturation of DNAPL as given by the following expression (Moreno- Barbero and Illangasekasre 2005, Jin et al. 1995),

\[ s_N = \frac{R - 1}{R + K_p + 1}. \]  

(1.34)

Where, \( K_p \) is the dimensionless partition coefficient, and \( R \) is the retardation factor of the partitioning tracer, equal to the ratio of the average travel times of the reactive and non-reactive tracers \( (t_p/t_c) \).
Dai et al. 2001, used column experiments to evaluate the performance of partitioning and interfacial tracers for the characterization of NAPL volume. They found that interfacial and partitioning tracer breakthrough curves predict NAPL volumes adequately in the case of uniform residual saturation, but they under-predict the volume in pooled NAPL entrapments. Moreno-Barbero and Illangasekare (2005) further studied the performance of partitioning interwell tracer tests (PITT) in aquifers with geological heterogeneity and complex DNAPL architecture for predicting DNAPL saturations. Their multiphase flow simulations of synthetic aquifers demonstrate that the reliability of the PITT technique depends not only on DNAPL architecture and aquifer heterogeneity, but also on PITT design.

Additional methods to quantify NAPL volumes are necessary. Geophysicists can aid environmental scientists and the public by applying non-invasive detection methods to determine extents of contamination, as well as source zone entrapment architecture. The electrical properties obtained from the crosswell radar data in this experimental PCE spill offer another method for the quantification of the volume of entrapped DNAPL, in particular the high saturation DNAPL pools and in areas near monitoring wells where DNAPL tracer interaction may not be complete.
2.1 Experiment Design

Two PCE spill experiments were performed in a building at the University of California Berkeley, Richmond Field Station in Richmond, California. The first was in May of 2004, and the second in September, 2005. The experimental setup was nearly identical for both spills, with two important exceptions. First, in 2004 the PCE broke through a clay barrier a few hours into the spill, and settled at the bottom of the tank. It was difficult to remove this contaminated sand after the spill ended because the PCE was no longer isolated. To allow for easier collection of the PCE, should this premature breakthrough recur in 2005, a nonmetallic false bottom was installed over a layer of water several centimeters above the floor of the tank. Second, the spill rates and volumes were decreased to nearly 1/3 of their 2004 values for the 2005 experiment. The duration of the spill was increased in 2005 to 72 hours, as compared to the 24 hour spill in 2004, again to mitigate the risk of premature breakthrough which had occurred in the previous experiment. The other differences are minor and concern the thickness of layers and slight variations in the percent (by weight) of clay used. When there is a difference in one of these parameters between the 2004 and 2005 experiments, the value for the 2004 experiment is given in parenthesis immediately following the 2005 value.

A 2.4 m diameter × 2 m deep cylindrical fiberglass tank with an open top was used to contain the spill. The tank was filled with layers of clay and sand (Figure 2.1). Ninety-five centimeters (one meter in 2004) below the surface of the sand was a 100% kaolinite layer about 3 cm thick. The purpose of this layer was to trap the PCE.
Figure 2.1 Sketch of tank showing thicknesses of the different sand and clay layers used in the 2005 PCE spill experiment.
Overlaying this clay layer was a 30 cm thick, 5% (by weight) (6% by weight in 2004) calcium montmorillonite (SAz-1, Source Clays Repository 2001) mixed with 90% Unimin Ottowa silica sand with grain sizes between 600μm and 850μm. A 20 cm clay-sand layer with only 3% SAz-1 montmorillonite was on top of the 5% (6% in 2004) clay layer. Horizontally surrounding the clay-sand layers a thin plastic membrane stopped the lateral migration of PCE. This plastic barrier, along with the kaolinite layer, formed a cup within the tank. In plan view the diameter of this cup was approximately 1.2 m. Surrounding this cup and overlaying the clay-sand layers and underlining the kaolinite was the clean Unimin sand, 0.35 m (.47m in 2004) thick under the kaolinite, and 0.42 m (.53m in 2004) thick above the upper clay-sand layer. The tank was fully saturated with a 0.001 molar calcium chloride solution (CaCl₂aq). About 1 cm of water was kept on top of the surface. This level was maintained throughout the experiment by inserting a length of one inch diameter flexible tubing into the sand tank below the desired water table. A cylinder was attached to the opposite end of the tube. The open end of the cylinder was attached to the side of the tank so that top of the cylinder lined up with the desired water table. A container was placed under the cylinder to collect overflow (Figure 2.2). A drop in water level in the cylinder would indicate loss of water to evaporation. This water could be replenished as necessary and any excess came out quickly into the overflow container. During the experiment water was displaced as PCE was injected into the tank. A volume of water equal to what was displaced went directly into the overflow container. A measure of the volume of the water displaced was equivalent to the volume of PCE injected (Aldo Mazzella, personal communication). The PCE was injected through a vertical tube into the uppermost layer of sand at an elevation approximately 20 cm below the water surface. A pump held the injection rate constant, at 5.5 ml/min for 72 hours (60 ml/min and 24 hours in 2004). During this time a total of 23.8 liters (85 liters in 2004) of PCE was spilled into the tank. Figures 2.3(a) and 2.3(b) show the volume of PCE spilled versus time.

Several wells penetrated the layers in the tank. Two of these, W1 and W2, were used for the crosswell radar monitoring, one for the transmitting antenna and one for the receiver. For most measurements, the transmitter was placed in well W1 and the receiver
Figure 2.2 Manometer for maintaining water level throughout spill experiment.
Figure 2.3 (a-upper) and (b-lower) Cumulative PCE injection rates for the 2004 and 2005 experiments.
in well W2. The wells were 0.75 meters apart and 7.6 cm diameter. For 2005, each antenna was fastened to the end of a 2 m long × 2” diameter PVC pipe. The PVC pipe-antenna assemblies were held concentric within the wells by sleeves of radio frequency absorbing material (to help minimize noise due to cable and air waves exhibited in the 2004 data). The antennas could be accurately positioned vertically using a locating pin inserted through radial holes in the PVC pipes and resting in notches at the top of each well. The locating holes in each PVC pipe were evenly spaced at 2.5 cm. Thus, the vertical antenna positioning was in 2.5 cm increments (3 cm in 2004). Figure 2.4 shows the tank, wells, transmitter and platform. To reduce crosstalk between the transmitting and receiving cables, they were suspended perpendicular to one another as they came out of the wells.

2.2 Instrumentation

The radar pulses sent to the transmitting antenna were generated by a Power Spectra PGS405 device, which was triggered from a 20 kHz free-running clock oscillator. The receiving antenna signal was passed through an RF amplifier before being sent to the Tektronics TDS 820 sampling oscilloscope (Figure 2.5). Measurements were stacked and averaged a user specified number of times to give each final waveform. The system was triggered by the operator to acquire the waveform and cause the PGS405 and TDS 820 to pulse and record. An adjustable delay on the scope was set to allow for the signal propagation delays. Additional delays were accounted for using air calibration measurements. The waveform data from the TDS820 scope was sent over a GPIB interface to a computer (PC). The PC, utilized a program written by Craig Moulton (USGS) to store and display the waveforms. The program also performed sequencing tasks during each cycle including, incrementing the antenna positions, acknowledging move confirmation, and arming the scope to acquire data.

The antennas used for the acquisition were vertical electric-dipoles made from semi-rigid solid copper sheathed coaxial cable without an insulating jacket. Dave Wright
Figure 2.4 Photograph taken during data acquisition showing tank, wells, transmitter cable and platform.
Figure 2.5 Instrumentation includes TDS820 oscilloscope, Power Spectra PGS405 pulser, keyboard for operator input, oscillator, voltage regulator and power supply, Tx, trigger and Rx cables, RF amplifier, monitor screen displaying waveform. The computer, with the acquisition and storage software, is located under the shelf holding the power supply.
(USGS-Denver) provided the electrical engineering expertise to suggest a design for the prototype using materials that were on hand. Dimensional sketches were developed by the author and provided to Ray Hutton (USGS-Denver) who constructed the antennas. Carl Stoddard, a machinist at the USGS constructed the cases. A short aperture was chosen in order to provide a high frequency signal within a saturated sand environment. The transmitter and receiver are identically configured. Figure 2.6 shows a cross section of the antenna, and a photograph of the antenna with the case removed. Ferrite beads cover the upper part of the coax leaving the transmitting portion of the antenna to be approximately 7 centimeters with a 4 mm gap cut into the copper sheath at the center point. The 32mm portion of antenna beyond the gap is soldered so that the sheath is in contact with the center wire. The radius of the antenna is 1.5 mm. The pulse is sent to the transmitting antenna through a shielded coaxial cable, designed for the transmission of high frequencies. The cable attaches to the antenna above the ferrites. The receiving antenna is also attached to its shielded coaxial cable above a set of ferrite beads. In 2005, additional ferrite beads were incorporated to help attenuate any signal that traveled back up the antenna cables. This modification was implemented to help minimize air and cable waves identified in the data from the 2004 experiment.

The pulse generated by the Power Spectra PGS405 had a rise time of 230 ps, a peak output of 400 Volts and a 1.3 ns pulse width at half amplitude (Abraham 1999). The amplitude of this pulse as a function of time is plotted in Figure 2.7. A typical air calibration wavelet and its associated frequency spectrum, are shown in Figures 2.7 and 2.8 respectively. The air calibration wavelet has a center frequency of 1.4 GHz with a resulting wavelength of 0.21m. Unfortunately, the amplitudes were clipped on the air calibration data, but this was not noticed at the time these data were acquired. This shortcoming was not detrimental to the experiment however, because the primary use of these calibrations was to determine the time lag and number of samples to shift each data record.
Figure 2.6 Photograph of the interior (the antenna was disassembled) and a cross section sketch of the borehole radar antenna used in the PCE spill experiment. The transmitting and receiving antennas were identical.
Figure 2.7 Typical air calibration trace showing clipping of the amplitude peaks. This was not apparent during the data acquisition. Radar traces acquired in air have larger amplitudes than those taken in a sand medium. The data acquired within the sand tank were not clipped.
Figure 2.8 Frequency spectra of typical air calibration. Note that the air calibrations were clipped at their highest amplitude. The center frequency represented above is accurate, but the magnitudes are lower than would be expected from an unclipped waveform.
2.3 Data Acquisition and Processing

A zero offset gather (ZOG) is sometimes referred to as a common offset gather or COG. A COG is a set of radar trace data recorded while maintaining a constant separation distance between transmitting and receiving antennas. A ZOG is a set of radar trace data recorded while the transmitter and receiver are at equal elevations. The set of measurements is acquired by simultaneously moving the transmitter and receiver in equal increments to maintain the ZOG or COG geometry. This provides a data set giving one-dimensional (vertical) information about the average properties between the two wells. ZOG and COG are often used interchangeably. In this experiment, the transmitting and receiving antennas were in vertically oriented wells (0.75 m apart), and at equal elevations. Zero offset gather surveys were acquired before the spill began, every twelve hours during the spill, and every 24 hours after the spill had stopped until there were no observable changes in the traces. A typical ZOG consisted of 45 traces, one trace every 0.025 m (0.03 m in 2004) depth. Each trace had a 20 picosecond (40 ps in 2004) sample interval and a length of 100 nanoseconds giving 5000 samples/trace (2500 samples/trace in 2004). The data were stacked 10 times and the average was recorded as the trace. The scope was set to begin recording about 110 ns after the beginning of the pulse. The first trace was recorded 0.075 m (0.137 m in 2004) below the saturated sand surface; the depth of the last trace in each ZOG was 1.175 m (1.457 m in 2004) below the surface.

In addition to the ZOG data recorded, two full common source gather (CSG) surveys were acquired during each experiment. The first set prior to the start of the spill and the second set after the spill had stopped. Each CSG consisted of positioning the transmitting antenna at a single depth in the transmitting antenna well and recording the signal at all 45 depths in the receiving antenna well. More than ten hours were necessary to acquire each common source gather data set. In 2004, in addition to the two full CSG surveys, several other CSG data sets were acquired at approximately twelve hour intervals during and after the spill. These data sets consist of 14 or 16 transmitter and receiver locations with a vertical spacing of 0.06 m. It took about 4 hours to acquire one
of these less spatially dense data sets. Table 2.1(a) and 2.1(b) show the different ZOG and CSG data sets acquired during the 2004 and 2005 experiments.

**Table 2.1(a)** Type and number of data sets acquired in 2005

<table>
<thead>
<tr>
<th>Time</th>
<th>Zero Offset Gathers</th>
<th>Common Source Gathers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prespill</td>
<td>2 – 24 hours apart</td>
<td>1 (48 Tx, 48 Rx)</td>
</tr>
<tr>
<td>+03 Hours</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>+13 Hours</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>+25 Hours</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>+37 Hours</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>+49 Hours</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>+61 Hours</td>
<td>2 – for repeatability</td>
<td>--</td>
</tr>
<tr>
<td>Postspill +01 Hours</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Postspill +13 Hours</td>
<td>2 – for repeatability</td>
<td>--</td>
</tr>
<tr>
<td>Postspill +36 Hours</td>
<td>2 – for repeatability</td>
<td>1 (43 Tx, 43 Tx)</td>
</tr>
<tr>
<td>Postspill +63 Hours</td>
<td>1</td>
<td>--</td>
</tr>
</tbody>
</table>

**Table 2.1(b)** Type and number of data sets acquired in 2005

<table>
<thead>
<tr>
<th>Time</th>
<th>Zero Offset Gathers</th>
<th>Common Source Gathers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prespill</td>
<td>2</td>
<td>1 (45 Tx, 45 Rx)</td>
</tr>
<tr>
<td>+01 Hours</td>
<td>--</td>
<td>1 (14 Tx, 14 Rx)</td>
</tr>
<tr>
<td>+10 Hours</td>
<td>--</td>
<td>1 (16 Tx, 16 Rx)</td>
</tr>
<tr>
<td>Postspill +43 Hours</td>
<td>--</td>
<td>1 (16 Tx, 16 Rx)</td>
</tr>
<tr>
<td>Postspill +61 Hours</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>Postspill +74 Hours</td>
<td>1</td>
<td>1 (45 Tx, 45 Rx)</td>
</tr>
</tbody>
</table>

In addition to the data sets shown in Table 2.1, air calibration measurements were made prior to, and sometimes during and after, taking ZOG and CSG measurements. The decision to obtain additional air calibration data was typically based on the duration of the primary data acquisition session. For shorter session, air calibrations were usually
recorded at the beginning and the end. For longer CSG measurements, calibrations were recorded roughly every three hours. For analysis, the data trace should only include information about the media of concern. However, the raw data include additional time due to instrumentation. To account for the travel time of the pulse and returning signal as it passed through the electronic instrumentation and cabling, the traces were shifted to zero time based on delays established from the air calibration data. This was accomplished by subtracting the travel time of an electromagnetic wave in air ($V_0 = 3.0E8 \text{ m/s}$) as it traverses the 0.75 m (0.762 m in 2004) separation between transmitter and receiver, from the air calibration time. The calculated travel time for the 0.75 m separation is 2.5 nanoseconds. The initial data show the first arrival at approximately 2.7 or 2.8 nanoseconds. This extra 0.2 or 0.3 nanoseconds is thus removed from the beginning of the trace. Depending on the data set, the corresponding average air calibration, the trigger delay, and the sample interval used, there were usually 9-15 samples that were due to cabling and instrumentation. To keep the length of the traces the same between data sets, zeros are added to the end of each trace in a number equal to the number of samples removed from the beginning of the trace.

2.4 Electrical Property Measurement Results

The electrical properties of the sand, clay, fluids and mixtures that were used in the sand tank were measured in the laboratory by Horton (2005, unpublished data). MC-50 resistivity is in $\Omega \text{m}$ measured in the BBL MC-50 three electrode parallel plate sample holder. RDP is relative dielectric permittivity measured in the MC-50 sample holder. 2-electrode resistivities are in $\Omega \text{m}$ measured in a 1"x3" sample holder. The samples consisted of 100% Unimin sand, 3% clay (3% SAz-1 clay available from Source Clays Repository, dry wt.) mixed with Unimin sand, 6% clay (6% SAz-1 clay, dry wt.) mixed with Unimin sand and 100% pyrophillite clay (non-swelling, limited cation exchange) containing a minor amount of kaolinite and a trace of smectite. The first three were
saturated with 1.0 mM CaCl\textsubscript{2} solution. These properties are summarized in Tables 2.2(a) and 2.2(b).

**Table 2.2(a) Resistivity of water, sand and clay mixtures (Horton 2005, pers. comm.).**

<table>
<thead>
<tr>
<th>Sand-Clay-Water Mixture</th>
<th>Electrical Resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimin Ottawa sand fully saturated with deionized H\textsubscript{2}O</td>
<td>290 Ω m</td>
</tr>
<tr>
<td>3% Ca clay-sand fully saturated with deionized H\textsubscript{2}O</td>
<td>110 Ω m</td>
</tr>
<tr>
<td>Deionized H\textsubscript{2}O</td>
<td>6700 Ω m</td>
</tr>
<tr>
<td>Deionized H\textsubscript{2}O in place with clean sand</td>
<td>40 Ω m</td>
</tr>
<tr>
<td>Deionized H\textsubscript{2}O in place with 3% Ca clay-sand</td>
<td>17 Ω m</td>
</tr>
</tbody>
</table>

**Table 2.2(b) Relative Dielectric Permittivity and Resistivity for laboratory measurements of sand and clay with residual PCE saturation (Horton 2005, pers. Comm.).**

<table>
<thead>
<tr>
<th>Sample</th>
<th>MC-50 Resistivity</th>
<th>2-Electrode Resistivity</th>
<th>RDP</th>
<th>PCE residual saturation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unimin Sand</td>
<td>73.1</td>
<td>178</td>
<td>23.9</td>
<td>16</td>
</tr>
<tr>
<td>3% Clay</td>
<td>27.4</td>
<td>46.7</td>
<td>23.4</td>
<td>9.5</td>
</tr>
<tr>
<td>6% Clay</td>
<td>18.7</td>
<td>34.2</td>
<td>31.4</td>
<td>5.4</td>
</tr>
<tr>
<td>100% Clay</td>
<td>20.6</td>
<td>--</td>
<td>7.6</td>
<td>--</td>
</tr>
</tbody>
</table>
CHAPTER 3

ONE DIMENSIONAL PCE SATURATION MODELING

3.1 Zero Offset Gather Results

Zero offset gather data provide one dimensional (depth) information about the medium between the two wells. The zero offset gather traces acquired during the 2005 spill are plotted in Figure 3.1 (a-k). The 48 radar traces in each record show the energy arriving at each depth between 5 and 15 nanoseconds. Figures 3.1(a) and 3.1(b) are the data records taken before the spill and 63 hours after the spill had ended. In the upper 20 cm of the sand tank, the direct arrival is followed by a second arrival representing reflections from the water-air interface. In Figure 3.1(a) (pre-spill) the highest amplitude arrivals are near the top and bottom of the tank. Some lower amplitude waves arrive at the top of the 3% clay, the top of the 5% clay and at the 100% clay layer. The first arrivals begin at about 10 nanoseconds.

The postspill record (Figure 3.1(b)) shows low amplitude arrivals at the bottom of the 5% clay and around the 100% clay layer. The 3% clay and upper sand layer traces are similar to those seen in the pre-spill record. The arrival times within the 3 and 5 percent clay layers and around the 100% clay layer have decreased in the post-spill data by as much as 4 nanoseconds. The first energy in the 5% clay layer is arriving near 10 nanoseconds before the spill began, and at approximately 7 nanoseconds after the spill had ended.

Figures 3.1(c) -3.1(k) show the sequence of traces acquired at 12 hour intervals during the spill and at 24 hour intervals after the spill had ended. As the spill progressed, the velocity increased. The first arrival times decreased due to the infiltration by low permittivity PCE.
Figure 3.1 (a) and (b) Common offset gather data acquired before and after 2005 PCE spill.
Figure 3.1c,d and e (left to right). Common offset gather data acquired during 2005 PCE spill at 3, 13 and 25 hours after spill began.
**Figure 3.1 f, g and h (left to right).** Common offset gather data acquired during 2005 PCE spill at 37, 48 and 61 hours after spill began.
Figure 3.1 i,j and k (left to right). Common offset gather data acquired after 2005 PCE spill at 1, 13 and 36 hours after spill ended.
The wavelets near the surface and below the 100% clay layer (from 0.00 to -0.15 m and below -1.00 m) aren’t affected by the PCE and exhibit consistent shapes and arrival times before and after the spill. Where the PCE has accumulated, there is a noticeable change in the shape of the arriving wavelets. The wavelets above the 100% clay layer decrease in amplitude and show dispersion as the spill progresses. This is due to the scattering of energy by heterogeneities that form as the PCE migrates into fingers, blobs and pools. This is discussed in greater detail in Chapter 5. The traces in Figures 3.1 (e, g, and i) exhibit a high amplitude low frequency noise of unknown origin. The only common factor between these three noisy records is that they were all acquired in the late evening around 10 p.m. Although it is less than ideal, the noise didn’t have a significant negative impact on the interpretation of the results.

Below the 100% clay layer the traces are consistent and repeatable throughout the entire spill. It is the first arrivals of waves traveling through the spill cup that change in time and shape. Above the 100% clay layer, a faster velocity zone moves downward throughout the duration of the spill. Not only are the travel times in the data different but the data exhibits dispersion over time. This can be due to interference, constructive or destructive, and it can be a result of the scattering losses discussed in Chapter 1.

3.2 Modeling One Dimensional Porosity and PCE Saturation

The process for modeling the non-wetting fluid saturation, or in this case PCE, begins with picking the first arrival travel times. These times are converted to velocity and then to permittivity. Next, application of the Bruggeman Hanai-Sen (BHS) mixing formula yields porosity of the sand/clay matrix. Finally PCE saturation is approximated by using a modified form of the BHS formula (Sneddon 2003). As discussed in Chapter 1, electrical properties control the velocity of the electromagnetic wave between the transmitting and receiving antennas. The electrical properties can be correlated to porosity and saturation by non-wetting and wetting fluids through various mixing formulas (Sen et al. 1981).
3.2.1 Velocity and permittivity

To calculate the velocity of the radar waves traveling in the tank, the travel time of the first arrival of energy at the receiver is picked for each trace. Due to the small separation distance between transmitter and receiver relative to the borehole radius in this experiment, it is necessary to modify the simple velocity formula to account for the borehole and minimize error in the resulting wave velocity. Equation 3.1 gives the velocity ($v$) in terms of first arrival travel time ($t_{fa}$), separation distance between the axes of the two antennas ($d_{Tx-Rx}$) and borehole radius ($R_{borehole}$).

$$v = \frac{d_{Tx-Rx} - 2R_{borehole}}{t_{fa} - 2\frac{R_{borehole}}{c}}$$  (3.1)

Neglecting the borehole radius consideration can result in permittivity values that are too low, by as much as 20%. Permittivity is related to velocity by Equation 3.2 which assumes that magnetic permeability is that of free space and conductivity is less than 28 mS/m at 500 MHz. When the medium is more conductive, or at lower frequencies the expression is more complicated (Powers 1995, p.33).

$$\sqrt{\varepsilon_r} = \frac{c}{v}.$$  (3.2)

$\varepsilon_r$ is the unitless relative dielectric permittivity, $c$ is the velocity of an electromagnetic wave in a vacuum or of light in free space ($3\times10^8$ m/s), and $v$ is the velocity of an electromagnetic wave in the medium between the two antennas, in meters per second. Before and after spill profiles of the RDP calculated from the 2005 zero offset gathers are shown in Figure 3.2. Figure 3.3 shows how the permittivity profile changed during the spill. Before the spill began the RDP is approximately 20, slightly lower in the clay layers possibly due to non-polarizable clay bound water molecules or air trapped within those layers. After the spill, the permittivity has stabilized near 8, and the profile demonstrates the pooling of the PCE on top of the 100% clay barrier. The experiment was designed so that the permittivity would remain constant below the 100% clay layer, however, the profiles show decreasing RDP below this barrier. This is an Artifact due mostly to aperture of the antennas and their interaction with energy that
Figure 3.2 Pre and post-spill relative dielectric permittivities from the 2005 PCE spill. The curve on the right is an average from ZOG measurements taken before the spill began. The group of curves on the left shows how the permittivity quickly stabilized once the spill had ended. Nevertheless, data sets were acquired as long as 62 hours after PCE spill stopped.
Figure 3.3 Relative dielectric permittivities from the 2005 Zero Offset Gather data acquired during the PCE spill. As time PCE is spilled the RDP decreases from slightly less than 20 in the to less than 9 in the 5% clay. The permittivity is fairly consistent in the clean sands above and below the clays where the PCE didn’t accumulate. The low RDP values present below the 100% clay layer are likely due to the aperture of the antennas and signal leakage around that barrier.
travels above and below the clay barrier (Olhoeft, pers.comm.). Additional minor contributing factors to the artifact are: trapped air below the clay layer that caused a decreased RDP; the low permittivity of the 100% clay layer, (the clay used (SAz-1) in the first Richmond PCE spill has a relatively low permittivity, and it doesn’t form a polarizable electric double layer, Horton, personal communication); simple dielectric mixing between the clay, sand and water; hydration of the clay that decreases the amount of polarizable water molecules.

The RDP from the 2004 zero offset gather measurements is shown in Figure 3.4. There were two pre-spill measurements followed by one taken +9 hours after the spill ended and another one +56 hours after the spill had ended. As in the 2005 profiles, the plots show lower RDP caused by pooling of PCE at the interfaces between layers with different clay content. There are also decreases in RDP that are artifacts from leaking signals around the 100% clay layer. However, it was in this (2004) experiment that the PCE broke through the 100% clay layer and migrated into the clean sand layer at the bottom of the tank. The +56 hour plot may be exhibiting lower permittivity due to the breakthrough, in addition to antenna signal leakage. Below the 100% clay layer, the RDP for the 2004 +56 hour plot is slightly smaller and less smooth than the RDP for any of the 2005 ZOGs.

### 3.2.2 Porosity and PCE saturation

The method chosen for determining porosity and PCE saturations is based on recursive application of the Bruggeman-Hanai Sen (BHS) mixing formula. This follows the work of Sander (1994), and Sneddon (2003), who showed that the BHS model can be applied to two phase fluid mixtures to predict porosity and DNAPL saturations. Applying the BHS model this way is not limited to the one dimensional data of the zero offset gathers. In Chapter 4 it is applied to the inverted common source gather data to get an estimate of PCE saturations in two dimensions. Other models for estimating moisture content are often used, including the complex refractive index method (CRIM
Figure 3.4 Relative dielectric permittivity from the 2004 Zero Offset Gather data. The first two curves on the right (overlaying one another) are from the radar measurements taken before the spill began. The data that made the two curves to the left were taken 9 hours and 56 hours after the spill had ended. The 9 hour curves (circles) tends to show pooling at interfaces. The 56 hour curve has an increased RDP.
model) and Topp’s equation, (Binley et al. 2001). Alumbaugh et al. (2002), found that Topp’s empirical equation overestimated moisture contents in a vadose zone study. They recommended developing a site specific relationship between velocity and moisture content, and found that problems with values from Topp’s equation are likely due to higher dielectric permittivity present in saturated clays and organic matter found within the vadose zone. The CRIM model, when applied to this experiment exhibited a tendency to predict non-wetting saturations somewhat too high to be physically realistic (>60%).

It has been demonstrated that the BHS mixing formula is a reliable model to apply at radar frequencies and when the composite mixture contains more than two phases (Sneddon 2003). The results of the work presented here confirm this by producing physically realizable PCE saturations, and saturation profiles that are in agreement with the controls of the spill experiment. The main caveat in applying BHS at radar frequencies is the assumption that there is no interaction between the elements of the composite. The first step is to use the permittivity values of the pre-spill zero offset gathers in the first iteration of the BHS mixing formula to calculate porosity,

$$\phi = \frac{\varepsilon^*_{\text{matrix}} - \varepsilon^*_{\text{comp}}}{\varepsilon^*_{\text{matrix}} - \varepsilon^*_{\text{fluid}}} \left(\frac{\varepsilon^*_{\text{fluid}}}{\varepsilon^*_{\text{comp}}}\right)^C,$$

(3.3)

where \(\phi\) = fractional porosity, \(\varepsilon^*_{\text{fluid}}\) is complex relative dielectric permittivity of the fluid, \(\varepsilon^*_{\text{matrix}}\) is complex relative dielectric permittivity of the matrix, \(\varepsilon^*_{\text{comp}}\) is complex relative dielectric permittivity of the composite mixture and \(C\) is a shape factor set equal to 1/3 required for the assumption of spherical grains. In the first application for determining the porosity throughout the tank, the values used in Equation 3.3 are as follows: the matrix permittivity is 4.5, the fluid is water with a permittivity of 81, and the composite permittivity is the RDP calculated from Equations 3.1 and 3.2 using the prespill first arrival times and assuming zero imaginary component.

Figure 3.5 is adapted from Sneddon 2000. It shows schematically the process used to calculate porosity and PCE saturations from permittivity measurements. Figure 3.5(a) is a plot of BHS mixing formula curves. For the upper curve, water was used as the fluid, sand as the matrix, and the composite permittivity was calculated from
Figure 3.5 (a) and (b) BHS Model Curves for water, sand and PCE as individual end members in the formula (a) and for water-sand and sand-PCE mixtures as end members in the formula (b). Also see Sneddon 2000, Figure 1.
Equation 3.2. The lower curve is calculated in an identical fashion, but uses PCE (instead of water) as the fluid. The porosity is then used to find the permittivity of the sand-water and sand-PCE end members ($\varepsilon_{\text{sand-water}}$ and $\varepsilon_{\text{sand-PCE}}$). Their values are obtained by rearranging Equation 3.3 and solving for the roots ($1/C$) at any given porosity. They also could be estimated graphically. The end members are shown on plot 3.5(a and b) for a porosity of 31%. In Equation 3.4, the saturation of PCE ($S_{\text{PCE}}$) is analogous to porosity ($\phi$). $\varepsilon_{\text{sand-PCE}}$ is substituted for $\varepsilon_{\text{fluid}}$, $\varepsilon_{\text{sand-water}}$ becomes the matrix. $\varepsilon_{\text{comp}}$ is calculated by Equation 3.2, and $C$ is the same shape factor. The BHS curve resulting from Equation 3.4 is plotted in Figure 3.5(b). In Figure 3.5(a) the horizontal axis is porosity, while in Figure 3.5(b) it becomes PCE saturation ($S_{\text{PCE}}$). The \textit{matlab} routines for performing these calculations are included in Appendix B.

$$S_{\text{PCE}} = \frac{\left(\varepsilon_{\text{sand-water}} - \varepsilon_{\text{comp}}\right)\left(\varepsilon_{\text{sand-PCE}} / \varepsilon_{\text{comp}}\right)}{\varepsilon_{\text{sand-water}} - \varepsilon_{\text{sand-PCE}}}$$

(3.4)

The PCE saturation values during and after the 2005 spill are plotted in Figures 3.6 and 3.7. The end-members ($\varepsilon_{\text{sand-water}}$ and $\varepsilon_{\text{sand-PCE}}$) were re-calculated for each porosity, representing the different layers within the tank. The behavior of the curves is as might be expected from the permittivity curves. In the three hour data, there is apparent pooling at the clean sand – 3% clay-sand interface. By 12 and 25 hours the PCE has overcome the entry pressure required to penetrate the 3% clay-sand and pools on top of the 5% clay-sand. By the 37th hour, the PCE has broken through the 5% clay-sand barrier and pools on top of the 100% clay layer, where it settles after the spill has stopped. The PCE seems to stop its movement by 36 hours after the spill ended. Figure 3.8 are the saturation curves for the 2004 data. As in the permittivity plots, the PCE does go to a slightly greater depth (below the 100% clay layer), demonstrating the detection of the breakthrough that occurred during that experiment. The curves also exhibit the expected pooling at the clay-sand interfaces.
Figure 3.6 PCE saturations during the 2005 spill, showing the expected pooling and breakthrough at the clay and sand interfaces. At +3 hours into the spill, PCE has begun to saturate the clean sand and 3% clay, with $S_{PCE}$ approaching 0.1. By the end of the spill $S_{PCE}$ is greater than 0.45 in the 5% clay. The higher saturations at the interfaces indicate pooling of PCE prior to its breakthrough into the next layer.
Figure 3.7 PCE saturation after the 2005 spill. Two measurements were taken at +13 hours, two at +36 hours and final one obtained 62 hours after the spill had ended.
Figure 3.8 PCE saturation within the tank calculated from 2004 Zero Offset Gather data using the BHS mixing formula. The data were taken 9 hours and 56 hours after the spill had ended. The nine hour curve shows pooling at interfaces. The 56 hour curve has an increased RDP.
3.3 **Volume of Investigation**

In these one dimensional results, all of the calculated velocities, permittivities and PCE saturations are representative of an average of the material intercepted as energy travels from the transmitter to the receiver. The path that energy travels between the antennas is more complex than a straight ray between the center points of the two antennas. Signals are being transmitted and received along the entire length of the antenna. Energy is scattered, focused and defocused along its path between the antennas whenever there is a velocity contrast, in addition to the conductive, magnetic and dielectric relaxation losses that can occur with changing electrical properties. Ray theory is an approximation that assumes the ray path is an integral of velocity along a straight line between the transmitter and receiver. The validity of this assumption depends upon the frequency. For the high frequency of this radar system it is a good first order approximation.

Even for the two dimensional case presented in Chapter 4 where the rays are allowed to bend, the ray segments are still considered to be straight between the cell boundaries of the 2-D model. Realizing that the straight ray path is a limiting assumption, two common methods exist for looking at the region, or volume of investigation, that is actually “seen” by the electromagnetic waves, antenna radiation patterns (ARP), and Fresnel volumes.

3.3.1 **Antenna radiation patterns**

Mike Powers (1995) demonstrated the relationship between antenna radiation pattern changes and variations in $\sigma$ and $\varepsilon$. His work shows that higher permittivity will cause an elongated pattern, while increasing conductivity causes both an elongated pattern and smoothing of the lobes. Two (pre-spill and post-spill) normalized antenna radiation patterns were calculated for the 2005 common source gather data. These are plotted for each transmitter depth in Figures 3.9(a)-3.9(d) with the label at the vertical axis indicating the depth of the transmitter. The highest point on each pattern is the
normalized signal received at .075 m below the surface (the shallowest receiver position). The lowest point on each pattern is the signal recorded at the deepest receiver position (-1.275 m). The horizontal axis is the normalized power at the receiver. The antenna radiation patterns (solid lines) present before the spill began, exhibit a focused beam of energy, corresponding to larger permittivities. The decreasing permittivity, and to some extent the increasing resistivity, after the spill (dashed lines) produces a broadened pattern with less energy in the horizontal direction and more energy scattered to the receiver located above the transmitter. A small lobe begins to protrude in the -0.525 m pre-spill ARP. It continues to grow until the -0.650 m ARP where the transmitter is at the interface between the 3 and 5% clay. The lobe reappears at -0.750 m getting larger until it reaches the -0.925 m ARP, where the transmitter is at the 100% clay layer. Both lobes demonstrate a focusing of energy, perhaps even a wave-guide at these sand-clay interfaces prior to the PCE spill. The amplitude of the radiation patterns is slightly less in the horizontal direction (Figures 3.9 b and c) for the transmitter and receiver positions above the clay barrier (-.55 m to -.975 m). However there is an increase in the energy postspill for the receivers in the upper part of the tank (receivers above transmitters). When the transmitter location is near the surface (Figure 3.9 a) or is .950 m or more below the surface (Figure 3.9 d), which corresponds to the 100% clay layer, there is little variation.

When the transmitter is located below the 100% clay layer, both the pre-spill and post-spill ARPs exhibit a strong elongated lobe of energy being received below the clay layer. Very little energy is being received at locations above the 100% clay layer. A matlab routine for calculating the antenna radiation patterns of a crosswell radar data set is included in Appendix B.

### 3.3.2 Fresnel volume and ellipse

The Fresnel volume provides a better approximation to an actual wavepath than ray theory allows (Spetzler and Snieder 2004) and Johnson et al. 2005). Waves are comprised of a bandwidth of frequencies that will propagate at different velocities.
Snell’s Law says that waves will be reflected and refracted at different angles depending upon their velocity. The result is group of wave paths that move through a finite volume, instead of single ray path traveling along a straight line or series of straight line segments between transmitter and receiver. The first order Fresnel volume, an ellipsoid, can be determined from the separation between the transmitter and receiver and the traveltime of the first arriving wavelet. The two focal points ($F_1$ and $F_2$) of the Fresnel ellipse (Figure 3.10) are defined by the locations of the transmitter and receiver. In a first order Fresnel volume, the lengths of the minor axes are related to the time ($\Delta t$) between the first break ($t_{s-r}$) and the first zero crossing ($t_{fv1}$) of the first arriving wavelet (Figure 3.10 adapted from Johnson et al., 2005). The Fresnel volume velocity ($v$) is estimated from the time of the first break ($t_{s-r}$) and the distance between source and receiver. The distance $b$ is given by, $b = v\Delta t$ where, $\Delta t = t_{fv1} - t_{s-r}$.

The area of an ellipse is given by $A=\pi(x_1)(x_2)$, and the volume by, $V=\frac{4}{3}\pi(x_1)(x_2)(x_3)$. ($x_1$) is $\frac{1}{2}$ the length of the major axis. ($x_2$) and ($x_3$) are $\frac{1}{2}$ the length of the two minor axes of an ellipsoid. In Figure 3.10, $x_1 = b/2 + c$ and $x_2 = b$. The same permittivity decrease that caused a broadening of the antenna radiation pattern also produces a broader radar pulse and larger Fresnel volume. The Fresnel volume becomes larger as velocity increases during the PCE spill and it can be used to approximate the volume of PCE based on the estimated PCE saturations. Although the one-dimensional zero offset gather data limit the accuracy in this experiment, the concept could be extended to the case where data were acquired in three dimensions.

### 3.3.3 Comparison of Fresnel volume with PCE volume

Extrapolating the volume of spilled PCE from estimates of PCE saturations requires information in three dimensions. The one-dimensional zero offset gather data and the two dimensional common source gather data (discussed in Chapter 4) can’t provide an accurate PCE volume, but the methods described below could be applied to a problem in which three dimensional data are available. Keeping in mind that the Fresnel volume is the volume investigated by the radar waves, and it may be smaller or larger
Figure 3.9 (a) Normalized antenna radiation patterns from the 2005 CSG data 0.075 m → 0.350 m below the surface. The horizontal axis is normalized amplitude. The transmitter position is indicated on the vertical axis. Receivers are positioned every .025 m between -.075 m and -1.125 m.
Figure 3.9 (b) Normalized antenna radiation patterns from the 2005 CSG data 0.375 m→0.650 m below the surface. The horizontal axis is normalized amplitude. The transmitter position is indicated on the vertical axis. Receivers are positioned every .025 m between -.075 m and -1.125 m.
Figure 3.9 (c) Normalized antenna radiation patterns from the 2005 CSG data 0.675 m→0.950 m below the surface. The horizontal axis is normalized amplitude. The transmitter position is indicated on the vertical axis. Receivers are positioned every .025 m between -.075 m and -1.125 m.
Figure 3.9 (d) Normalized antenna radiation patterns from the 2005 CSG data 0.975 m→1.125 m below the surface. The horizontal axis is normalized amplitude. The transmitter position is indicated on the vertical axis. Receivers are positioned every .025 m between -.075 m and -1.125 m.
than the area infiltrated by the PCE. Three basic approaches were taken in this work to approximate the volume of PCE spilled. First, a Fresnel volume for each \((i\text{-th})\) transmitter and receiver pair \((FV_i)\) were calculated. The volumes were then multiplied this by the corresponding PCE saturation \((S_{PCEi})\), and finally the resulting products were summed,

\[
V_{PCE_{ext}} = \sum_{i=1}^{#T\times Rx} FV_i S_{PCEi} .
\]  

(3.5)

The second approach was to create an elliptical disk \((FA_i)\) with an area equal to the cross sectional area (major and minor axis) of the Fresnel volume and a thickness equal to the 0.025 m transmitter spacing,

\[
V_{PCE_{ext}} = \sum_{i=1}^{#T\times Rx} FA_i S_{PCEi} .
\]  

(3.6)

Results from these first two methods are shown in Figure 3.11 as “Fresnel volume” and “Fresnel ellipse disk,” respectively. These approximations significantly underestimate the volume of PCE.

The third approach assumes that the PCE spread uniformly from the injection point so that data taken through any cross sectional plane would be identical to the data that were actually acquired. Intuitively, it doesn’t seem that this would be a reliable assumption, but the result was surprising. The long axis of the Fresnel volume was used as the diameter of a circular disk (“Fresnel major axis round”, \((FMAR_i)\)) with a thickness equal to the separations in transmitter height (0.025 m). The volume of PCE is based on saturations, and the summation is performed as in the previous two methods,

\[
V_{PCE_{ext}} = \sum_{i=1}^{#T\times Rx} FMAR_i S_{PCEi} .
\]  

(3.7)

Although this method overpredicts PCE volume at the beginning of the spill, it more closely approximates the volume after the spill ends (Figure 3.11). At the beginning of the spill the disk is larger than the PCE occupied volume. It comes to some average after the spill has progressed and then is smaller after the spill has ended, and the DNAPL has migrated further outward onto the clay layer. This result suggests the possibility of improving the approximation by using a conical volume, increasing the diameter with
Figure 3.10 The parameters used to define a first order Fresnel volume, $\Delta t$ is the difference in travel time between $t_{s-r}$ (the first arrival time) and the time of the first zero crossing ($t_{fv1}$). $x_1$ and $x_2$ are the major and minor axis of the ellipse. $x_2$ would be the second minor axis of an ellipsoid. $F_1$ and $F_2$ are the focal points and the position of the transmitter (Tx) and receiver (Rx). $C$ is the circumference.
Figure 3.11 Comparison of the different methods utilizing Fresnel volume to predict the volume of PCE in the tank with the actual volume spilled over the 72 hour period for the 2005 experiment.
depth. This approach may be tried in the future. A fourth curve provides an upper bounds estimate, demonstrating what the maximum estimated volume of PCE could be, had it spread laterally to the farthest extent possible within the clay cup and with the same saturations used for the first three methods. The “clay cup disk” curve in Figure 3.11 is calculated using circular disks with diameter equal to that of the PVC membrane barrier and a thickness of 0.025 m. The volume of PCE is calculated as in equations 3.5 through 3.7. A three dimensional data set would certainly allow a greatly improved volume estimate using similar methods.

3.4 Error Analysis

There are numerous sources for error in the determination of permittivity and PCE saturation. One such source occurs during data acquisition where placement and/or alignment of antennas within the borehole is not identical, as required for repeated measurements. In spite of the RF absorbing centralizers used in the 2005 experiment, this tended to happen near the top of the well with the antennas becoming more centrally located as they approached the bottom of the borehole. In 2005, it was also noticed that the west well, the one that contained the receiving antenna, was slightly off vertical. It is also possible that a few of the traces were not acquired at the correct location because the antennas were moved manually. When it was noticed that a mistake had been made during data acquisition, the trace was reacquired. In most cases the borehole radar system was the only instrument in use while the data were being acquired. In a couple of instances the logistics of the experiment required that different instruments be used simultaneously. This created the potential for interference.

There are other sources of noise in the data that can make first arrival picking difficult. On some traces the direct arrivals are clearly identifiable, while on others they are not. In 2004, noise caused by energy traveling along the cables caused some distortion in the first arrivals. In the traces from the uppermost measurements there may be refracted arrivals traveling along the higher velocity air layer that can constructively and destructively interfere with the direct arrivals. It is important to have an idea of
where in time these air waves will arrive so that a strong air wave is not picked in lieu of the true direct arrival. The location of airwaves is dependent upon the depth of the transmitter and receiver, and their separation. A plot of common source gather data taken in the first experiment (2004) is shown in Figure 3.12. The red line is the approximate location of an air wave arrival based on transmitter and receiver depth and separation. The first arrival travel time picks are indicated with short green lines. Because the size of the data sets was limited, it was feasible to pick the first arrivals by hand. In an automated scheme the accuracy of the first arrival picks might be suspect. Because in this case the small separation distance between the transmitter and receiver create conditions in which it is quite likely that the air and cable waves will be mistaken for direct arrivals. In larger field data sets this close geometry, and thus the attendant interference, may not exist. Also, with large data sets, an automated picking method may be the only practical solution. Errors within the data acquisition and first arrival picks aren’t the only ones to consider, video logs from the wells showed that the depth of the interfaces between sand and clay layers can vary by over one centimeter limiting the ability to precisely define the boundaries of the different layers. In addition, it is typically assumed that energy is being transmitted and received at the center of the antenna. But, the 0.07 m aperture of the antenna must also lead to some ambiguity in the interpretation of the data.

The preceding factors can cause errors in arrival times which will effect the calculation of permittivity and PCE saturation. The box-whisker plot in Figure 3.13 demonstrates the repeatability of the data and first arrival picking technique for the 2005 zero offset gathers by showing the mean, the mean of the upper and lower half of the data (quartiles), the median, and the outliers. The six depths are at the bottom of the tank below the 100% clay layer where electrical properties of the tank should remain constant throughout the duration of the spill and first arrival times should be consistent. Each of the six depths contains first arrival picks from all 13 of the zero offset gathers. These mean first arrival values fall between 10.4 and 10.6 nanoseconds with a range of 0.3 to 0.5 nanoseconds depending on the depth and trace of interest.
Figure 3.12 A sample of the 2004 common source gather data traces measured at depths from -0.3 m to -1.2 m. The red line indicates the approximate location of an air wave traveling between the source and receiver. The green lines are the first arrival picks. In some cases the air wave can destructively and constructively interfere with the first arrival. The first arrivals are distorted here between -0.5 and -0.7 m.
Figure 3.13 Box-whisker plot of first arrival picks for the 13 different zero offset gather data sets using 6 traces below the 100% clay barrier, where the electrical properties and travel times should remain constant.
The plot in Figure 3.14 shows the range for permittivity values calculated from the first arrival time data presented in Figure 3.13.

Recall that velocity is related to permittivity by Equation 3.2. By taking the derivative of Equation 3.2 with respect to time, a simple error analysis can be applied to this result to help predict the amount of error for a variety of situations. $r$ is the distance between wells, $c$ is the speed of light, $t$ is the travel time for a given permittivity and distance.

$$d\varepsilon = \frac{c^2}{r^2} 2tdt$$

(3.8)

This would indicate that, for a given separation, $r$, when the travel times are greater and permittivity is higher the absolute error in permittivity will be greater. Conversely the relative error, as a portion of the permittivity, decreases as permittivity increases.
Figure 3.14 The range for permittivity values calculated from the first arrival time data presented in Figure 3.13.
CHAPTER 4

TWO DIMENSIONAL SLOWNESS AND PCE SATURATION MODELS
FROM COMMON SOURCE GATHER DATA

The variation of PCE saturation with depth was presented in Chapter 3 using the zero offset gather traveltimes. The next step was to use the two dimensional common source gather data (CSG) to examine the lateral variations in PCE saturation. This process required an inversion routine to fit the observed two dimensional common source gather data to a slowness model. Two electromagnetic models were employed. The first used a straight raypath between transmitter and receiver. This allowed for a forward traveltime model that is linear with respect to slowness and raypath length. This simplifying assumption resulted in relatively rapid fitting of a model to the observed traveltimes. The second method uses a regularization technique to smooth the final models. The forward model is non-linear with respect to its parameters, and the raypaths are allowed to bend according to Snell’s law, resulting in a more realistic scenario than the straight rays used in the first method.

4.1 Straight Raypath Inversion of CSG Traveltimes for Slowness (linear model with no regularization)

In general, traveltime tomography consists of solving the problem, \( Ax=b \), where given \( b \) (measured traveltimes) find the spatial variation of the slowness along the path between the transmitter and receiver. If it is assumed that the number of cells is less than or equal to the product of the number of transmitters and number of receivers, and the raypaths follow a straight line, of length \( x \), between the transmitter and receiver, then the number of knowns (measured traveltimes) will be equal to or greater than the number of equations formed by \( Ax=b \), and the problem is considered overdetermined. When the system is overdetermined a slowness model, \( A \), can be found using the known distances,
The size and number of cells in the model must be sufficient to provide data density that can adequately represent the geology of the subsurface, or in this case the PCE saturated areas in the tank. The validity of the straight raypath assumption depends on the velocity (or permittivity) distribution between the two antennas, the radar frequency, and the distance between the antennas. For this case, a linear forward model was developed for the crosswell radar problem with varying numbers of cells and antenna locations in the borehole. After verifying the forward model accuracy, a non-linear regression routine to estimate the model parameters (slowness) following minimization of a least squares objective function (Hansen 1998) was implemented. The objective function was composed of the difference between the modeled and the observed traveltimes, \( \phi = (t_{\text{obs}} - t_{\text{mod}}) \). Additional discussion and results of the straight ray path inversion are presented in Appendix A.

### 4.2 Curved Raypath Inversion of CSG Traveltimes for Slowness (non-linear model with regularization)

According to Fermat’s principle, the correct raypath between the transmitter and receiver is one that comprises the least overall traveltime and not necessarily the shortest path. Snell’s Law describes the path of least traveltime, but the expression relating traveltime to slowness and distance (time = slowness × distance) must be considered in the context of bending rays. Whereas, traveltimes were observed during the geophysical survey, the raypath coverage and velocity structure are unknown (Berryman 1991). Unlike the previous investigation (Section 4.1) which assumed a straight raypath and had as many equations as unknown parameter values, the curved ray problem is non-linear in regards to model parameters and it is underdetermined, since rays may not travel through all of the cells in the two dimensional model. The forward model and regularized travelt ime inversion routine written and provided by Karl Ellefsen (USGS, pers. comm.) is designed to solve this type of problem. The generalized steps used in this approach are outlined in the flow diagram (Figure 4.1)
Zero Offset Gathers
Convert *.tdf to *.su format

Air Calibrations
Convert *.tdf to *.su format

Common Source Gathers Convert *.tdf to *.su format

Apply time shift to account for instrumentation delays

Zero Offset Gathers
Convert *.tdf to *.su format

Air Calibrations
Convert *.tdf to *.su format

Common Source Gathers Convert *.tdf to *.su format

Apply time shift to account for instrumentation delays

Zero Offset Gathers
Convert *.tdf to *.su format

Air Calibrations
Convert *.tdf to *.su format

Common Source Gathers Convert *.tdf to *.su format

Apply time shift to account for instrumentation delays

Figure 4.1 Flow diagram illustrating the steps for regularized inversion and determination of PCE saturation for the 2004 CSG data.
The model consists of a rectangular mesh with cell sizes chosen so that they are appropriate for the frequency and wavelength of the GPR and the expected range of permittivities to be encountered. Additionally, the impact of cell size on resolution must be considered as part of the model parameterization process. The resolution of crosswell radar and seismic techniques has been studied by numerous authors including Schuster (1996). In general they have found that resolution of objects that scatter energy is limited to the shortest wavelengths being propagated by the radar system. Therefore, frequency of the transmitted signal is the most significant limiter in a crosswell radar investigation. However, frequency is not the only factor limiting the performance of a crosswell radar investigation. Other limiting factors include the spatial density of the data acquired, aperture, raypath coverage, well separation, inclusion or lack of surface acquisition measurements, and the inversion routine used to generate the models (Ellefsen 2007, personal communication). Schuster (1996) gives the following formulas to estimate the nominal size limits for vertical and horizontal resolution of crosswell tomography respectively,

\[ \Delta_{z\text{tomo}} \approx \sqrt{\lambda x_0} \]  \hfill (4.1a)
\[ \Delta_{x\text{tomo}} \approx \frac{4x_0}{L} \left( \frac{3x_0\lambda}{4} \right) \]  \hfill (4.1b)

\( x_0 \) is the well separation, \( L \) is the borehole length, and \( \lambda \) is the source wavelength. The horizontal resolution is more than \((2\sqrt{3})x_0/L\), and therefore more difficult to achieve than the vertical resolution. Therefore the larger \( L \) is relative to \( x_0 \), the better the horizontal resolution. In this experiment, the borehole length is 1.47 m, and well separation is 0.76 m, resulting in horizontal resolution of approximately \( 1.6\sqrt{\lambda \Delta_{z\text{tomo}}} \).

The expression \( v = \lambda f \) relates frequency and wavelength to velocity. As permittivity increases from its free space value the velocity decreases according to, \( v = c/\sqrt{\varepsilon} \). At a given frequency, the wavelength decreases if the velocity decreases. For a permittivity of 20 (saturated sand) the wavelength, \( \lambda_s \), of a 1.4 GHz electromagnetic source wave will be 5 cm, \( (\lambda_{0.5m} \rightarrow \lambda_{2m}) = (v_{20} \rightarrow v_{20})/(1.4GHz) \). This is considered to be the lower limit for wavelengths propagated by the crosswell radar system used in this experiment. Considering the limits of resolution and the ease of mesh design, square
cell sizes of 0.04 m were chosen for the forward model. The rectangular mesh used in the finite element calculations was created using these square cells, their assigned slowness values and the x and y coordinates of their nodes. The dimensions of the model are larger than the region that is covered by the source and receiver locations, and air filled boreholes are included in the inversion routine.

The radar measurements used to constrain the curved raypath inversion are from the 2004 CSG measurements. They include one background, one postspill and two intermediate surveys. The prespill and postspill measurements were acquired with a vertical spacing of 0.03 m. Survey 01 was acquired approximately 1.5 hours after the spill had begun, and Survey 02 was conducted 9 hours later. These two surveys had a 0.06 m vertical separation between subsequent transmitter (and receiver) locations. After shifting the time series traces for the instrumentation delays, the traveltimes associated with direct arrivals were determined and assigned a confidence weight representing their relative reliability and quality. The weight values are 0.00, 0.25, 0.5, and 1.00, with 1.00 being a reliable first arrival pick, and 0.00 effectively eliminating that first arrival from the data set. A one dimensional forward model (Figure 4.2) was created with effort directed at finding a close fit to the first arrivals. The fit between the one dimensional forward model and the first arrival traveltimes is shown in Figure 4.3. The dark lines form an envelope showing the forward model traveltimes, while the dots are the weighted observed traveltimes. The red dots are first arrival traveltime picks that were considered unreliable and have a weight of zero. Green dots represent a weight of 1.00, orange dots a weight of 0.50, and yellow dots are for a weight of 0.25.

Like the straight raypath method discussed in Section 4.1 and Appendix A, a least-squares procedure, minimizing the sum of the squared residuals, was applied. However, the objective function contains a regularization term to reduce fluctuations in the properties of adjacent cells and smooth the final result. Regularization also provides a solution in the underdetermined case, so there is no restriction on the number of cells in horizontal or vertical direction. The mathematical representation of the objective function being minimized is given by Equation 4.2 (Ellefsen pers. comm.).
Figure 4.2 Initial model used in the cross borehole traveltime inversion. This model was created from the traveltime fits in Figure 4.4. The symbols × and · represent transmitter and receiver locations.
Figure 4.3 Initial model fit to first arrival traveltime picks. The red dots on the left are traces where the first arrival pick was unreliable due to noise. These are assigned a confidence weight of zero and not included in the traveltime inversion. The black lines are the first arrivals of the initial model. The green, orange and yellow, dots are the first arrival picks that are included in the traveltime inversion. They are weighted with confidence values of 1.0, 0.5, and 0.25 respectively. The initial model is designed such that it envelopes the first arrivals of the data.
\[ \Phi = (d - g(m))^T C^{-1}_{dd} (d - g(m)) + \gamma (Km)^T (Km). \] (4.2)

The first term on the right hand side represents the data residual, the sum squared difference between observed and modeled traveltimes. \( C_{dd} \) is the covariance matrix of the observed data (with confidence weights greater than zero), \( d \) is a vector of observed traveltimes, and \( g(m) \) is a vector of traveltime values calculated for the forward model. The second term on the right hand side smoothes the model. \( \gamma \) is the square root of the applied weight. Larger values of \( \gamma \) produce smoother models. \( K \) is the first order derivative regularization parameter. The forward traveltime model computes the length of the raypath and traveltime from the slowness within the cell. The individual ray traveltimes are summed to give the total traveltime for each composite ray.

4.3 Model Quality and Trade Off Between Data Fitting and Model Smoothness

The traveltime inversion routine produces pixel based tomograms of slowness, and information about residuals and raypath coverage. The quality of the inversion depends on the traveltimes themselves, first arrival picks, their assigned confidence weights, and the initial model, along with other inputs to the inversion routine. If too many, poorly resolved, first arrival times are included in the traveltime picks, the inversion will be forced to fit noise. If too few are included or if the weights are too low, there may be insufficient ray coverage. Leaving some cells without any rays, and no way to accurately resolve velocity in those cells.

The quality of the traveltime picks depends primarily on the noise present in the data. In the 2004 data sets there was an airwave that tended to interfere with the first arrivals. Where rays passed through the 100% clay layer attenuation of amplitudes added to the difficulty of accurately identifying first arrivals. Weighting the first arrival traveltimes, and eliminating those with a confidence weight of zero improved the inversion results. However, where the first arrivals were decimated, because of noise, the models essentially had no ray coverage through crucial areas. In addition to accurately identifying and assigning confidence weights to the first arrivals, it was
necessary that the initial parameter values provide a good fit to the first arrival traveltimes as demonstrated in Figure 4.3. A good initial model can facilitate convergence, ultimately requiring fewer iterations, as well as avoiding local minima.

Once a set of inversions was obtained, the appropriate model was chosen considering the smoothness and residual criteria along with information about geology and error when it was available. Each value of smoothness parameter \( \gamma \) produces a different model that minimizes the objective function. The inversion process was usually begun with the largest \( \gamma \). This resulted in a smooth model that could be used as the initial model for the next smaller \( \gamma \). As \( \gamma \) gets smaller, the regularization term (second term on the right hand side in Equation 4.2) is less dominant and the model favors a fit to the data and coincidentally the noise. The inversion routine provides numeric values that represent the model roughness and data residuals. These numeric values are related to the solution and residual norms (Ellefsen pers. comm.), and provide a heuristic method to interpret the model quality with regards to achieving balance between model roughness (MR) and data residual (DR). Plotting the square root of the data residual value versus the square root of the model roughness value for a range of \( \gamma \) values yields a “trade-off” curve (Figures 4.4(a), 4.5(a), 4.6(a) and 4.7(a)). The point of maximum curvature is interpreted as the balance between roughness and data fit. Parabolas were fit to each arm of the curve, to find the point of maximum curvature. Where the slope becomes asymptotic along each arm, the asymptote (horizontal and vertical) was constructed. A line extending from the origin passing through the intersection of the asymptotes crosses the trade off curve, approximately at the point of maximum curvature. This point is located between two of the plotted points produced by separate \( \gamma \) values, identifying a range of smoothness parameters that produce balanced tomograms in terms of data residual and model roughness.
4.4 Curved Ray Analysis from 2004 Common Source Gather Data

Curved raypath inversion results for each of the four surveys (Background, Survey 01, Survey 02 and Postspill) are illustrated in Figures 4.4 through 4.7: a tradeoff curve for choosing the upper and lower $\gamma$ values (4.4 a through 4.7 a), the corresponding tomogram (4.4 b1 and b2 through 4.7 b1 and b2) histogram of the traveltime residuals (4.4 c1 and c2 through 4.7c1 and c2), and a plot of the traveltime residuals versus the source and receiver offset from inversion of the background data for each of the two chosen $\gamma$ values (4.4 d1 and d2). In order to visualize where the inversion results are most strongly influence by velocity structure, the plots have individual scales.

The tomograms in Figure 4.4 b1 and b2 result from the background data set. The slowness (a result of permittivity) is anticipated to vary as a function of the fraction of clay in the sand and layering within the tank, because these physical characteristics affect the porespace and water content in the media. The upper plot, b1, has slowness values between 12.8 ns/m and 14.75 ns/m. The slowness of plot b2 ranges between 12.2 ns/m and 14.84 ns/m. The inversion routine results are characterized more by velocity structure when using $\gamma = 0.474$. Lower $\gamma$ values favor a fit to the noise as opposed to the smoothing that is favored in plot b1, where $\gamma = 0.64$. The diagonal patterns present in both models, but to a greater extent in the model with the lower $\gamma$ value, are considered an artifact.

In the histogram of residuals (Figure 4.4 c1 and c2) the radar traveltimes converge to within -0.07 ns +0.05 ns. Both residual plots are centered near 0.0 with slight skew towards positive values. In the crossplot of residuals (Figure 4.4 d1 and d2), the positive and negative residuals congregate relative to the receiver and source locations. The skew seen in the histograms is also evident in the crossplots. It appears that the positive values occur when the source is above the receiver (the lower diagonal half of the cross plot). There are several reasons for this. It may be a result of inaccurate traveltime picks. Perhaps when the receiver was above the transmitter the traveltimes to pick were clearer. The borehole may not be vertical thereby affecting coordinates used in the inversion. We know that in 2005 the borehole was slightly tilted. Possibly, there was an error in
locating the transmitter or receiver. An error in depth is not occurring in the actual data files, or the source and receiver location files. If there is a depth error it would have most likely occurred during the acquisition. As described in Chapter 2, the ability to accurately locate the source and receiver was limited, as it was performed manually.

The tomograms illustrate how the slowness decreases as the PCE spill migrates through the subsurface. High velocity regions are beginning to form above the 100% clay layer (-1.00 m on the vertical scale). In Figure 4.6 b2 the slowness value is below 12.5 ns/m over a large region above the 100% clay layer and to the left side of the tomogram. The residual histograms for Survey 01 (Figures 4.5 c1 and c2) demonstrate a fairly uniform distribution about zero. For Survey 02 the residuals are slightly skewed toward positive values (Figures 4.6 c1 and c2). The lower counts in these two surveys, compared to the background and postspill surveys, are due to the fact that fewer traces were acquired in the intermediate acquisitions (Survey 01 and Survey 02). The postspill survey (Survey 05) shows another decrease in the minimum slowness value (9 ns/m in Figure 4.7 b2). There also is a spreading of the high velocity region. It is no longer localized on the left side of the tomogram, but has spread out above the clay (100%) barrier. A high velocity layer has formed just below the clay barrier in the center of the tomogram. It is noteworthy that PCE did penetrate the 100% clay barrier through a crack near one of the wells. The residual histograms are slightly skewed toward positive values. The ray coverage for the postspill data is presented in Figures 4.8 e1 and e2. Radar energy is reflected and refracted according to Snell’s law, so whether or not a raypath intersects a cell will depend on its initial trajectory, and the velocity of the cell and its neighbors.
**Figure 4.4(a)** Trade-off curve for 2004 CSG background data set. The data residual (DR) and model roughness (MR) terms are output from the tomography inversion program (Ellefsen USGS). The balance between MR and DR provide a heuristic method to find the regularization parameter much the same way as the residual and solution norms are used in constructing L-curves (Hansen 2005, Ellefsen pers. comm.).
Figure 4.4(b1-upper and b2-lower) Cross borehole slowness tomograms 2004 CSG background data set
Figure 4.4(c1-upper and c2-lower) Histograms for the 2004 CSG background data set
Figure 4.4(d1-upper and d2-lower) Residuals as a function of the source and receiver depths for the 2004 CSG background data set
Figure 4.5(a) Trade-off curve for 2004 CSG Survey 01 acquired approximately 1.5 hours after the spill began. The data residual (DR) and model roughness (MR) terms are output from the tomography inversion program (Ellefsen pers. comm.). The balance between MR and DR provide a heuristic method to find the regularization parameter much the same way as the residual and solution norms are used in constructing L-curves (Hansen 2005, Ellefsen pers. comm.).
Figure 4.5(b1-upper and b2-lower) Cross borehole slowness tomograms for 2004 CSG Survey 01 acquired approximately 1.5 hours after the spill.
Figure 4.5 (c1-upper and c2-lower) Histograms for the 2004 CSG Survey 01 acquired approximately 1.5 hours after the spill began.
Figure 4.6(a) Trade-off curve for 2004 CSG Survey 02 acquired approximately 10.5 hours after the spill began. The data residual (DR) and model roughness (MR) terms are output from the tomography inversion program (Ellefsen pers. comm.). The balance between MR and DR provide a heuristic method to find the regularization parameter much the same way as the residual and solution norms are used in constructing L-curves (Hansen 2005, Ellefsen pers. comm.).
Figure 4.6(b1-upper and b2-lower) Cross borehole slowness tomograms for 2004 CSG Survey 02 acquired approximately 10.5 hours after the spill began.
Figure 4.6 (c1-upper and c2-lower) Histograms for the 2004 CSG Survey 02 acquired approximately 10.5 hours after the spill began.
Figure 4.7(a) Trade off curve for 2004 CSG postspill (Survey 05) data set. The data residual (DR) and model roughness (MR) terms are output from the tomography inversion program (Ellefsen pers. comm.). The balance between MR and DR provide a heuristic method to find the regularization parameter much in the same way as the residual and solution norms are used in constructing L-curves (Hansen 2005, Ellefsen pers. comm.).
Figure 4.7(b1-upper and b2-lower) Cross borehole slowness tomograms 2004 CSG postspill data set.
Figure 4.7(c1-upper and c2-lower) Histograms for the 2004 CSG postspill data set
Figure 4.8 (e1-upper and e2-lower). Example of ray density. The darkest areas have the fewest rays, with the number of rays intersecting a cell dependent upon the velocity of the cell and its neighbors as the ray path is computed with Snell’s law.
4.5  2-D PCE Saturation

The Bruggeman-Hanai Sen (BHS) formula has been applied to the two dimensional models of permittivity (slowness) estimated in the traveltime inversion using the approach described in Chapter 3. Once an acceptable model was chosen for the background data set (Figure 4.4 b1) it was used with the BHS formula to calculate porosity in each pixel (cell). As in Chapter 3, the porosity was used to calculate the permittivities of the sand-pce and sand-water end members. These permittivity values were used with the inverted models (from subsequent data sets, taken at 1.5 hours and 10.5 hours after the spill began, and 18 hours after the spill ended) to determine how the PCE saturation changed during the experiment. Plots of the contoured PCE saturations, shown in Figure 4.9, reveal that the PCE saturation is increasing during the spill and pooling along the clay barrier. There is also evidence of PCE below the 100% clay layer in the postspill saturation plot, consistent with the breakthrough that occurred during the experiment.
Figure 4.9 Two dimensional PCE saturation for 2004 CSG Left to right: Survey 1 (1.5 hrs), Survey 2 (10.5 hrs) and Survey 5 (18 hrs postspill). S\textsubscript{PCE} (indicated in red) increases as the spill progressed. Black rectangles indicate area with ray coverage.
CHAPTER 5

ATTENUATION ANALYSIS AND WAVEFORM MODELING

The radar traces acquired in this experiment vary in shape, amplitude, and traveltime as the spill progressed. Electromagnetic properties changed and heterogeneities developed within the tank. Traces from the 2005 and 2004 experiments are shown in Figures 5.1 and 5.2 respectively. Notice that the background data have larger amplitudes than the data taken during and after the spill. There is attenuation present in the post-spill data that can’t be explained by changes in electrical properties. Specifically, there is a resistivity increase with increasing PCE saturation that ought to result in larger amplitudes. However, the subsurface is typically a complex environment, even in this situation where the tank was well characterized before the spill began. As the volume of the PCE spill increased complicated three dimensional structures formed. Their presence resulted in the attenuation visible in the waveforms.

As discussed in Chapter 1, changes in the propagating wavelets that are due to acquisition geometry and antenna properties are assumed to remain fixed throughout the experiment. This implies that the changes in waveforms that are of interest can be limited to a study of traveltime and attenuation. Traveltime tomography is the subject of Chapter 4. To study the mechanisms of attenuation exhibited by the radar traces throughout the spill, this chapter examines how the electrical properties influence amplitude of a radar wave, how the frequency of the waves being propagated influence electromagnetic loss, and how increasing the number and size of heterogeneities during the spill causes energy to be scattered.

In this chapter three approaches are used to illustrate the interaction of electrical properties and scattering and their effect on the waveforms. First, a radar trace is calculated from the propagation of a Ricker wavelet through a homogeneous medium to demonstrate the effects of changes in conductivity and permittivity on GPR. In the second, the power and frequency content of data traces acquired during the experiment
Figure 5.1 Time lapse image of normalized amplitude of traces from data acquired before, during, and after the 2005 experiment. As the spill progresses the traces exhibit earlier first arrival times due to a decreasing permittivity and change in shape and amplitude due to scattering of energy. The prespill and +27 hour traces are relatively smooth compared with the data acquired at +63 hours and postspill. The 100% clay layer is near -1.0 m on the depth scale.
Figure 5.2 Prespill and postspill traces from the 2004 experiment. As the spill progresses the traces exhibit earlier first arrival times due to a decreasing permittivity, change in shape, and amplitude due to scattering of energy.
are investigated, and the information is used to construct forward waveform models of traces from one and two dimensional pre and postspill permittivity models. Finally, an investigation of attenuation and phase parameters and the electromagnetic and scattering loss tangents is used to show how different loss mechanisms dominate with varying frequency, and how scattering losses increase during the spill. The results demonstrate that the presence of PCE post-spill does cause a decrease in electromagnetic loss, while an increase in scattering loss is manifested as attenuation in the radar traces.

5.1 Electric Field in a Homogeneous Medium

Losses that are due to variations in electrical properties can be studied by propagating a wavelet through a homogeneous medium. Applied to crosswell radar data, this involves solving the homogeneous Helmholtz equation, \( \nabla^2 E + k^2 E = 0 \), for the vertical electric field. To find a solution to the wave equation it is typical to express the field, in this case the electric field, \( E \), in terms of potential. In this case, the Hertz potential (\( \Pi \)) was chosen. Equations 5.1 through 5.8 may be used for future work where the expressions for the field, \( E \), may be expanded to the case of layered media with the different transmitter and receiver heights found in common source gather geometry. For the vertical electric field in homogeneous media, \( \Pi \) is expressed as (Ellefsen 1999),

\[
\Pi(r, z, \omega) = -M \frac{i}{2} \int_{-\infty}^{\infty} H_0^{(2)}(k, r) k \frac{k_z}{k^2} e^{-ik|z-z_0|} dk, \tag{5.1}
\]

Where, the moment of the source is \( M \),

\[
M = \frac{I(\omega)}{4\pi(\sigma + i\epsilon \omega)}. \tag{5.2}
\]

The current \( I \) can be simulated by a Ricker wavelet. One of several possible expressions defining a Ricker wavelet is given in equation 5.3,

\[
I(t) = \frac{1}{4\pi} \left( 1 - \frac{1}{2} \left( \frac{2\pi f_0}{f(t-t_0)} \right)^2 \right) \exp \left( \frac{-(2\pi f_0)^2(t-t_0)^2}{2} \right). \tag{5.3}
\]

The frequency \( f_0 \) is arbitrarily chosen to be 300 MHz. \( t_0 \) is the time delay that honors causality and is greater than one half the period of the source Ricker
wavelet with a frequency $f_0$. $\omega = 2\pi f$, while $k_r$ and $k_z$ are the horizontal and vertical wavenumbers (which are equivalent in a homogeneous medium), $z$ and $z_t$ are the receiver and transmitter heights, $r$ is their horizontal separation. The right hand side of equation 5.1 can be written (Sommerfeld 1926) as,

$$\Pi_z(r, z, \omega) = -M \frac{e^{ik_z R}}{R},$$

(5.4)

where,

$$R = \sqrt{r^2 + (z - z_t)^2}.$$  

(5.5)

The exponential of Equation 5.4 is more stable than the integration of the Bessel function in Equation 5.1 (Wait 1970, and Ellefsen 1999). Hertz potential is analogous to the vector potential described in Ward and Hohmann 1987, p.173. Furthermore, as shown by others (Ward and Hohmann 1987, p.161, Wait 1970, p. 138 and Ellefsen 1999) the vertical electric field (TM due to electric sources) is,

$$E_z(r, z, \omega) = \left( \frac{\partial}{\partial z^2} + k^2 \right) \Pi_z(r, z, \omega).$$

(5.6)

Performing these operations on the expression for the Hertz potential (Equation 5.4) yields the vertical component of the electric field intensity in the frequency domain,

$$E_z(r, z, \omega) = Me^{-ikR} \left[ \frac{3(z - z_t)^2}{R^5} + \frac{3ik(z - z_t)^2}{R^4} - \frac{k^2(z - z_t)^2 + 1}{R^3} - \frac{ik}{R^2} + \frac{k^2}{R} \right].$$

(5.7)

The inverse Fast Fourier Transform of Equation 5.7 yields the vertical component of the electrical field in the time domain,

$$e_z(r, z, t) = \int_{-\infty}^{\infty} E_z(r, z, \omega) e^{i2\pi\omega t} d\omega.$$  

(5.8)

The expressions given by Equations 5.3, 5.4, 5.7, and 5.8 are calculated by the Matlab routine, epssigd.m (Appendix B). In a lossless homogeneous medium with magnetic permeability of zero and all components of the wavenumber real and frequency independent, there will be a time delay due to permittivity changes and amplitude attenuation due to increasing conductivity. Figure 5.3 shows traces that represent the vertical electric field in a homogeneous medium. This is the component that is measured by an infinitesimal vertical dipole approximating the antennas used in this experiment.
**Figure 5.3** Electric field and varying permittivity or conductivity. The moment of the source contains a Ricker wavelet with a center frequency of 300 MHz. The figure on the left shows the time lag due to increasing permittivity and subsequent velocity decrease. \( \sigma \) is fixed at 0.1 mS/m and \( \varepsilon_r \) increases from 4 for the lowest trace to 24 for the upper trace. The traces on the right show the amplitude decrease resulting from increases in electrical conductivity. For these traces, \( \sigma \) increases from 0.1 mS/m for the bottom trace to 30 mS/m for the upper trace. The relative dielectric permittivity is fixed at 20.
The homogeneous medium is changed by varying permittivity and conductivity with the wavenumber $k$. The magnetic permeability is assumed to be that of free space. The traces in the left hand side of the figure are for a fixed conductivity with varying permittivities that range between 4 and 24. The traces on the right hand side are for a fixed permittivity of 20 with varying conductivities between 0.1 and 30 mS/m, a range similar to the electrical property values expected in the experiment. If the propagating energy were to pass above and below a horizontal layer with velocity contrast, the result would be a superposition of wavelets with constructive and destructive interference.

### 5.2 Frequency Content of Observed Data

The frequency content of the 2004 zero offset gather data is shown in Figure 5.4. This information is required to define the frequency of the source and the bandwidth of frequencies used to calculate the waveforms in Section 5.3. It is also used to find the wavelengths that are considered in the discussion of scattering in Section 5.4. The mean of the 45 traces was calculated for each of the ZOGs. This is plotted as normalized amplitude versus time in the four panels on the left side of the figure. The upper two rows are from background (prespill) data. The third row down is for data acquired 9 hours after the spill had ended (Survey 4). The bottom row is from data taken 56 hours after the spill had ended (Survey 6). At this point the spill was considered to be stabilized and the data were no longer changing in a measurable way. A tapered window filter was created by picking two points on each averaged trace (indicated by arrows on Figure 5.4). The window had a maximum amplitude of one for a number of points equal to the number of points spanning the two points and was tapered from zero to one (at the beginning) by an arbitrary value of $1/6^\text{th}$ the number of points between the first and second traveltime picks (indicated by arrows on Figure 5.4). The taper on the right (from one to zero) was $1/3^\text{rd}$ the number of points between that number, such that the left taper was steeper. The vector $y(t)$ was calculated by multiplying the average trace by the tapered window. $y(t)$ was transformed into the frequency domain by the Fast Fourier Transform, $Y(\omega)=\text{fft}(y(t))$. The power spectra $P(\omega)$ is the product of $Y(\omega)$ and its
Figure 5.4 Normalized frequency content of 2004 ZOG data. The plots on the left are an average trace constructed from the 45 traces in each of the 4 ZOG measurements. From top to bottom, they are the two prespill data sets, Survey 4 and Survey 6. The plots on the right are the Power spectra calculated from a window of the traces on the left.
Transform, \( Y(\omega) = \text{fft}(y(t)) \). The power spectra \( P(\omega) \) is the product of \( Y(\omega) \) and its complex conjugate \( Y(\omega)^* \) divided by the number of points \( n \) in the \text{fft}. 
\[ P(\omega) = \frac{|Y(\omega)Y(\omega)^*|}{n}. \]

The Power spectra as a function of frequency are plotted for each of the normalized average traces in the panels on the right side of the figure. Typical center frequencies appear to be several hundred megahertz. At half amplitude, the highest central frequency is approximately 650 MHz, as established by the middle frequency at half amplitude for the postspill data.

### 5.3 Two Dimensional Waveform Modeling

As shown in Figure 5.1 and 5.2 there is significant attenuation when comparing the prespill and postspill zero offset gather data sets. Note the changing wavelet shapes and the decreasing amplitudes in the traces above the 100% clay layer. Recall from Figure 5.3 that increasing electrical conductivity will cause a decrease in amplitude. However in this experiment as PCE infiltrates and displaces water, the overall resistivity within the tank should increase. There have been some reports of conductivity increases being observed when PCE was introduced into sands and clays. It is thought that PCE may wash salts from the sand and clay grains into the pore water (Olhoeft 2007, pers. comm.). Barring that possibility, scattering remains as the dominant mechanism responsible for dispersion and attenuation of the radar traces. The original conditions within the sand tank were axisymmetric, what happens to the waveforms when the medium becomes two and three dimensional? Are there amplitude losses similar to what is observed in the data traces? A two dimensional full waveform forward model is used in this section to further demonstrate the dominance of electromagnetic energy scattering as the attenuation mechanism responsible for the dispersed and low amplitude wavelets exhibited by the traces above the 100% clay layer.
5.3.1 2-D Waveform forward model description

The 2-d full waveform modeling program used here was provided by Karl Ellefsen (USGS, Denver). It is described as a hybrid method that calculates traces by multiplying two functions in the frequency domain,

\[
E_x(x, y, z, t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} dk \, e^{i\omega t} \int_{-\infty}^{\infty} e^{ik(x-x')} g(x, k, z, \omega) S(\omega).
\]

(5.9)

The first function comes from the calculation of Green’s functions, \(g(x, k, z, \omega)\), using the finite element method. The Greens functions are found for a range of frequencies whose maximum is determined by the power spectra (Figure 5.4). The second is a source function \(S(\omega)\), whose center frequency is also determined by the power spectra. This source plays an important role. In the experiment, the measured value represents the current along the dipole receiving antenna measured as a voltage. It has the shape of a wavelet but is not in units of electric field (V/m). This is acceptable for most of the analysis but in modeling the full waveform, data must be compared with the modeled electric field, so a suitable approximation to the transfer function must be used. This is accomplished via the source function. The full waveform model provides the option of a Kelly source, Ricker wavelet or Gaussian pulse for the source. Experimentation by Moulton and Ellefsen (pers. comm. 2006) demonstrated that the Kelly source provides a good approximation to the appropriate transfer function between the measured voltage on the antenna and its electric field, thus it is used herein as the source for the full waveform modeling. Finally, the Fast Fourier Transform is used to obtain the time domain traces of the product of these two functions (Ellefsen 2006).

In addition to files specifying source type and the central and maximum frequencies, the model requires a grid of cells whose size is less than \(1/10\)th of the shortest wavelength. If the cell dimension is too large relative to the highest frequency, the result will be plagued with numerical dispersion problems evidenced by ringing in the calculated waveforms. The \((x, y)\) coordinates of the grid are defined in an input file that also contains the relative dielectric permittivity, magnetic permeability, and electrical conductivity associated with each grid point. The RDP for each cell was obtained from
the inverted slowness tomograms presented in Chapter 4. The relative magnetic permeability was equal to the value for free space (1.0), and the conductivity was assigned values given by Horton and presented in Table 2.2. The source and receiver location for the desired traces are defined in a separate input file and are representative of those used in the experiment.

Following the above considerations, the best grid spacing was found to be 5 mm. The center frequency was chosen to be 650 MHz with the highest frequency at 2 GHz. This choice resulted in calculation of Green’s Functions for 41 frequencies. The time necessary for calculation of the waveforms is primarily dependent upon the number of cells in the model, and the speed of the computer performing the calculations. The amount of random access memory available for the computation is the limiting factor in the number of cells in the model. For the models presented in Section 5.4.2, the typical time needed to obtain the waveforms was slightly less than four minutes per each of the 41 frequencies on an Intel® Pentium D® 2.80 GHz processor. More recent versions of the Waverform2d modeling program require less time for the calculations (Ellefsen pers. comm. 2007).

5.3.2 2-D Waveform forward modeling results

Recall Figure 5.2, which shows the traces from ZOG background and postspill datasets for the 2004 experiment. Note the dispersion in the wavelets and particularly the amplitude loss after the spill when conductivity and permittivity are low. To explore the impact of heterogeneities caused by PCE on the wavelet, traveltimes and amplitude, modeled traces were created using Waverform2d. The models were generated from the tomograms presented in Chapter 4. Figure 5.5 shows the results. The modeled traces overlay the observed traces. The background model is created from the prespill inversion result presented in Chapter 4 (Figure 4.5 b1). It is one dimensional. The postspill traces are from the postspill inversion result presented in Chapter 4 (Figure 4.8 b2). The model varies in two dimensions. Note the smooth uniform wavelets in the background (one dimensional) modeled traces versus the dispersion of the wavelets in the two dimensional
Figure 5.5 2-d waveform models calculated from the traveltine inversion results obtained from the prespill and postspill CSG data.
postspill modeled traces. This supports the idea that scattering losses are responsible for much of the wave attenuation present in the postspill data. These should be similar in characteristics and traveltime to the ZOG traces in Figure 5.2. However, near the 100% clay layer the first arrival of the model is coming in 1-2 nanoseconds before the first arrival present in the ZOG. In addition to offsets in traveltime, other differences between the data and the modeled traces exist. The amplitudes at the top and bottom of the model are smaller than the amplitudes of the actual data. The traces between -0.8 and -1.0 m show some faint similarity in their overall shape. But there is not a good match between the data and the forward model. There are several reasons that the dissimilarity between the data and models can occur. Common source gathers were used in the inversion to create the permittivity model. Zero offset gathers acquired at slightly different times, but under assumedly similar conditions are used for the comparison. The first arrival traveltime picks may be inconsistent between the ZOG and CSG data sets resulting in discrepancies in first arrival traveltimes. The model does not contain air filled boreholes or the tank bottom and other reflectors that were present in the actual experiment. This can account for the first arrival traveltime discrepancy and the stronger reflections above -0.6 m and below -1.2 m in the observed data relative to those same depths in the modeled data traces. The fact that the modeled traces are created from an infinitesimal dipole source, while the actual antennas have an aperture of 0.07 m is a significant factor in the wavelet shapes. The antennas are transmitting and receiving signal along their entire length in an asymmetric pattern as opposed to the infinitesimal dipole of the model. In addition to the above possible explanations, the observed data represent energy that has propagated through three dimensions. The traveltime inversion and waveform models are limited to two dimensions.

To qualitatively compare the observed and modeled traces a shift, of the modeled traveltimes is employed so that the first arrivals of the model and actual traces are better aligned. An overlay of the shifted models and the actual data are presented in Figures 5.6 and 5.7. Similarities between the model and data are evident, but the amplitude discrepancies, particularly at the top and bottom of the model still need additional consideration. The shift accounts for the error in the 2-D waveform model due to air in the borehole and variations in velocity due to lateral heterogeneities. Waveforms are a
Figure 5.6 Overlay of the prespill ZOG data already shown in Figure 5.2 (grey) with the shifted 2-D waveform models (black) calculated from the traveltime inversion results obtained from the prespill CSG data. The shift accounts for the error in the 2-D waveform model due to air in the borehole. The background waveform model has a constant -0.7 ns shift.
Figure 5.7 Overlay of the postspill ZOG data already shown in Figure 5.2 (grey) with the shifted 2-D waveform models (black) calculated from the traveltime inversion results obtained from the and postspill CSG data. Each trace of the postspill model is shifted to line up first arrivals.
rich source of information. The combination of traveltime inversion, forward waveform modeling, and 2-D waveform inversion will eventually lead to physically realistic models with improved resolution.

5.4 Electromagnetic and Scattering Loss

Plots of attenuation ($\alpha$ [Np/m]) and phase ($\beta$ [Radians/m]) parameters show the frequencies where each one will dominate, and the frequency where the displacement currents begin to dominate conduction currents. Figure 5.8, shows the attenuation and phase parameters calculated from the Cole-Cole permittivities (Equation 1.1), using 2 and 32 as the low and high frequency RDP values with a resistivity of 20 $\Omega$m over the frequency range of 1 MHz to 10 GHz. Above several hundred megahertz, the frequencies important to this experiment, conduction losses ($\alpha$) are less important than those due to dielectric permittivity ($\beta$). The phase parameter, where permittivity plays a dominant role, makes a large contribution to the total electric loss tangent. At 1 GHz, $\beta$ is more than an order of magnitude larger than $\alpha$. However, the main loss mechanism at the frequencies of this experiment is not electromagnetic losses but instead is due to scattering, as would be expected at frequencies above 300 MHz (Olhoeft 1986). This is also observed in the antenna radiation patterns in Chapter 3 that exhibit broadening with the lower permittivity values that occur as the PCE spill progressed.
Figure 5.8 Attenuation ($\alpha$) and Phase ($\beta$) parameters as a function of frequency. Above 100 MHz the phase parameter, $\beta$, begins to dominate. This is the point where displacement currents will dominate over conduction currents.
As discussed in Chapter 1, the flow of DNAPL in the subsurface is complex. PCE will create fingers, blobs and pools and leave behind partially saturated areas. Scattering can result from minute PCE particles that fit into individual pore spaces up to large heterogeneities where the PCE saturated region encompasses dimensions larger than a wavelength. There may also be water saturated pockets that form interfaces and induce scattering.

Scattering of electromagnetic energy is a phenomenon that is dependent upon the smoothness of the incident surface, the frequency, or wavelength, of the energy being propagated relative to the size of scatterers, and the angle of incidence. Figure 5.9 shows the difference between scattering patterns for interfaces of varying surface roughness. The roughness of a surface depends upon the height of irregularities and the angle of incidence. A surface can be considered approximately smooth as defined by the Rayleigh criterion, \( d < \frac{\lambda}{8 \cos \theta} \). Where \( d \) is the root-mean square of the roughness height measured from a reference plane, \( \lambda \) is the wavelength of the incident energy and \( \theta \) is the angle of incidence. Therefore a surface can be rough at some frequencies and smooth at others (AMS-Glossary of Meteorology). The concern in this experiment is the scattering

**Figure 5.9** Surface scattering patterns for an incident wave on smooth, medium and rough surfaces (Ulaby et al. 1982)
that occurs as electromagnetic energy interacts with the numerous interfaces of varying size that are created by the PCE. As with electromagnetic losses, scattering losses may be expressed in terms of a loss tangent. Borrowing from the study of radar propagation in the atmosphere, the scattering loss tangent can be calculated using the Mie scattering model (Skolnik 1971, Schaber et al. 1986, Balanis 1989, Cox et al. 2002, Mätzler 2002).

For a propagating electromagnetic wave incident on a particle, a fraction, \( q_s \), of the incident energy, \( E^i \), is scattered by an amount, \( E^{0s} \), such that, \( q_s = E^{0s} / E^i \). Likewise, when the refractive index or dielectric permittivity is complex (Equation 1.1) energy is removed by absorption, \( q_a = E^{0a} / E^i \). \( q_a \) and \( q_s \) are the absorption and scattering cross sections of the particle. Their sum, \( q_t = q_a + q_s \), is the total attenuation cross section (Skolnik, 1971, p.24-19). For a plane wave incident upon a sphere placed in the far field of the source (\( 2D^2/\lambda \)), where \( D \) is the diameter of the sphere, and \( \lambda \) is the wavelength of the incident field, the extinction efficiency, \( Q_{ext} \), is the sum of the scattering and absorption efficiencies and is related to their respective cross sections by,

\[
Q_{ext} = Q_{sca} + Q_{abs} = \frac{q_{sca} + q_{abs}}{\pi r^2}.
\]

The extinction efficiency is given by (Mätzler, 2002)

\[
Q_{ext} = \frac{2}{\lambda^2} \sum_{n=1}^{\infty} (2n + 1) \text{Re}\{a_n + b_n\}.
\]

Scattering efficiency of a sphere results from the integration of scattered power over all directions, (Mätzler, 2002).

\[
Q_{sca} = \frac{2}{\lambda^2} \sum_{n=1}^{\infty} (2n + 1) \left( |a_n|^2 + |b_n|^2 \right).
\]

In the case of monostatic radar where the transmitting and receiving antennas are colocated, the backscattering efficiency is (Mätzler, 2002),

\[
Q_{bsca} = \frac{1}{\lambda^2} \sum_{n=1}^{\infty} (2n + 1)(-1)^n \left| (a_n - b_n) \right|^2.
\]

The coefficients \( a_n \) and \( b_n \) are given by the following two expressions,

\[
a_n = \frac{m^2 j_n(mx) \left[ y_j(x) \right]'}{m^2 j_n(mx) \left[ xj(x) \right]'} - \mu_i j_n(x) \left[ mj_j(mx) \right]'.
\]

\[
b_n = \frac{m^2 j_n(mx) \left[ xh(x) \right]'}{m^2 j_n(mx) \left[ yj(x) \right]'} - \mu_i j_n(x) \left[ mj_j(mx) \right]'.
\]
and,
\[ b_n = \frac{\mu_r^m j_n(m x)(x j_n(x))' - j_n(x)(m x j_n(m x))'}{\mu_r^m j_n(m x)(x h_n^{(1)}(x))' - h_n(x)(m x j_n(m x))'} . \tag{5.15} \]

The parameters used in Equations 5.9 through 5.14 are the radius of the particle, \( r = D/2 \), the size parameter, \( x = kr \), and the wavenumber, \( k = 2\pi/\lambda \). \( m \) is the ratio of the index of refraction of the sphere to the index of refraction of the background medium. In this case, where magnetic permeability is that of free space, the index of refraction values simplify to the square root of the respective relative dielectric permittivities, \( \epsilon_r\text{-sphere} \) and \( \epsilon_r\text{-medium} \). \( j_n \) is the spherical Bessel function of the first kind and order \( n \). \( h_n^{(1)} \) are spherical Hankel functions of order \( n \). The primes indicate first derivatives with respect to the arguments \( mx \) or \( x \). Equations 5.10 – 5.12 are valid for all particle radii. Therefore, they encompass the Rayleigh (\( r < 0.1\lambda \)), Mie (\( 0.1\lambda \leq r \leq 2.0\lambda \)) and Thompson (optical) scattering regions (\( r > 2.0\lambda \)) (Balanis, 1989). The Mie scattering efficiency (\( Q_{\text{sca}} \)) is plotted as a function of \( mx \) in Figure 5.10. Rayleigh scattering falls on the linear portion of the model and is inversely proportional to \( \lambda^4 \).

The scattering and absorption efficiencies can be summed over an appropriate grain size distribution to obtain the combined extinction efficiency for a unit volume. The same can be done with the associated scattering cross sections. In this analysis the pre-spill grain size distribution is assumed to be made up of spherical sand grains. Summing \( q \) over the number of particles in a unit volume, \( N \), yields an expression for the scattering for a unit volume, \( \eta \),
\[ \eta = \sum_{i=1}^{N} q_{s,i} . \tag{5.16} \]
Figure 5.10 Mie scattering efficiency “$Q$” as a function of $mx$. $m$ is the ratio of the index of refraction of the sphere to the index of refraction of the background medium. $x$ is the size parameter and is equal to $kr$, where, $k=2\pi/\lambda$ is the wavenumber and $r$ is the particle radius.
5.4.2 Scattering and electromagnetic loss tangents

The scattering loss tangent, $\delta_s$, as a function of frequency is simply the volume scattering, $\eta$, divided by the phase parameter $\beta$,

$$\delta_s = \frac{\eta}{\beta}. \quad (5.17)$$

The loss tangents for dry and wet sand are shown in Figure 5.11. The DC conduction, dielectric and scattering losses are summed for each. Examining the curves from left to right, DC conduction is represented in the down sloping part of the curve, at the minima scattering and dielectric losses begin to dominate and the curve slopes upward. In the wet sand the dielectric relaxation peak is near 20 GHz. In general, the wet sand has both larger electromagnetic losses (sum of DC conduction and dielectric loss) and scattering losses.

The loss tangent for the prespill data is calculated for a grain size distribution consisting of spherical grains with a cubic packing. The number of sand grains, $N$, within a unit volume depends on the radius of the grains. Two approaches were used for the post-spill grain size distribution and calculations of loss tangents. Both depend on non-wetting saturation, $S_{nw}$, which was chosen based on the maximum average PCE saturation obtained by the one dimensional zero offset gather data discussed in Chapter 3. First, the grain size distribution incorporates small PCE particles that occupy 45% of each pore space, simulating uniform saturation with $S_{nw} = 0.45$ and $S_w = 0.55$. The radius of the PCE particles is $r_{PCE} = \sqrt[3]{(A_p S_{nw})/\pi})$. Second, also using $S_{nw} = 0.45$, the PCE particles increase in size to 0.0175 m, mimicking a PCE blob, and no longer occupy every pore space. In addition the number of particles, $N$, decreases.

A complete set of loss tangents for the prespill and postspill conditions are plotted in Figures 5.12 through 5.14. The loss tangents include DC conduction, dielectric relaxation, Mie scattering, Rayleigh scattering, as well as absorption ($\delta_{DC} = \sigma/\omega\varepsilon_0\varepsilon_r$, $\delta_{DIELECTRIC} = \varepsilon''/\varepsilon'$, $\delta_{MIE}$, $\delta_{RAYLEIGH}$, and $\delta_{ABS}$). Note the dominance of conduction losses at low frequencies, followed by increasing losses due to scattering. The water (dielectric) loss peaks above 20 GHz. Figures 5.15 and 5.16 are of the total loss tangents for the prespill and postspill conditions. Scattering loss is largely dependent on particle radius.
The large increase in scattering loss postspill can account for the observed amplitude loss. Particularly in the 2005 experiment (Figure 5.1), there are amplitude losses in the traces above the 100% clay layer that increase as the spill progresses. In general, the complexity of the PCE movement makes for wavelength scale heterogeneity that scatters the energy.

Figure 5.11 Model curves showing dc conduction, water, and scattering losses as a function of frequency for dry and wet sand. The particles are uniform spheres with radius, $r$. Other inputs to model are fluid type (AIR or H$_2$O), porosity ($\phi$), $S_{nw}$ (applies only to PCE as non-wetting fluid), Cole-Cole parameters for sand and fluids. This result compares favorably to the model results presented by Olhoeft, in Schaber et al. 1986.
Figure 5.12 Loss tangent model curves for the prespill electrical and scattering properties of the sand tank. Sand grains are assumed to be spheres. The background fluid is water. The tank is fully saturated with water. Inputs to the model are porosity ($\phi = .32$), radius of the sand grains ($r = 350 \mu m$), electrical conductivity ($\sigma = 12.3$ mS/m), and Cole-Cole parameters $\varepsilon_s$, $\varepsilon_\infty$, $\tau$, $\alpha$, for sand and water.
Figure 5.13 Loss tangent model curves for the postspill electrical and scattering properties of the sand tank. Sand grains are assumed to be spheres. Magnetic permeability is equal to that of free space. PCE saturation is at its maximum average value, $S_{nw} = .45$. With a spherical PCE particle occupying 45% of each pore space. Additional inputs to the model are ($\phi = .32$), radius of the sand grains ($r = 350 \mu$m), electrical conductivity ($\sigma = 12.3$ mS/m) and Cole-Cole parameters $\varepsilon_s$, $\varepsilon_\infty$, $\tau, \alpha$, for sand, water, and PCE. Absorption losses were not significant over this frequency range.
Figure 5.14 Loss tangent model curves for the postspill electrical and scattering properties of the sand tank. Sand grains are assumed to be spheres. Magnetic permeability is equal to that of free space. PCE saturation is at its maximum average value, $S_{nw} = .45$. PCE particles form blobs with large interfaces $r = 0.0175$ m, but do not occupy all pore spaces as in Figure 5.13. Additional inputs to the model are ($\phi = .32$), radius of the sand grains ($r = 350 \mu$m), electrical conductivity ($\sigma = 12.3$ mS/m) and Cole-Cole parameters $\varepsilon_a$, $\varepsilon_x$, $\tau, \alpha$, for sand, water, and PCE. Absorption losses were not significant over this frequency range.
Figure 5.15 Sum of dc conduction, dielectric and Mie scattering loss tangents. The pre-spill curve represents the losses for fully saturated (water) spherical sand grains. In the post-spill curve 45% of each pore space is occupied by spherical PCE particles (shown in red).
Figure 5.16 Sum of DC conduction, dielectric and Mie scattering loss tangents. The pre-spill curve represents the losses for fully saturated (water) spherical sand grains. In the post-spill curve the PCE particle radii are .0175 m. They occupy a total of 45% of the equivalent pore space.
CHAPTER 6

SUMMARY AND CONCLUSIONS

This thesis has resulted in three major contributions toward solving the problems of locating and characterizing volumes of DNAPL contaminants as well as improving imaging resolution of subsurface heterogeneity by crosswell GPR. Changes in the frequency, polarization, and angular GPR responses provide evidence of scattering processes. These are indicative of changes in fluid pore space properties and processes that occur when DNAPL displaces water. This is the first GPR study to explore all three measures of scattering. Second, the scattering and electromagnetic loss tangent analysis of prespill and postspill PCE distributions provides additional indicators of fluctuating pore scale heterogeneities and fluid-solid interactions (such as wetability) when DNAPL is present that is not observed in the water and sand without DNAPL. Including this type of radar wave scattering analysis improves the sensitivity of the GPR method to the presence of DNAPL and allows characterization of heterogeneities which are too small to be directly imaged. Third, the high frequency of the radar system combined with traveltime inversion enabled the highest resolution imaging ever obtained of DNAPL contamination without invasive exhumation.

The work contained herein demonstrates that high frequency crosswell GPR can quantify PCE saturations, and indicates that it would be a useful method for monitoring remediation and changes in subsurface contaminants over time. In this experiment, PCE was injected into a large tank filled with water saturated sand/clay layers. The spill was monitored by a 1.4 GHz crosswell radar system built at the United States Geological Survey in Denver, Colorado. The zero offset gather data show excellent vertical resolution, limited by the antenna aperture and spatial density of measurements. The common source gather data produced inverted tomograms with lateral resolution higher than predicted by Schuster (1996). The high frequency and subsequent data analysis allowed for the characterization of porosity and quantification of PCE saturation to within
a few percent in one and two dimensions. From the saturations, it is possible to estimate the contaminant volume.

When designing GPR data acquisition, the geophysicist must be attentive to the characteristics of the experiment or field site as well as the capabilities of the radar system. The frequency of the radar system is paramount to its ability to resolve heterogeneities and dominantly controls the depth of investigation. Electrical, magnetic, and geometric properties, including spatial heterogeneity, and their dependence on frequency via surface and volume scattering, have a significant impact on GPR performance. Other considerations include acquisition geometry, radar system properties, and capability of the method to resolve differences vertically and horizontally. In general densely spaced and densely timed common source gather data provide the best opportunity to accurately characterize the subsurface geometry; while zero offset gather data provide a fast method for obtaining one dimensional information about properties.

The one dimensional PCE saturation profiles clearly demonstrate how the PCE pools as it encounters layers composed of finer grained sand and clay. PCE flow is unpredictable, but generally speaking, when the PCE pool height is large enough to overcome entry pressure, the PCE will break through and flow into the finer grained material. The BHS mixing formula provides a method for determining PCE saturations within a few percent. However, PCE contaminates and becomes mobile at a much lower concentration (ppb to ppm) than is detectable by GPR imaging (ppt). The PCE volumes within the tank could be quantified because of prior knowledge about the geometry of the clay cup that trapped the PCE. Once the PCE began to settle within the tank, the volume interpreted from the data was within 3 to 15 percent of the volume actually spilled. This result was obtained by calculating the volume of 2.5 cm thick disks, each with diameter equal to the length of the major axis of the Fresnel ellipse associated with each ZOG measurement. Each disk was multiplied by the corresponding PCE saturation, yielding the PCE volume per disk. The total volume was obtained by summation of the individual disk volumes. This indicates that three-dimensional data might be used to accurately predict PCE volume. The ability to quantify PCE saturation at a real contaminated site will depend on the prior information that is available including answers to questions such as: is the volume of spilled PCE known, and what data are available regarding the
geologic characterization of the site? A multidisciplinary approach that integrates geophysical methods with the environmental sciences, engineering, hydrology, chemistry, geology, and others, can provide solutions to environmental contamination problems associated with DNAPL in soil.

An inversion of traveltime data provides models that suffer from non-uniqueness; many models may fit the data equally well. In the linear inversion (Appendix A) the models are fitting the data, but are plagued with artifacts that manifest as high-low-high patterns. Regularization will smooth fluctuations in the properties of adjacent cells, but at the cost of decreased resolution. This requires that a balance be achieved between model smoothness and resolution. Initially, in this work, attempts were made to find this balance by using an L-Curve method (Hansen 1998 and 2005), but difficulties were encountered in extracting the norms of the regularization solution and data residual required by Hansen’s corner finding routine (Hansen 1998). The L-curves that I was able to calculate were not reliable in their ability to locate the point of maximum curvature. The shapes were not truly an “L.” Perhaps this is an artifact due to the noise present in the data. Therefore, the method suggested by the author of the inversion routine (Ellefsen pers. comm.) was used instead. This method (including a technique for finding the range of weights to use in the regularized inversion routine) was improved by calculating the asymptotes of each arm of the trade off curve hyperbola, and locating their intersection. Once the range of weights was known, model choice then became a matter of examining histograms of data residuals looking for a normal distribution, and eliminating tomograms that appeared to contain artifacts inherent to the inversion process or lack of ray coverage.

The high frequency of the radar system and spatial density of the data acquisition allowed better resolution imaging than previously obtained in a crosswell GPR study. The tomograms demonstrate how lateral resolution is limited by the lack of vertically traveling waves, and how these results compare with the expected resolution described by various authors who give formulas for lateral and vertical resolution based on borehole length and separation. Tomograms exhibit resolution at the pixel scale (0.04 m) and correspond to the shortest wavelengths propagated by the 1.4 GHz radar. However, PCE flows into smaller fingers and blobs and leaves behind small residual saturations that a
traveltime inversion cannot resolve. The length of time required to obtain a CSG data set also limits the resolution capability of this experiment. For the CSG data acquisitions during the spill, which took several hours, the PCE underwent significant movement. This resulted in a smearing of information and resolution.

While the first arrival times can be used to provide a wealth of information including porosity, saturation, and Fresnel volume size, the waveforms are a rich source of information that goes beyond the first arrivals. Initially, an increase in amplitude was expected as the spill progressed due to the high resistivity of PCE. As resistivity increases the electromagnetic losses should substantially decrease. However, the opposite was observed as the amplitudes of the received wavelets decreased. An analysis of the electromagnetic loss and Mie scattering loss mechanisms indicated that scattering by PCE accounts for the attenuation visible in the radar traces. As PCE blobs or fingers become larger than one-tenth of a wavelength (about 2 cm for the 1.4 GHz radar) Mie scattering dominates all of the electromagnetic losses present between 100 MHz and 10 GHz, which is a new finding. The degree of scattering losses suggests that crosswell radar at this frequency needs to be acquired in smooth boreholes. A borehole with irregularities that approach $0.1 \lambda$ ($\lambda$ = wavelength) would scatter energy and limit the penetration of radar waves into the formation.

To capitalize on the additional information contained in the waveform, two dimensional forward modeling was performed, and the forward models were compared to the observed data. The mesh requires small cells, less than $1/10^{th}$ of $\lambda$, compared to the cell size for the traveltime tomography which was approximately equal to $\lambda$. The small cell size helps to overcome numerical dispersion error in the waveform modeling program. It also provides the potential for increased resolution. Some of the modeled traces are comparable to the observed data. This indicates that the 2-D slowness tomograms provide a good starting point for two dimensional forward waveform modeling and inversion. A recent report by Ellefsen (2007) shows that waveform inversion of crosswell radar data improves lateral resolution by two to three times that available from traveltime tomography. Olhoeft et al. (1993), found a factor of 9 improvement when the whole wavetrain was used.
While the work in this thesis demonstrates that 1.4 GHz crosswell GPR can be used to detect and quantify PCE in the saturated zone, the results would have been improved with denser data sets acquired at more frequent intervals. This could be achieved by automating the data acquisition and providing a mechanism that places the antennas at the correct depth. As more data are acquired, a method for rapidly and accurately picking first arrivals would be beneficial. Tomograms could be produced more quickly if that method were automated as in Olhoeft (1993).

In addition to waveform inversion, future work should include experiments in three dimensions. This would likely lead to the ability to quantify the size and shape of the heterogeneities that cause scattering due to the presence of the DNAPL in the subsurface. It would also allow for more accurate quantification of PCE volumes. As it currently exists, the method described in this thesis might be used to monitor remediation of PCE contaminated sites. While characterization of vadose zone hydrogeologic properties with lower frequency commercial crosswell GPR has been done in the past (Alumbaugh et al. 2002), the ability to locate DNAPL within the unsaturated zone remains elusive. This is a result of lower dielectric permittivity and electrical resistivity contrasts for PCE displacing air in dry sand. Time-lapse measurements, for example during remediation, make it easier to detect changes in DNAPL saturations (Sander 1994 and Sneddon 2002). The relationship between the scattering losses and the attenuation in the radar traces should be explored further. The scattering models, particularly the one containing the 0.0175 m PCE particles indicate that it may be possible to resolve PCE and grain size distributions that are too small to be imaged by crosswell radar tomography. Nonlinear Complex resistivity (NLCR) can detect clay organic reactions due to the presence of DNAPL at parts per million concentrations (Grimm et al. 2005). The sensitivity of NLCR is due to the large surface areas of clay where reactions occur as contrasted to the volume dependence in GPR. Incorporating a GPR survey and scattering process analysis such as the one presented in Chapter 5, may indicate surface scattering at a similar scale, where mobilization of DNAPL becomes a concern.
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APPENDIX A

STRAIGHT RAYPATH TRAVELTIME
FORWARD MODELING AND INVERSION

The two dimensional forward model, tomo2dfwd.m, assumes straight ray paths to calculate the radar traveltimes based on permittivity values assigned to a cell array. The difference between the modeled traveltimes and the observed traveltimes is minimized by the matlab optimization routine nonlinls.m (Hansen 1998).

A.1 Forward Model

Each ray in the forward model is assumed to be a straight line between a source and receiver. This assumption does have limitations. For the tank experiment, the change in length and traveltimes due to refraction would not be significant until the refracted wavelet has traveled an extra 0.5 ns. This value was obtained in the error analysis presented in Chapter 3. The refracted travel path, \( R_T = R + dr \), where \( R \) is the antenna and receiver separation and \( dr \) is the additional distance traveled by the wave, would not be able to exceed an additional length of \( dr = 0.15 \text{ m} \) in free space, or \( dr = 0.0375 \text{ m} \) when the relative permittivity is 16,

\[
dr = v \left[ \frac{m}{ns} \right] 0.5 ns .
\]

\( \text{tomo2dfwd.m} \) was written using Matlab 6.5. Inputs to the forward model include the cell size, and number and locations of transmitters and receivers. The output provided by the model is a vector of traveltimes for the transmitter and receiver pairs. The region simulated by the model is represented by a grid of cells that are assigned a permittivity value. The cells are rectangular, with the sum of their heights encompassing the transmitter and receiver depths. The sum of their widths is equal to the transmitter and receiver well separation. The model computes the length of the ray and traveltimes within
each cell based on the geometry and the assigned permittivity value. The individual traveltimes for each cell are summed to give the total traveltime for each complete path.

The forward model is able to accommodate any rectangular cell size and vertical distribution of transmitters and receivers. The geometric method used to calculate the ray lengths is shown in Figure A.1. The numerical calculation begins by finding the row of cells containing the first transmitter depth. The total length and slope of each ray between that transmitter and each receiver is then calculated. Next the length of ray segment within the cell is calculated by finding the slope for a line segment extending from the beginning of the ray segment across the cell to a node (dotted arrows in Figure A.1). The value of the intermediate slope is compared to the slope of the full ray between the transmitter and receiver allowing determination of the $x$ and $z$ values, and thus the calculation of ray segment length. The forward model then increments to the next appropriate cell and the process is repeated. To verify that the forward model is correct, the sum of the incremental ray lengths is compared to the length of the ray between the transmitter and receiver using the following criteria, $R = \sum r$.

![Figure A.1 Schematic of the computation of the individual ray segments, showing the full ray, $R$, from transmitter, Tx, to the receiver, Rx and the incremental ray segments. The intermediate slopes are shown as dotted arrows from where the ray crosses a cell boundary to the next appropriate node. These slopes are compared to the slope of the main ray and the length of the incremental ray “$r$” is computed. The forward model increments to the next appropriate cell.](image-url)
A.2  Inversion

Although the forward model can accommodate varying cell sizes and transmitter and receiver locations, there is a limited amount of information available for the inversion. To keep the problem linear the number of independent equations must be greater than or equal to the number of unknown parameter values. Therefore, when used in the inversion, the forward model is limited to having the number of rows equal to the number of transmitters and receivers, and the number of horizontal cells (columns) cannot exceed the number of rows. Even with this limitation, under the current application the cell sizes are only a few centimeters in depth and width.

The Matlab Optimization Toolbox (Hansen 1998) provides a minimization routine “nonlinls.m”, a least squares method to minimize the sum of the square of the difference between observed and modeled traveltimes (called the objective function), using a large scale reflective Newton method (Hansen 1998). The successful minimization using this least squares approach produces a two dimensional slowness tomogram and distribution of permittivity values. The objective function, $\Phi$, is the sum of the squares of the differences between the observed and modeled traveltimes ($t_{obs}$ and $t_{fwd}$, respectively), without any regularization parameters.

$$\Phi = \sum (t_{obs} - t_{fwd})^2.$$

(A.2)

The forward model is used to calculate traveltimes from the permittivity values, beginning with the initial guess for each cell. The computed traveltimes are compared with the measured traveltimes, and the vector of permittivity values is updated within the inversion routine. Then the forward model is recalculated. Iterations continue until the difference in traveltime is less than the set tolerance or an established maximum number of iterations have been reached. Lower and upper bounds of permittivity may be applied to reflect known physical limits for each cell of the model or permittivity may fluctuate freely. When the permittivity hits a boundary or becomes physically unrealistic, it is an indication that there is not enough ray coverage or information to get achieve a reliable inversion.
A.3 2004 Common source gather data

A larger number of common source gather data sets were acquired in the 2004 PCE spill experiment than in that of 2005. In 2004 full sets using 3 cm vertical spacing were acquired before and after the spill and three sets using 6 cm spacing were acquired during the spill. In the 2005 experiment there were only full sets using 2.5 cm spacing taken before and after the spill. Although the 2004 experiment didn’t behave as anticipated the common source gather data are inverted here to demonstrate the types of information that can be obtained from a CSG acquisition.

The data processing flow from acquisition of the data through inversion is shown in Figure A.2. Due to the relatively close transmitter and receiver separations and small scale of the experiment, it is possible for air waves to interfere with direct arrivals, especially in the upper portions of the tank. It is important that the first (direct) arrivals be identified accurately and not confused with air wave traveltimes. To help minimize the ambiguity in identifying first arrival times a spreadsheet of expected air wave traveltimes was created for reference. To process the common source gather data, the radar records were first shifted in time according to the air calibrations taken before, during, and after the common source gather data were acquired. Direct arrivals were then identified or “picked,” using Ellefsen’s TVision software (Ellefsen 1999a). The traveltime data were read into the Matlab two dimensional tomography inversion routine, runti.m, which calls the forward model tomo2dfwd.m and nonlinls.m.

The first thing to note in the slowness tomograms, Figures A.4 through A.6 (Survey 01 was acquired 1.5 hours after the spill began, Survey 02, 10.5 hours after the spill began, and Survey 03, 17.5 hours after the spill began), is the general behavior of the high velocity areas with time. As the PCE plume gets larger; the permittivity decreases, and the velocity increases. As expected, the slowness values are erroneous at the edges of the final model. However, there is a high-low-high pattern in the resulting tomograms. This pattern indicates that the inversion is fitting the data, but it may not be doing so in a physically realistic manner. These artifacts of over and under fitting of data are not uncommon, (Friedel and Olhoeft, personal communication). The use of a regularization parameter and curved ray paths could smooth artifacts over the cells.
Nevertheless, the straight ray path inversion and simple measurements objective function result is sufficient to show the distribution of the two dimensional velocity (high and low permittivity), and that the velocity is increasing as the spill progresses. Smoother models were obtained using the regularization method described and presented in Chapter 4.

### A.4 Reliability of tomographic inversion results

In the common offset gather data the ray coverage is limited near the top and bottom of the tank (Figure A.7). For this reason, the inverted results are not as accurate here as in areas with more ray coverage. A simple statistical inference can demonstrate the reliability of the inverted model and quantify where it breaks down. For example, one simple test was involved to determine the standard deviation of a 14×14 cell model. In this test the traveltimes for the model were calculated where each cell had a fixed relative permittivity of 16. This became the “true” model. Next the inversion was performed to try and fit this model, \( n = 30 \) times, letting the initial permittivity guess be a uniform random distribution between 1 and 81 for each of the \( n \) inversions. The values of permittivity, 1 and 81, were chosen because they are the physically limiting values that permittivity can attain, although the same method could be applied without choosing boundaries. \( n \) was chosen to be large enough that the 30 results would have an approximately normal distribution with a mean \( \bar{x} \) and samples \( x_i \). The measure of this distribution is the standard deviation given by the following expression,

\[
s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}.
\]

(A.3)

A plot of the standard deviation of relative dielectric permittivity is shown in Figure A.7. As expected, the standard deviation is higher in the cells with decreased ray coverage.
Data acquired in .tdf format

Convert * .tdf to * .su format

Shift time according to air calibration information

Pick direct arrivals considering air wave interference using “TVision.prj”

Put direct arrival traveltimes into * .xls spreadsheet

Read traveltimes into matlab tomographic inversion routine “runti.m”

Specify global variables including transmitter and receiver separation, horizontal and vertical cell size, Transmitter and receiver locations, lower and upper bounds and initial permittivity guess.

Call forward model and inversion routines with “runti.m”

Calculate forward model from “tomo2d.m”

Compute difference between model and measured travel times in “myfuninv.m”

Iterate minimization with “nonlinls.m” until convergence is reached

$$\Phi = \sum (t_{\text{obs}} - t_{\text{fwd}})^2$$

Output model permittivity, horizontal and vertical axis values. Grid “xyz” data in surfer and plot.

**Figure A.2** Flow diagram for linear traveltine inversion of common source gather data
Figure A.3 Geometry of ray coverage for 14 transmitter and receiver pairs
Figure A.4 Slowness in ns/m for Survey 01 from 2004 common source gather data.
Figure A.5 Slowness in ns/m for Survey 02 from 2004 common source gather data.
Figure A.6 Slowness in ns/m for Survey 03 from 2004 common source gather data.
**Figure A.7** Standard deviation in relative dielectric permittivity. The initial model had an RDP of 16 assigned to every cell. The number of inversions was $n=30$. Lower and upper bounds of RDP were set to 4 and 30.
APPENDIX B

INDEX OF FILES INCLUDED ON CD-ROM

These .m files are included in the directory: \MlabFiles\*.m

Areaddata.m
Reads *.su data files

ARPCsg.m
Calculates the antenna radiation pattern for a set of common source gather data in seismic unix (.su) format

bhs.m
Calculates Bruggeman Hanai-Sen mixing formula porosity and PCE saturations without plotting.

BHSCURVES.m
Calculates the Bruggeman Hanai-Sen mixing formula permittivities and PCE saturations and plots BHS curves for water-sand, sand-PCE, and end members at a given porosity.

bhmie.m
This matlab routine was obtained from:
http://www.igf.fuw.edu.pl/meteo/stacja/kody/mie.m
It was written by Krzysztof Markowicz, Institute of Geophysics Warsaw University, Warsaw, Poland, who states, “This code is published in the appendix of Bohren and Huffman light scattering book and is probably one of the most heavily used Mie codes.”

callpcesat04.m
Provides input parameters in a call to pcesat04.m and plots the resulting PCE saturations.

callpcesat05.m
Provides input parameters in a call to pcesat04.m and plots the resulting PCE saturations.

callpcesat2d.m
Provides input parameters (from traveltime tomography tank models) in a call to pcesat2d.m and outputs an ascii file of the resulting PCE saturations.

deltaepsb.m
Calculates the ricker wavelet amplitude as a function of permittivity and conductivity in a homogeneous medium then plots the result
LTMultipcesf.m
Calculates grain and pore sizes for prespill and postspill models, then calls ScatEff.m.
Also calculates the dc conduction and dielectric loss tangents.

NewScatTest.m
Calculate Mie Scattering cross sections using *matlab* Bessel functions, also calculates Rayleigh scattering.

pcesat2d.m
Calculates the two dimensional PCE saturations for 04 and 05 using:

- pcesat04.m
- pcesat05.m

Runti.m
Contains the objective function and calls the forward model tomo2dfwd.m and Hansen’s (1998) nonlinls.m to minimization.

ScatEff.m
Calls function bhmie.m to calculate the mie and then rayleigh scattering

tomo2dfwd.m
Computes straight ray path travel times between boreholes for a variety of transmitter and receiver combinations and a rectangular mesh, where the number of cells doesn’t exceed the product of number of transmitters and number of receivers.

tracecomps.m
Reads *seismic unix* (.su) files, normalizes data and plots radar traces.

The thesis front matter is contained in the file:
WallinFrontmatter.doc

The main body of the thesis is contained in the file:
WallinMainBody.doc

*xls* files for the COG data are in the files:
\XLSFiles\2004COG.xls
\XLSFiles\2005COG_traces.xls

A list of data files for 2004 is contained in the text file:
\CWR2004_DATA\FileList.txt
The 2004 data are contained in the folder:
\CWR2004_DATA\n
A list of data files for 2005 is contained in the text file:
\CWR2005_DATA\cwr_2005_datafile_list.txt

The 2005 data are contained in the folder:
\CWR2005_DATA\n