AN EXAMINATION OF SOIL TEXTURE AND WATER CONTENT
ESTIMATES FROM NUCLEAR MAGNETIC RESONANCE

by

Yonghui Peng

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ABSTRACT OF THE DISSERTATION

An examination of soil texture and water content estimates from nuclear magnetic resonance

By Yonghui Peng

Dissertation Director:
Prof. Kristina Keating

An accurate description of soils is critical to agricultural practices because water and nutrients accessible to crops are stored in shallow soils at ~1–2 m depth. Traditional methods used for soil characterizations involve invasive, sparse, and time-consuming direct soil sampling techniques. Geophysical methods have shown promise to infer the physical properties of soils non-invasively and spatially. Nuclear magnetic resonance (NMR), the only geophysical method that directly measures the water content, has been increasingly used in soil science. This thesis focuses on exploring the use of NMR to characterize soil properties in agricultural practices.

The first laboratory study investigates the effect of clay, silt, and sand content in synthetic samples on NMR relaxation times. NMR measurements are collected on mixtures of 1%–60% kaolinite clay, 5%–85% glass beads, and 8%–94% quartz sand by mass. The effect of silt and sand content can be seen in soils with low clay content (<10%) but do not have an impact on soils with high clay content (>10%). The clay content dominates the NMR response for soils with >10% clay. The strong effect of the clay content on the NMR responses is due to the high specific surface area and
the distribution of clay throughout the soil samples.

The second laboratory study explores the use of NMR as an alternative method to estimate soil texture of water-saturated soil samples collected in three agriculture sites in Moline, IL, USA. NMR presents a possible alternative method to determine the soil texture as other commonly used methods, such as textural analysis or laser diffraction, are time-consuming or need to be calibrated. To determine the soil texture using NMR, NMR transverse relaxation time ($T_2$) distributions are separated into three regions using two $T_2$ cutoff times, which are further used to estimate the clay, silt, and sand fractions. The NMR-derived soil texture is compared to that estimated by the sieve-pipette and laser diffraction method. NMR data with site-specific $T_2$ cutoff times obtained from quantitative comparison with the sieve-pipette method offers a better estimation of soil texture than the laser diffraction method for soils with low magnetic susceptibility.

While the NMR method has been widely used to characterize saturated systems, its use in partially saturated systems (e.g., agriculture sites) is still being developed. The third study examines the use of a small-diameter NMR logging probe to estimate soil water content during two experiments in June and September 2016 at an agriculture site in central California. The NMR data can monitor the changes in water content from the two experiments at each borehole; however, at each experiment, NMR water content is lower than the water content derived by the reference time-domain reflectometry method because of the presence of soils with high magnetic susceptibility. A proposed calibration method, which used a linear model to account for the magnetic susceptibility, fail to accurately capture the total NMR estimated water content. Other mechanistic models are needed for more accurately calibrating.
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Chapter 1

Introduction

1.1 Motivation

Water use for agriculture, which accounts for 70% of global freshwater withdrawals [WWAP, 2018], is usually seen as the main factor behind increasing freshwater scarcity. In the United States, for example, in the year 2015, about 118 billion gallons of fresh water were used for irrigation every day, which accounted for 42% of the total [Dieter et al., 2018]. Some areas in the western regions of the US corn-belt are facing long-term pressures to reduce the usage of water in agriculture [Cooper et al., 2014]. Meanwhile, globally, the food demand is estimated to increase by 60% from 2018 levels by 2050 [WWAP, 2018]. To support the increasing demand for crop production with the increasingly precious water resources, it is critical to increase water use efficiency and improve irrigation water management for agriculture.

The common method of irrigation water management is through measuring or monitoring the soil water content. The amount of water stored in a soil is primarily influenced by the soil texture. Water and nutrients that are accessible to crops are stored in shallow soils (∼1–2 m depth) that, traditionally, are characterized through direct point-scale soil sampling, which is known to disturb the natural state of soils and are time-consuming. Geophysical methods, however, can be used in the field condition, many are non-invasive (i.e., do not require soil samples or an augured hole), and the data of which can be collected quickly, have been successfully applied for soil characterizations and agricultural applications [Robinson et al., 2008b; Allred
et al., 2010; Romero-Ruiz et al., 2018]. In particular, one geophysical method that is increasingly used in soil science is nuclear magnetic resonance, NMR, which directly measures the soil water content and provides details of pore-scale soil properties. This thesis aims to examine NMR as a geophysical method for estimating the soil properties, soil texture is of particular interest.

NMR measurements are sensitive to water content in geologic materials because the amplitude of the measured NMR signal is directly related to the number of protons in water, that is, the signal magnitude of the NMR measurement is proportional to the water content in the pore spaces. NMR measurements can provide details of pore sizes of water-saturated materials through interpreting the obtained NMR relaxation times. NMR logging has been widely used for a few decades in the petroleum industry to quantify water and hydrocarbons in consolidated rocks [Coates et al., 1999]. The more recent development of NMR logging tools [Sucre et al., 2011; Walsh et al., 2013]. appropriate for groundwater and environmental investigations has led to the successful application of NMR in a variety of soil science studies [Claes et al., 2019; Crow et al., 2020].

This thesis focuses on exploring how the NMR relaxation times relate to soil texture, which mainly affects the soil water content, and how NMR data can be used to directly detect water. A laboratory study that explores the effect of clay, silt and sand content in synthetic soils on NMR relaxation times is presented in Chapter 2. Subsequently, in Chapter 3 NMR is used as an alternative method to estimate the soil texture of soil samples collected from three agricultural fields in Moline, IL, USA. Results from a field study evaluating the use of NMR relaxation times to estimate the soil water content from one agricultural site in central California are presented in Chapter 4, followed by summarizing and proposing future research directions given in Chapter 5.
1.2 Background

1.2.1 Soil texture analysis

Soil texture is important in assessing soils as it affects soil functions such as the soil water retention characteristics, nutrient retention and supply, and hydraulic conductivity. The texture of the soil is determined by the percent (by weight) of the three primary soil particles: clay, silt, and sand, and can be grouped into different classes based on the U.S. Department of Agriculture soil classification system. Traditionally, for soil scientists, the standard procedure used to determine the particle size distribution is a combination of sieving and sedimentation methods, the latter is often performed using a pipetting apparatus or a hydrometer [Gee and Bauder, 1986; Gee and Or, 2002]. However, this commonly used method in soil science is time-consuming, especially for the determination of clay particles (over a couple of hours). New techniques used in the laboratory such as laser diffraction offer rapid analysis, high reproducibility, and can measure a wide range of particle size, have been increasingly applied in quantifying the particle size distributions of soils [Yang et al., 2019]. However, many researchers have suggested calibration with the standard method when using a laser particle size analyzer [Eshel et al., 2004; Taubner et al., 2009; Di Stefano et al., 2010]. Geophysical methods are widely used to characterize soils [Kuang et al., 2012; Romero-Ruiz et al., 2018], however, the texture of soils can only be indirectly estimated through the relationship between the geophysical parameters and the physical properties of soils.

1.2.2 Soil water content

The goal of irrigation is to ensure the amount of water in the soil is enough and available for good plant growth. Understanding the basic concepts of soil water is critical to effective irrigation management. Water content in soil can be directly
measured using the difference in weight before and after drying a soil sample, referred
to as gravimetric water content, and using the difference in volume referred to as
volumetric water content. These direct methods are accurate; however, they are
invasive (using disturbed soils) and time-consuming.

Practical measurements for monitoring soil water content are mostly indirect [Bittelli, 2011]; soil moisture was estimated by a calibrated relationship with some mea-
surable physical properties of soils such as electrical resistivity and dielectric constant.
The neutron probe has been used for soil moisture measurement since it was proposed
more than 50 years ago [Van Bavel, 1961; Bell, 1987]. The neutron probe is still fre-
quently used in deep borehole measurement because there is little option, although
the data collection is relatively slow and rules for using radioactive materials are
increasingly strict Yao et al. [2004]. Over the last few years, the time-domain re-
fectometry (TDR) technique has been widely accepted for estimating soil moisture
[Robinson et al., 2003; Walker et al., 2004]. The dielectric constant of soils is deter-
mined by measuring the travel time of an electromagnetic wave traveling back and
forth on the probe [Jones et al., 2002]. The water content of soils was estimated
from the empirical relationship that relates the soil dielectric constant and soil water
content [Topp et al., 1980; Quinones et al., 2003].

Geophysical methods have been widely applied to monitor the soil water content
[Allred et al., 2008], and most of them provide non-destructive and in situ measure-
ments which are useful for the effective management of irrigation. Electrical resistivity
tomography (ERT), which measures the distribution of the electrical resistivity in the
subsurface, is one of the geophysical methods widely used in agricultural applications
range from small-scale to field-scale [Michot et al., 2003; Samouelian et al., 2005;
Brunet et al., 2010; Araya Vargas et al., 2021].
1.2.3 Geophysical methods in soil science

Geophysical methods have been increasingly used in many agricultural applications including hydrology, precision agriculture, and irrigation management. Successful applications of geophysical methods to characterize soils have been steadily growing over the last few decades [Corwin and Lesch, 2005; Kuang et al., 2012; Romero-Ruiz et al., 2018; Zajícová and Chuman, 2019]. The three geophysical methods that are commonly used for agricultural purposes are resistivity, electromagnetic induction (EMI), and ground-penetrating radar (GPR). These methods can be applied noninvasively (i.e., do not require soil samples or an augured profile) in the field condition. For example, direct current resistivity and EMI measurements have been widely used in determining soil water content using electrical conductivity and are sensitive to the clay content—clay has a high electrical conductivity compared to sands or silts—and are used to map changes in clay content across a field [Robinson et al., 2008b,a; Sudduth et al., 2010, 2013]. GPR measurements of water content are used in conjunction with soil texture measurements to improve the characterization of soil texture distribution across a site [Grote et al., 2010]. The induced polarization (IP) method is also widely used for characterizing soils, for example, studies have shown that a near linear relationship exists between IP parameter (e.g., imaginary conductivity) and specific surface area (or the cation exchange capacity) of soils [Slater et al., 2006; Revil et al., 2017]. However, no direct or global relationship exists between EC, EMI, GPR, or IP signal response and the estimated physical properties of soils so these geophysical measurements require local calibration for effective use in the prediction of soil properties including soil texture. A combined approach with different geophysical methods may eliminate the need for calibration.
1.2.4 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) has been used in near-surface geophysics for measuring hydrogen, which is primarily found in water and hydrocarbons, in the subsurface. NMR is the only geophysical method capable of measuring the water content directly. NMR has been adopted as a mature logging technique in the petroleum industry [Kenyon, 1997]. Although this method shows great potential for helping to determine the water content and to estimate the pore size distributions in soils [Bird et al., 2005; Jaeger et al., 2009; Meyer et al., 2018], it is rarely applied in soil science [Bayer et al., 2010]. To make full use of the NMR technique for soil science, it is necessary to gain a more comprehensive understanding of this method.

The basic principle of NMR

The NMR phenomenon occurs in atoms with an odd number of protons that possess spin angular momentum. The charged nucleus spinning about an axis will form a current loop that generates a magnetic moment. Near-surface geophysics mainly focuses on measuring hydrogen because of its abundance in water. When a large number of hydrogen atoms are placed in a static magnetic field $B_0$, the magnetic moments align with $B_0$, which will produce a net magnetization moment $M$, and precess around $B_0$ at the Larmor frequency $f_L$ where,

$$f_L = \frac{\gamma}{\pi}B_0$$  \hspace{1cm} (1.1)

$\gamma$ is the gyromagnetic ratio ($\gamma = 2.68 \times 10^{-4}$ for hydrogen), $B_0$ is the strength of the magnetic field.

For NMR logging tools used in the oilfields where the static magnetic field is generated using permanent magnets, the typical resonance frequency for hydrogen nuclei ranges from 500 kHz to 2 MHz. In laboratory NMR applications, the resonance
frequency often ranges from 1–900 MHz, whereas in surface NMR applications, lower frequencies (∼1.3–2.5 kHz with earth magnetic field $B_0 \approx 30–60 \, \mu T$) are used.

At thermal equilibrium state, $\mathbf{M}$ will be pointed in the direction parallel to $\mathbf{B}_0$, which is referred to as the longitudinal direction (or z-axis). The magnitude of $\mathbf{M}$ is too small and cannot be measured directly. However, if $\mathbf{M}$ is tipped away from the equilibrium direction, the precession of $\mathbf{M}$ around $\mathbf{B}_0$ will induce a measurable signal. Normally an alternating magnetic field $\mathbf{B}_1$, oscillating at $f_L$, is applied to tip $\mathbf{M}$ away from the longitudinal direction to the transverse plane. The proton spins and therefore $\mathbf{M}$ will be affected by both $\mathbf{B}_0$ and $\mathbf{B}_1$. Typically, a tipping angle of either 90° or 180° is applied, and the corresponding pulse is referred to as 90° pulse or 180° pulse, respectively.

Once $\mathbf{B}_1$, which is defined as a function of time, is terminated, $\mathbf{M}$ will relax back to the equilibrium state and resume precession around $\mathbf{B}_0$. Two different kinds of relaxation are considered: the longitudinal or spin-lattice relaxation, the return to equilibrium along the z-axis characterized by the longitudinal relaxation time constant $T_1$, and the transverse relaxation or spin-spin relaxation, the decay of transverse magnetization $M_{xy}$, characterized by the transverse relaxation time constant $T_2$. This study will focus on the transverse relaxation $M_{xy}$.

In laboratory and borehole NMR applications, a pulse sequence consists of an initial 90° pulse followed by a series of 180° pulses (the CPMG pulse sequence, named after Carr and Purcell [1954] and Meiboom and Gill [1958]) is applied. In the case of observing transverse relaxation, the NMR signal in porous media, such as soils, is a superposition of exponential decays,

$$M_{xy}(t) = I_0 \sum I_i e^{-t/T_2}$$

where $I_0$ is the signal magnitude at $t = 0$, $I_i$ is the $i^{th}$ signal fraction with relaxation time $T_2$, $I_0$ is proportional to the number of energized protons in the pore space;
therefore, in water-saturated soils, $I_0$ relates to total porosity and in partially saturated soils $I_0$ is proportional to the volumetric soil water content.

**NMR relaxation of porous media**

In water-saturated soils, the $T_2$ relaxation time consists of three relaxation mechanisms that occur in parallel:

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}} \quad (1.3)$$

where $T_{2B}$ is the bulk fluid relaxation time, $T_{2S}$ is the surface relaxation time, and $T_{2D}$ is the diffusion relaxation time. $T_{2B}$, in most cases, is much longer than other components (e.g., $T_{2B} \ll T_{2S}$) of equation 1.3 [Dunn et al., 2002] and is assumed to be negligible.

$T_{2S}$ occurs due to the relaxation of the spinning protons at pore-grain interfaces [Kleinberg et al., 1994]. It is typically the dominant relaxation mechanism in water-saturated geologic material. In the case of fast diffusion $T_{2S}$ is given by the following equation [Brownstein and Tarr, 1979]:

$$\frac{1}{T_{2S}} = \rho_2 \frac{S}{V} = \rho_2 \frac{\alpha}{r_{pore}} \quad (1.4)$$

where $S/V$ is the pore surface-to-volume ratio, $\rho_2$ is a material-specific constant called surface relaxivity, which is dependent on the presence of paramagnetic ions on the surface, such as Fe(III) [Bryar et al., 2000; Keating and Knight, 2008] and Mn(II) [Kenyon and Kolleeny, 1995], and $\alpha$ is a shape factor (i.e., $\alpha = 1$ for planar, $\alpha = 2$ for cylindrical, and $\alpha = 3$ for spherical pores). The fast diffusion assumption can be verified by calculating the control parameter [Brownstein and Tarr, 1979; Ryu, 2009; Keating and Knight, 2012]

$$\kappa = \frac{\rho_2 V}{D S} \quad (1.5)$$
where \( D \) is the self-diffusion coefficient of water \((\approx 2.5 \times 10^{-9} \text{ m}^2\text{s}^{-1} \text{ at } 20 \degree \text{C})\). The assumption of fast diffusion regime is valid if \( \kappa \ll 1 \). In the fast diffusion regime, hydrogen protons can diffuse through the entire pore space and can interact with the solid surface within the time interval of the NMR experiment. Outside the fast diffusion regime, relaxations are in slow or intermediate diffusion regimes where \( \kappa \gg 1 \). Hydrogen protons in the slow diffusion regime are unable to diffuse through the entire pore during the time scale of the NMR measurement.

\( T_{2D} \) accounts for the dephasing of hydrogen spins in the presence of an inhomogeneous magnetic field, which is given by

\[
\frac{1}{T_{2D}} = \frac{(D\gamma G t_E)^2}{12}
\]

where \( G \) is the average internal gradient of the magnetic field, and \( t_E \) is the echo time, which is the time between two 180° pulses in the CPMG pulse sequence Meiboom and Gill [1958]. The average internal gradients are caused by the differences in magnetic susceptibility between the solid material and the pore fluid. The presence of magnetic grains such as magnetite can contribute to the magnetic field gradients [Keating and Knight, 2007; Fay et al., 2015]. Equation 1.6 shows that \( T_{2D} \) can be reduced with a sufficiently short \( t_E \), which becomes a more dominant relaxation mechanism in a pore environment with strong field gradients. For example, \( T_{2D} \) is often assumed to be negligible when measured in a 2 MHz lab NMR systems for small \( t_E \) Dunn et al. [2002].

**NMR measurements and data analysis**

NMR experiments in this thesis were conducted in the laboratory and a well, but they can also be collected at the ground surface. Laboratory NMR data were collected with a 2.0 MHz Rock Core Analyzer (Magritek Ltd., Wellington, New Zealand). Laboratory NMR measurements provide data with high signal-to-noise ratios from
well-controlled experiments. The standard laboratory typically has a volume of about 40 cm$^3$ or less [Behroozmand et al., 2017]. The borehole measurements in this thesis were collected using a Dart NMR probe (Vista Clara, Mukilteo, WA, USA). This probe can operate at two distinct frequencies within the range from 245–290 kHz, providing a radial depth of sensitive zone of 10–14 cm from the surface of the tool to the surrounding formations [Walsh et al., 2013].

The recorded NMR data, which are multiexponential decays, are inverted to produce a $T_2$ distribution using a least-squares algorithm. As the inverse problem is ill-posed, the solution has to be regularized. The typical technique uses the second-order Tikhonov regularization [Tikhonov, 1963; Aster et al., 2013] and obtains a solution through minimizing the following expression:

$$\min \| G(m) - d \|^2 + \alpha^2 \| Lm \|^2$$

(1.7)

where $\| \cdot \|$ denotes the norm of a matrix, $G$ is the forward operator, $m$ is the model vector, $d$ is the data vector, $Lm$ is the second derivative of $m$ when $L$ is the second-order Tikhonov regularization matrix, and $\alpha$ is the regularization parameter, which can be determined using the L-curve criterion Costabel and Yaramanci [2013]. The first term in equation 1.7 reflects the difference between the modeled and measured data, and the second term is the second-order smoothness constraint of the resulting $T_2$ distribution. The inversion algorithm will yield a sufficiently smooth $T_2$ distribution once a proper regularization parameter $\alpha$ is chosen.

A $T_2$ distribution of a soil sample can be characterized by a single relaxation time, typically use the mean-log (logarithmic mean) value of the $T_2$ distribution or $T_{2ML}$. This parameter characterizes the entire pore spaces of a sample. If $T_{2B}$ and $T_{2D}$ are considered to be insignificant, $T_{2ML}$ is related to the mean-log pore radius of the soil
sample by the following equation:

$$\frac{1}{T_{2ML}} \approx \frac{1}{T_{2S}} = \rho_2 \frac{\alpha}{T_{ML}}$$

(1.8)

This equation relates the relaxation time to the specific pore size and is the basis for the estimates of the hydraulic parameters of soils (e.g., permeability and hydraulic conductivity) from NMR data.

### 1.3 Summary of research

The objectives of the thesis were (i) to explore how NMR relaxation times relate to soil texture, which affects the soil water content; (ii) to find suitable $T_2$ cutoff times for using NMR data to estimate soil texture; (iii) to investigate the factors that can affect the relaxation times in the laboratory and field; and (iv) to examine the estimate of soil water content from borehole NMR measurements. This thesis approaches these research topics in three chapters. Chapters 2 and 3 are laboratory work focus on defining the relationship of NMR relaxation times to soil texture. Chapter 4 focuses on evaluating the estimates of soil water content from borehole NMR measurements collected during two growth stages of corn at one agriculture site.

**A laboratory study of the effect of clay, silt, and sand content on low-field nuclear magnetic resonance relaxation time distributions**

Chapter 2 presents a systematic study of a controlled variation of clay, silt, and sand synthetic mixtures and examines the corresponding changes in the NMR relaxation time distributions. Although no study has expansively investigated the impact of clay, silt, and sand content on NMR measurements, a few studies have explored the effect of clay content on the NMR response for synthetic mixtures and natural soils [Pohlmeier et al., 2009; Osterman et al., 2019]. The NMR measurements were
collected from 36 water-saturated unconsolidated sediment mixtures of 1–60% kaolinite clay, 5–85% silt-size glass beads, and 8–94% quartz sand by mass. Clay content is shown to have significant impacts on the NMR relaxation time distributions, both on the dominant relaxation times but also the relaxation distribution shape. Sand and silt content affect the relaxation times for mixtures with low clay content but show no impact for mixtures with high clay content. Clay content dominates the NMR response when the clay is present in quantities greater than 10% and is enough to fill in the interparticle space throughout the mixture. This chapter has been published in the journal *Geophysics* [Peng and Keating, 2021].

**NMR relaxation time for soil texture estimation in the laboratory: A comparison to the laser diffraction and sieve-pipette methods**

Chapter 3 explores an approach to estimate the soil texture of soil samples based on the NMR measurements; the approach is examined using soil samples collected from three agricultural fields near Moline, IL, USA. A previous study by Keating and Falzone [2013] has shown that NMR $T_2$ relaxation time distributions of water-saturated unconsolidated soil samples can be linked to the grain size distributions. In this study presented in chapter 3, the hypothesis that NMR $T_2$ distributions can be used to estimate the soil texture was tested on soil samples with a wide range of soil textures from clay, clay/silt loam, to sand. The $T_2$ distributions were separated with two $T_2$ cutoff times into three regions to calculate the clay, silt, and sand fractions. Two approaches for determining the cut-off times were used: the first used $T_2$ cut-off times determined from the data from all sites and the second used site-specific $T_2$ cutoff times. The results show that there is no universal cut-off time for estimating the sand, silt, and clay fraction based on NMR $T_2$ distributions. The NMR-derived soil textures with the site-specific $T_2$ cut-off times applied were found reliable, when compared to those determined from the sieve pipette method, for soils with low magnetic susceptibility ($< 2 \times 10^{-4}$ SI). These estimates closely match, and in some
cases are better than, the soil texture determined from laser diffraction particle size analysis. This chapter was published in the journal *European Journal of Soil Science* [Peng et al., 2021].

**An examination of NMR logging to determine soil water content for agricultural investigations**

Chapter 4 is about a field project that takes place at an agriculture site in central California, which focuses on evaluating the estimates of soil water content from borehole NMR data and aims to find a solution to calibrate the NMR estimated water content by taking into account the effect of magnetic susceptibility on NMR measurements. The NMR field data were collected using a small-diameter NMR probe in 6 PVC-cased boreholes during two different growth stages of corn in June and September 2016. Soil water content at each borehole was also measured using TDR right after the NMR measurement. The results show that changes in water content from the June and September NMR experiments are comparable to those from the two TDR experiments; however, the NMR-derived water content during each experiment is lower than the TDR estimated soil water content at all boreholes. The laboratory NMR measurements collected on water-saturated soil samples with high magnetic susceptibility also underestimated the total saturated water content. A linear equation developed in the laboratory, which takes into account the magnetic susceptibility, was successfully applied in the calibration of NMR estimated porosity in the laboratory but failed to calibrate NMR estimated water content in the field.
Chapter 2

A laboratory study of the effect of clay, silt, and sand content on low-field nuclear magnetic resonance relaxation time distributions\(^1\)

2.1 Abstract

We have developed a laboratory nuclear magnetic resonance (NMR) study to investigate the effect of clay, silt, and sand content on the NMR relaxation time distribution. Transverse NMR relaxation times \((T_2)\) are determined for water-saturated unconsolidated sediment mixtures of 1\%–60\% kaolinite clay, 5\%–85\% silt-size glass beads, and 8\%–94\% quartz sand by mass. Nearly all of the mixtures are characterized by a unimodal \(T_2\) distribution. When the clay is present in quantities greater than 10\%, the clay content dominates the response. For these samples, the mean-log relaxation times \((T_{2ML})\) range from 0.03 to 0.06 s, regardless of silt or sand content. For mixtures with \(<10\%\) clay, \(T_{2ML}\) decreases with increasing clay content. When the clay content is kept the same, \(T_{2ML}\) decreases with increasing silt content and increases with increasing sand content. The strong effect of the clay content on the NMR response is due to the high specific surface area of clay and the distribution of clay throughout the samples. These results will help improve the interpretation of NMR field data in soils and unconsolidated sediments.

\(^1\)Published in Geophysics as Peng and Keating [2021]
2.2 Introduction

Geophysical nuclear magnetic resonance (NMR) data are used in the evaluation of petroleum reservoirs and are increasingly being used in near-surface geophysics investigations including for applications in hydrogeophysics, soil physics, and environmental science [Yaramanci and Müller-Petke, 2009; Behroozmand et al., 2015]. However, although the interpretation of NMR data is well-established for water- and oil-saturated sandstones and carbonates, it is still being developed for soils and unconsolidated sediments. In our work, we are interested in understanding the effect of grain size on the interpretation of NMR data collected on water-saturated unconsolidated sediments.

The NMR signal is a multiexponential decay characterized by initial signal intensity and distribution of relaxation times. NMR can directly detect hydrogen protons in water, and the signal intensity is proportional to the number of hydrogen protons or the water content. Thus, the primary use of NMR in near-surface geophysics is to estimate porosity in water-saturated geologic materials and water content in partially saturated geologic materials [Freedman, 2006; Walsh et al., 2013; Flinchum et al., 2018]. The relaxation time distribution (\(T_2\) distribution) is sensitive to the physiochemical environment of hydrogen protons, so NMR measurements can also yield information about the pore structure, such as the pore size distribution (PSD) and the characteristic pore size of water-saturated geologic material [Bird et al., 2005; Jaeger et al., 2009; Stingaciu et al., 2010; Meyer et al., 2018]. The PSD and characteristic pore size can then be used to determine the hydraulic conductivity [Dlubac et al., 2013; Dlugosch et al., 2013; Maurer and Knight, 2016; Ren et al., 2019]. Because the PSD of soils and sediments depends on the grain size distribution (GSD) and aggregation of these grains, NMR measurements also can be used to obtain information about the GSD. Keating and Falzone [2013] show that a simple linear transformation of the NMR \(T_2\) distribution could be used to obtain the GSD in fine to coarse sands with low iron content. A recent study also shows that NMR data can be used to
predict the soil texture (i.e., clay, silt, and sand content) for natural soils with low magnetic susceptibility [Peng et al., 2021]. However, what has not been performed, and is necessary for improving the interpretation of NMR data in unconsolidated sediments and soils, is a systematic study of the impact of clay, silt, and sand content on NMR measurements.

In soil and sediments, the movement of water and air through the pore space is governed by the clay, silt, and sand content, or soil texture; quantifying the soil texture and GSD thus allows us to predict water movement and nutrient and contaminant transport. Improving our understanding of soil texture on NMR measurements will help to expand the use of NMR for applications in soil physics. Although no study has systematically examined the impact of sand, silt, and clay content on NMR measurements, a few studies have shown that the presence of clay has a strong effect on the $T_2$ distribution. Laboratory data have shown that the $T_2$ distribution shifts to shorter $T_2$ values when the clay content increases for water-saturated sand-clay mixtures with clay contents ranging from 1% to 15% by mass [Moss and Jing, 2001; Anand et al., 2008; Osterman et al., 2019] and for natural soils with clay content ranging from 4% to 15% by mass [Pohlmeier et al., 2009]. Osterman et al. [2019] further show that this effect depends on the distribution of clay within the measured volume (e.g., homogeneously distributed throughout the sample or present in aggregates). Clays are known to have the high surface area and small pores; thus, they affect the fast relaxation part of the NMR signal [Osterman et al., 2019]. Although previous studies have examined the effect of clay on the NMR response, they are limited in the range of clay content (up to 15%) and they do not also systematically test the influence of silt content.

In this study, we address the following research question: how does the clay, silt, or sand content impact the NMR response? To answer this question, we perform laboratory NMR measurements on water-saturated synthetic samples with known sand-silt-clay proportions. To limit the impact of swelling on the NMR measurements,
we use the nonswelling clay kaolinite. The samples are mixtures of kaolinite clay (1%–60% by mass), clean silt-size glass beads (5%–85% by mass), and clean quartz sand (8%–94% by mass). The laboratory results from our study will help to improve the interpretation of further NMR measurements in the field.

2.3 NMR relaxation theory in porous media

The NMR phenomenon occurs in hydrogen protons because they possess angular momentum. In an NMR experiment, the spinning protons will align with and precess around a static magnetic field, $B_0$, at the Larmor frequency, which is proportional to the strength of $B_0$. At equilibrium, spinning hydrogen protons in water produce a bulk magnetization aligned with $B_0$. Because the bulk magnetization cannot be measured directly in laboratory measurements, the NMR signal is measured by moving the magnetization away from equilibrium using a series of energizing pulses. Laboratory and borehole near-surface geophysics applications typically apply the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [Carr and Purcell, 1954; Meiboom and Gill, 1958; Behroozmand et al., 2015], which consists of a 90° pulse that excites the spinning protons and tips them out of alignment with the static field, followed by a series of 180° pulses separated by the echo time $t_E$. As the spinning protons relax back to their equilibrium positions, the time-varying transverse component of the decaying signal $A_{xy}(t)$ is measured inductively between 180° pulses. The term $A_{xy}(t)$ is a multiexponential decay characterized by the initial signal amplitude $A_0$ and distribution of transverse relaxation times, $T_2$ distribution. The term $A_0$ is proportional to the number of hydrogen protons and thus the volume of water in the porous media [Coates et al., 1999]. Consequently, the NMR-estimated porosity $\phi_{NMR}$ for a saturated sample can be determined from its initial signal amplitude $A_0$ calibrated by $A_0$ measured on an equivalent sample volume of water.

Each $T_2$ value in the $T_2$ distribution can be described as a sum of three relaxation
processes occurring in parallel [Brownstein and Tarr, 1979]:

\[
\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}}
\] (2.1)

where \(T_{2B}\) is the bulk fluid relaxation time, \(T_{2S}\) is the surface relaxation time, and \(T_{2D}\) is the diffusion relaxation time. In most cases, \(T_{2B}\) is much longer than \(T_{2S}\), and is assumed to be negligible (i.e., \(\frac{1}{T_{2B}} \ll \frac{1}{T_{2S}}\)) [Dunn et al., 2002]. The term \(T_{2D}\) accounts for the dephasing of spins that occurs when relaxation takes place in an inhomogeneous magnetic field. Inhomogeneities in the magnetic field can be applied, associated with the NMR magnet, or caused by the presence of magnetic minerals such as magnetite [Keating and Knight, 2007, 2008].

The surface relaxation time \(T_{2S}\) occurs due to relaxation of the nuclear spins at pore-grain interfaces [Kleinberg et al., 1994]. If relaxation occurs in the fast diffusion regime, then each value of \(T_2\) in the \(T_2\) distribution represents a different pore environment (i.e., different pore size and/or pore with different surface chemistry) and \(T_{2S}\) is given by (Kleinberg and Horsfield, 1990)

\[
\frac{1}{T_{2S}} = \rho_2 \frac{S}{V} = \rho_2 \frac{\alpha}{r}
\] (2.2)

where \(\rho_2\) is the surface relaxivity, \(\alpha\) is a shape factor accounting for pore space (one for planar, two for cylindrical, and three for spherical pores), \(r\) is the pore radius, and \(S/V\) is the pore-volume normalized surface area. In this experiment, \(\rho_2\), which measures the capacity of the grain surface to cause the relaxation of hydrogen, is assumed to be constant across all pores within all samples; in this case, the \(T_2\) distribution can be linearly transformed to the PSD (e.g., [Bird et al., 2005]).

The diffusion relaxation \(T_{2D}\) is assumed to be negligible for samples with low magnetic susceptibility. This assumption can be tested by comparing CPMG measurements collected at multiple \(t_E\); if \(T_2\) does not change with \(t_E\), then it is valid [Kleinberg et al., 1994; Keating and Knight, 2007]. The \(T_2\) distribution of a sample
can be characterized by the mean-log relaxation time $T_{2ML}$ and, assuming bulk and diffusion relaxations are negligible,

$$\frac{1}{T_{2ML}} \approx \frac{1}{T_{2S}} = \rho_2 \frac{\alpha_{rML}}{r_{ML}}$$

Thus, $T_{2ML}$ is related to the mean-log pore radius $r_{ML}$ and $S/V$.

For samples with narrow grain size distributions, in general, the grain diameter can be transformed to the pore radius by assuming proportionality [Arya and Paris, 1981; Haverkamp and Parlange, 1986]. Then, the GSD of the media can be linearly related to the PSD and thus to the $T_2$ distribution of the material.

### 2.4 Materials and methods

The effect of clay, silt, and sand content on the NMR response of synthetic water-saturated sediment samples was examined using measurements made on samples with systematically varied clay, silt, and sand content. Wedron quartz sand (supplied by Wedron Silica Co.) was used as the sand, glass beads (grain diameters from 0 to 50 µm; manufactured by Sigmund Lindner GmbH, Warmensteinach, Germany) were used as an analog for silt-sized sediments, and kaolinite (sourced from Fisher Scientific) was used for a nonswelling clay. The specific surface area $S_{SA}$ (surface area per unit mass of the solid phase) and particle density ($\rho_p$) for all materials are shown in Table 2.1. The data for kaolinite and Wedron sand were from Osterman et al. [2019], and data for the glass beads were measured using the Brunauer, Emmitt, and Teller (BET) nitrogen gas adsorption method [Brunauer et al., 1938] with a Micromeritics ASAP 2020 surface area analyzer.
Table 2.1: Specific surface area $S_{SA}$ and particle density $\rho_p$ of kaolinite, silt-sized glass beads, and Wedron sand.

<table>
<thead>
<tr>
<th></th>
<th>Kaolinite</th>
<th>Glass beads</th>
<th>Wedron sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{SA}$ (m$^2$/g)</td>
<td>11.552±0.0179*</td>
<td>0.2074±0.003</td>
<td>0.0388±0.0001*</td>
</tr>
<tr>
<td>$\rho_p$ (g/cm$^3$)</td>
<td>2.6*</td>
<td>2.5†</td>
<td>2.65*</td>
</tr>
</tbody>
</table>

* Data from Osterman et al. [2019]
† Data from Sigmund Lindner GmbH.

2.4.1 Sample preparation

Mixtures were prepared with clay content ranging from 1% to 60% by mass, silt content ranging from 5% to 85% by mass, and sand content ranging from 8% to 94% by mass. To prepare the homogeneous mixtures, the kaolinite, glass beads, and sand were first oven-dried overnight at 80 °C. Then, the desired mass of each material was weighed out and added together. The materials were stirred together using a glass rod to homogeneously mix the materials, with special care taken to break apart any clay clusters. The final mixture weighed 20 g. Besides, pure (100%) materials were also used. In total, 36 mixtures were created. The percentage of clay, silt, and sand for each mixture is plotted on the ternary diagram shown in Figure 2.1. The term SSA for each mixture given in Table 2.2 was a weighted average, which was calculated using the $S_{SA}$ value of the pure material multiplied by the mass fraction of that material in the sample.

To make a sample for NMR measurements, the mixture was packed into a cylindrical sample holder with a lid (3D printed with polylactic acid filament, an inner diameter of 25.02 mm, an inner height of 20.34 mm, and a volume of 10 ml) according to the wet packing method detailed by Oliviera et al. [1996]. Two replicate NMR samples were created for each mixture resulting in 72 measured samples. The gravimetric porosity $\phi_{grav}$ of each sample was calculated gravimetrically from the mass difference between the saturated and dry samples normalized by the volume of the sample holder. Parafilm was placed at the top of the sample holder to ensure that
Table 2.2: Physical properties and NMR parameters for samples used in this study.

<table>
<thead>
<tr>
<th>Clay %</th>
<th>Silt %</th>
<th>Sand %</th>
<th>$S_{SA}$ (m$^2$/g)</th>
<th>$\phi_{grav}$ (-)</th>
<th>$D_{10}$ (µm)</th>
<th>$\phi_{NMR}$ (-)</th>
<th>$T_{2ML}$ (s)</th>
</tr>
</thead>
<tbody>
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<td>25</td>
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<td>0.72</td>
<td>0.7</td>
<td>0.74</td>
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</tr>
</tbody>
</table>

Physical properties include the specific surface area $S_{SA}$, the gravimetric porosity $\phi_{grav}$, and $D_{10}$ from the laser particle size analysis (LDPSA). The geophysical parameters include the NMR-estimated porosity $\phi_{NMR}$ and the mean-log relaxation time $T_{2ML}$. 
Figure 2.1: The percentages of clay, silt, and sand used for all samples plotted on the United States Department of Agriculture ternary diagram.

The sample material and water did not escape during the NMR experiment.

### 2.4.2 Measurement methodologies

NMR data were collected using a 2.0 MHz Rock Core Analyzer (manufactured by Magritek) using the CPMG pulse sequence with echo times of 200, 400, and 800 $\mu$s. The number of echoes ($n = 15,000$) was chosen so that the signal fully decayed within the time frame of the measurement. All CPMG measurements were stacked 32 times to ensure a high signal-to-noise ratio.

To process the NMR data, the background signal (from an empty sample holder placed in the instrument) was first subtracted from the NMR measurement on a
water-saturated sample. The background-removed NMR data were then inverted to obtain the $T_2$ distributions using a nonnegative least-squares inversion algorithm with the second-order Tikhonov regularization [Tikhonov, 1963]. In this algorithm, the data were logarithmically subsampled to 5000 points and then fit a predetermined set of 200 log-spaced $T_2$ values, ranging from 0.01 ms to 10 s. The regularization parameter, which controls the smoothness of the $T_2$ distribution, was selected corresponding to the point of highest curvature in the root-mean-squared (RMS) errors versus regularization parameter curve, as described by Costabel and Yaramanci [2013].

The GSD of each mixture was measured using laser particle size analysis (LDPSA) with a Beckman Coulter LS 13 320 instrument. The instrument contained a 5 mW laser diode with a wavelength of 750 nm, and it can measure particle sizes ranging from 0.017 to 2000 µm using the Polarization Intensity Differential Scattering (PIDS) option. Further details about LDPSA, the PIDS system, sample preparation, and the instrument set up can be found in Xu [2001] and Zobeck [2004]. LDPSA measurements were collected following the NMR measurements. First, the sediments were removed from the sample holder and dried at room temperature. Three subsamples ranging from 500 mg to 1 g (larger amounts were used for sandier soils) of each mixture were used for LDPSA measurements; measurements on each subsample were repeated three times and then averaged. The effective particle size $D_{10}$, which represented the particle diameter such that 10% of all particles are smaller by mass was determined from the LDPSA measurements.

2.5 Results

The physical properties ($S_{SA}$, $\phi_{grav}$, and $D_{10}$) and characteristic NMR parameters ($\phi_{NMR}$ and $T_{2ML}$) for all samples used in this study are reported in Table 2.2. For all samples, $S_{SA}$ varies between 0.04 and 11.55 m$^2$/g and increases with clay content. The term $\phi_{grav}$ varies from 0.21 to 0.33 for samples with <10% clay content and from
0.34 to 0.72 for samples with clay contents >10%.

2.5.1 The specific surface area $S_{SA}$ and clay content

Figure 2.2 shows the relationship between the specific surface area $S_{SA}$ and clay content for all samples: $S_{SA}$ increases linearly with clay content indicating that the clay content is the primary factor controlling $S_{SA}$.

![Regression curve](image)

Figure 2.2: Specific surface area $S_{SA}$ as a function of clay content (%) for all samples. The regression equation and the fit to the data (the dashed line) are also shown in the figure.

The GSDs determined from the LDPSA measurements for the pure materials and mixtures are shown in Figure 2.3. Figure 2.3a shows the GSDs for the 100% silt, sand, and clay samples; the silt and sand have narrow and unimodal GSD, whereas the clay has a broader GSD. For clay, the peak of the GSD is between 1 and 60 $\mu$m;
for silt, the peak is between 10 and 60 \( \mu m \); and for sand, the peak is between 100 and 600 \( \mu m \).

Figures 2.3b–e show the results for mixtures with 1%, 3%, 5%, and 7% clay content, respectively; Figure 2.3f shows the results for mixtures with >10% clay content. For all of the mixtures, the GSD is bimodal. We refer to the mode centered at small particle sizes as the small-grain mode and the mode centered at larger particle sizes as the large-grain mode.

For all mixtures, a consistent trend is found with silt or sand content: increasing silt content corresponds to an increase in the size of the small-grain mode; increasing sand content increases the size of the large-grain mode. For the mixtures with \( \leq 10\% \) clay content, the small-grain mode is located between 10 and 60 \( \mu m \), and the large-grain mode is located between 100 and 600 \( \mu m \). For these samples, the location and peak (at approximately 40 \( \mu m \)) of the small-grain mode are comparable with the pure silt sample, and the location and peak (at approximately 300 \( \mu m \)) of the large-grain mode is comparable with the pure sand sample. For mixtures with >10% clay (Figure 2.3e), the small-grain mode is broad and is located between 1 and 60 \( \mu m \); as the clay content increases, the peak of the small-grain mode shifts to smaller particle sizes. We note that the shape of the small-grain mode for the sample with 60% clay content is similar to the GSD for the pure kaolinite sample, with the same peak location at a particle size of approximately 7 \( \mu m \). For the high-clay content samples, the large-grain mode is located between 100 and 600 \( \mu m \) and is, again, comparable with the pure sand sample.

The \( D_{10} \) values are 0.7, 17, and 177 \( \mu m \) for clay, silt, and sand, respectively. The \( D_{10} \) values for samples with \( \leq 10\% \) clay content range from 4.7 to 111 \( \mu m \), whereas the \( D_{10} \) values for samples with >10% clay content range from 1.1 to 6.2 \( \mu m \). For samples with the same clay content (\( \leq 10\% \)), the \( D_{10} \) values decrease as the silt content increases.
Figure 2.3: The GSDs for (a) pure kaolinite clay, silt-size glass beads, and Wedron sand samples and for sand-silt-clay mixtures with clay contents of (b) 1%, (c) 3%, (d) 5%, (e) 7%, and (f) >10%.
2.5.2 NMR data: \( T_2 \) distributions, \( \phi_{NMR} \), and \( T_{2ML} \)

Figure 2.4 shows the \( T_2 \) distributions for the pure sand, silt, and clay samples as well as the mixtures. All data are collected at an echo time of 200 \( \mu s \). As with Figure 2.3, Figure 2.4a shows the pure samples. Figure 2.4b–e shows mixtures with 1%, 3%, 5%, and 7% clay content, and Figure 2.4f shows mixtures with clay content \( \geq 10\% \). Similar to the GSDs, each of the pure samples has a unimodal and narrow distribution. However, unlike the GSDs, for nearly all mixtures in Figure 2.4, the \( T_2 \) distribution is unimodal and narrow. Broad \( T_2 \) distributions are observed for mixtures (Figure 2.4b–d) with low clay content (1%-5%), low silt content (5%), and high sand content (\( \geq 90\% \)). For the mixture (Figure 2.4b) with 1% clay, 5% silt, and 94% sand, there is evidence of a bimodal \( T_2 \) distribution. For samples with <10% clay, as shown in Figure 2.4b–e, the \( T_2 \) distribution has a longer peak relaxation time than the pure kaolinite sample that decreases with clay content. For samples with >10% clay in Figure 2.4f, the peak relaxation times of the \( T_2 \) distributions are shorter than the peak relaxation time of the pure kaolinite sample. For nearly all mixtures (with the exceptions of the mixture with 1% clay, 5% silt, and 94% sand, and the mixture with 1% clay, 25% silt, and 74% sand), the peak relaxation times are shorter than that of the pure silt sample. For all mixtures, we find that the peak relaxation times of the \( T_2 \) distributions are shorter than the peak relaxation time of the pure sand sample.
Figure 2.4: Representative $T_2$ distributions obtained for water-saturated mixtures with (b) 1%, (c) 3%, (d) 5%, (e) 7%, and (f) >10% clay content. Also shown for reference on (a) are the relaxation time distributions for the pure sand, silt, and clay samples.
The NMR estimated porosity $\phi_{NMR}$, given in Table 2.2, varies from 0.21 to 0.74 and compares favorably with $\phi_{grav}$ for all samples regardless of mixture type. A comparison of $\phi_{grav}$ and $\phi_{NMR}$ is shown in Figure 2.5 and the calculated RMS errors are 0.022 from $RMS = \sqrt{\frac{1}{N} \sum_{i=1}^{N} y_i - \hat{y}_i}$ where $y_i$ represents $\phi_{grav}$, $\hat{y}_i$ represents $\phi_{NMR}$.

![Figure 2.5: The NMR-estimated porosity plotted versus the gravimetric porosity for all samples. The dashed line represents the one-to-one curve.](image)

The mean-log relaxation time $T_{2ML}$ determined from the NMR measurements for all samples is shown in Table 2.2. The $T_{2ML}$ value for the pure kaolinite, glass beads, and sand is 0.05, 0.14, and 0.67 s, respectively. This is consistent with previous studies [Matmon and Hayden, 2003] because kaolinite clay, with small particles, should have small pore sizes. We note that $T_{2D}$ is negligible for these samples because all mixtures do not have a dependence on the square of echo time.

To better assess the trends in the $T_2$ distributions, the $T_{2ML}$ values for each
mixture are plotted versus the clay, silt, sand content as shown in Figure 2.6a–c, respectively. At low clay content (<10%), clay content tends to be the major factor governing the $T_2$ distribution of these mixtures. We find that a threshold clay percentage of 10%, separates the NMR response. For mixtures with <10% clay, $T_{2ML}$ decreases with increasing clay content. For mixed samples with $\geq 10\%$ clay, $T_{2ML}$ is nearly constant with increasing clay content. For mixtures with the same and low clay content (<10%), $T_{2ML}$ decreases with increasing silt content, whereas it increases with increasing sand content.
Figure 2.6: The mean-log relaxation time $T_{2ML}$ for all mixtures versus the (a) clay, (b) silt, and (c) sand content. The size of the circle represents the clay content, which ranges from 0% to >10%. Mixtures with >10% clay content are plotted in the same size circle because very few changes are observed in the values of $T_{2ML}$. 
2.6 Discussion

Our results show that, at low clay content (<10%), $T_{2ML}$ values decrease with the increasing clay content in the mixtures, whereas at clay contents >10%, the $T_{2ML}$ values stay approximately the same. These results suggest that a 10% clay content represents a threshold of clay distributed throughout the sample due to the homogeneous packing of the mixtures. When clay content within the soil is above the threshold point, clay dominates the NMR relaxations.

The distribution of the clay, silt, and sand within a ternary mixture is conceptualized by Fiès and Bruand [1998]. This work describes the pores in clay, silt, and sand mixture as lacunar pores, which arise due to the presence of the clay particles between the silt and sand particles, as shown in Figure 2.7a and 2.7b, and from clay pores due to the packing of clay particles as shown in Figure 2.7c. A clean sand sample with no clay content contains large lacunar pores with unimodal PSD. For mixtures with low clay content (<10%), pore sizes are reduced because the clay particles tend to form a coating on the silt and sand particles in the mixture [Fiès and Bruand, 1998], and the PSD can be bimodal.
Figure 2.7: A schematic diagram showing how the clay will be accumulated in the larger pores of sand and silt. (a) Sand-Silt-Clay mixture: circle, sand fraction; grey, silt-clay phase. (b) Clay-silt mixture: circle, silt fraction; grey, clay fraction. (c) Clay fraction: black, clay particles; white, clay pores. SL, lacunar pore due to sand-sized particles; ZL, lacunar pore due to silt-sized particles. Figure modified from Fiès and Bruand [1998]

The increasing clay content leads to the shifting of the $T_2$ relaxation peak to shorter times. As shown in Figure 2.8, for mixtures with a low clay content (<10%), the $T_2$ relaxation time decreases with increasing $S_{SA}$, which is primarily due to the clay content. Our results are supported by the findings of Matmon and Hayden [2003], which show that, in a mixture of clay and beads with 10% kaolinite, the clay coats the beads and fills in small pores and narrow wedges of larger pores. For mixtures with high clay content (>10%), the $S_{SA}$ of mixtures increases with the increasing clay content. However, the T2ML remains constant despite increases in $S_{SA}$, as shown in Figure 2.8 because clay particles are filling the interstitial space between silt and sand. The T2 distributions of mixtures with more than 10% clay content are centered at short relaxation times varying between 0.02 and 0.04 s and are unimodal for mixtures with more than 10% clay, which suggests that, at this 10% threshold, clay can be found in every interstitial space within the sample.
The clay used in this study was kaolinite, a nonswelling clay, and the mixtures were all prepared homogeneously. We used a nonswelling clay to focus our work on the effect of particle size on the NMR response of water-saturated sediments. However, we recognize that clay mineralogy may have additional impacts not observed in this study and, as such, should be the focus of future studies. Similarly, all of the mixtures in this study were prepared homogeneously, but as reported in Osterman et al. [2019], in addition to the clay content, the packing structure has a strong influence on the NMR response of water-saturated sediment samples. Future study is necessary to expand on the work of Anand et al. [2008] and Osterman et al. [2019] and to test the NMR responses of mixtures with clustered or laminated clays with a wider range of clay contents.

2.7 Conclusion

We systematically examined the influence of sand, silt, and clay content on the NMR $T_2$ relaxation times of synthetic sand-silt-clay mixtures. Bimodal distributions of the grain sizes are observed in all mixtures measured from LDPSA. However, the $T_2$ distribution is unimodal for nearly all mixtures. The findings of this study suggest that the 10% threshold for clay content is critical for interpreting NMR data on
unconsolidated materials because clay dominates the NMR relaxations when clay content is above the threshold point. The sand and silt content are found to affect the mean-log relaxation times $T_{2ML}$ for mixtures with low clay content (<10%) but show no impact on $T_{2ML}$ for mixtures with a high clay content (>10%). Future testing is required to understand how different types of clay impact the NMR responses on synthetic mixtures and realistic soils.
Chapter 3

NMR relaxation times for soil texture estimation in the laboratory: A comparison to the laser diffraction and sieve-pipette methods

3.1 Abstract

Nuclear magnetic resonance (NMR) relaxation time ($T_2$) distributions are well known to be linked to the pore size distribution and show promise as a method of estimating soil texture. As traditional laboratory methods used for soil texture estimates in soil science are generally time-consuming, in this study, we explore an alternative approach based on NMR $T_2$ distributions to estimate the soil texture of water-saturated soil samples collected from three field sites. Using two $T_2$ cut-off times, $T_{2a}$ and $T_{2b}$, the $T_2$ distribution of soil was partitioned into three regions, short, intermediate, and long relaxation times, each of which represents the fraction of clay, silt, and sand, respectively. Two approaches for determining the cut-off times were used: the first used $T_2$ cut-off times determined from the data from all sites and the second used site-specific $T_2$ cut-off times. The NMR estimates of soil texture were compared to measurements of soil texture made using the sieve-pipette method and laser diffraction particle size analysis (LDPSA). The results show that there is no universal cut-off time for estimating the clay, silt, and sand fraction based on the NMR $T_2$ distributions. The accuracy of NMR measurements to estimate the soil texture depends on the magnetic susceptibility of the measured material. For soils with low magnetic

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susceptibility ($<2 \times 10^{-4}$ SI) using site-specific cut-off times, the NMR-derived soil texture (root mean squared error RMSE = 9.43%) more closely matches the soil texture measured from the sieve-pipette method than the soil texture determined using LDPSA (RMSE = 11.88%). However, the NMR estimate of soil texture breaks down for soils with high magnetic susceptibility ($>4 \times 10^{-4}$ SI). These results suggest that the NMR method can provide reasonable estimates of the soil texture for soils with low magnetic susceptibility.

3.2 Introduction

Soil texture, that is, the percent of sand, silt, and clay in the soil, affects important soil functions including soil-water retention characteristics, nutrient retention and supply, leaching and erosion potential, hydraulic conductivity, and the carbon-sequestration capacity. Quantifying soil texture is thus critical to assessing physical, chemical, and biological soil function and in developing best practice soil management [Kettler et al., 2001]. However, despite the importance of soil texture in assessing soils, it remains difficult to measure in the field, is usually collected sparsely compared to the natural spatial variability, and can only be obtained with high accuracy via measurements made in the laboratory.

There are two primary laboratory methods by which soil texture is measured: the sieve-pipette method or the hydrometer method. Briefly, sand fractions are determined by sieving, and clay and silt fractions are calculated from the density of a suspension measured using settling rates, based on the principle of sedimentation, with a hydrometer or a pipetting apparatus [Gee and Bauder, 1986; Gee and Or, 2002]. Once the clay, silt, and sand fractions have been determined, the soil texture can be classified by the use of a textural triangle (see e.g., Jury and Horton [2004]). However, both methods require field samples to be tested in the laboratory and are time-consuming, especially for the determination of clay particles (over a couple of hours). Small errors in dispersion and sampling lead to errors in estimates of clay,
silt, and sand fractions and so great care and attention must be taken when making these measurements.

Laser diffraction particle size analysis (LDPSA) is an alternative method for determining the soil texture [McCave et al., 1986; Zobeck, 2004]. However, it requires field samples and can only be performed in the laboratory with specialized equipment. Furthermore, LDPSA tends to underestimate the clay fraction in soil with respect to the pipette method because of deviations from spherical shape and heterogeneity of soil particle density [Bah et al., 2009]. Thus researchers have suggested that the LDPSA method should not be used for soil texture classification without verification using another method such as the pipette method [Eshel et al., 2004; Taubner et al., 2009].

Geophysical methods have been used extensively to characterize soils (e.g., [Binley et al., 2015; Romero-Ruiz et al., 2018]). These methods can be used in the field, many are non-invasive (i.e., do not require soil samples or an augered profile) and the data can be collected relatively quickly. For example, electrical conductivity (EC) or electromagnetic induction (EMI), which measures the EC of soils [Robinson et al., 2008a; Sudduth et al., 2010, 2013], ground-penetrating radar (GPR), which measures the dielectric constant [Grote et al., 2010], and the induced polarization (IP) method which measures the imaginary conductivity and is related to the specific surface area and the cation exchange capacity of soils [Slater et al., 2006; Revil et al., 2017], have been widely used to characterize soils. However, no direct or global relationship exists between EC, dielectric constant or the imaginary conductivity and soil texture and these geophysical measurements require local calibration for effective use in the prediction of soil properties, including soil texture. An emerging geophysical measurement in soil science, nuclear magnetic resonance (NMR), is sensitive to the pore-size distribution of water-saturated soils [Hinedi et al., 1997; Jaeger et al., 2009; Stingaciu et al., 2010; Behroozmand et al., 2017] and is related to the water retention curve [Costabel and Yaramanci, 2013; Falzone and Keating, 2016]. In this laboratory study,
we examine the use of NMR for providing a quantitative estimate of soil texture.

The NMR measurement yields a signal amplitude, which is proportional to the water content, and distribution of transverse relaxation times (or $T_2$ distribution). In water-saturated geologic media, the $T_2$ distribution is often thought to be a linear transformation of the pore-size distribution (PSD) [Hinedi et al., 1997; Bird et al., 2005], where long $T_2$ values correspond to large pores and short $T_2$ values correspond to small pores. The linear transformation between the $T_2$ distribution and the PSD has been validated for materials with various soil textures, for example, agricultural sand, loam and clay soils [Jaeger et al., 2009], artificial sand, and mixtures of sand and clay [Stingaciu et al., 2010; Osterman et al., 2019]. Various studies have shown that the PSD of soil can be related to the grain-size distribution (GSD) [Arya and Paris, 1981; Haverkamp and Parlange, 1986; Nimmo et al., 2007]. Assuming spherical particles and cylindrical pores, Arya and Paris [1981] showed that the PSD is a linear transformation of the GSD. As the NMR $T_2$ distribution can be linearly transformed to the PSD for water-saturated samples, these models indicate that the $T_2$ distribution can be linked to the GSD as demonstrated in Keating and Falzone [2013]. Here we hypothesize that $T_2$ distribution can also be used to estimate the soil texture.

To test this hypothesis, we made NMR measurements on 65 water-saturated agricultural soil samples, with a broad range of soil textures from clay, clay/silt loam, to sand. The NMR estimates of soil texture were compared to measurements of soil texture made using LDPSA and sieve-pipette methods. The results from this study represent a step toward applying NMR to estimate soil texture in the field and broadening the application of NMR data to agricultural investigations.

### 3.3 NMR theory

In the presence of a static magnetic field, the nuclear spins of hydrogen protons in water align themselves along the magnetic field and create a net magnetization $M$. The
magnetization can be perturbed from equilibrium using a series of energizing electromagnetic pulses, such as the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [Carr and Purcell, 1954; Meiboom and Gill, 1958]; the pulses tip the nuclear spins out of alignment and the transverse component of $M$, $M_{xy}$, can be measured inductively as the spins relax back to the equilibrium. When measured using the CPMG pulse sequence, as is commonly used in NMR laboratory and logging measurements [Behroozmand et al., 2015], $M_{xy}$ is a multiple exponential decays characterized by an initial signal amplitude and a distribution of transverse relaxation times or $T_2$ distribution. The initial signal amplitude is proportional to the number of hydrogen protons and thus yields the water content in the measured sample [Coates et al., 1999].

For a water-saturated soil, assuming that relaxation occurs in the fast diffusion regime [Brownstein and Tarr, 1979; Ryu, 2009], each $T_2$ value in the $T_2$ relaxation time distribution represents a different pore environment (i.e., different pore size and/or pore with different surface chemistry). Each $T_2$ value can then be described by three relaxation processes occurring in parallel,

$$\frac{1}{T_2} = \frac{1}{T_{2B}} + \frac{1}{T_{2S}} + \frac{1}{T_{2D}},$$

(3.1)

where $T_{2B}$ is the bulk fluid relaxation time, $T_{2S}$ is the surface relaxation time, and $T_{2D}$ is the diffusion relaxation time. In most cases, the bulk relaxation time is much longer than the surface relaxation time and is assumed to be negligible (i.e., $\frac{1}{T_{2B}} \ll \frac{1}{T_{2S}}$). $T_{2S}$ occurs due to the relaxation of the nuclear spins at pore-grain interfaces [Kleinberg et al., 1994]. $T_{2D}$ accounts for the dephasing of spins that occurs when relaxation takes place in an inhomogeneous magnetic field. Inhomogeneities in the magnetic field can be applied, associated with the NMR magnet, or caused by the presence of magnetic minerals such as magnetite.

When bulk and diffusion relaxation are negligible and the sample material is
homogeneous, each $T_2$ value corresponds to specific pore size and is represented by [Brownstein and Tarr, 1979]

$$\frac{1}{T_2} \approx \frac{1}{T_{2S}} = \rho_2 \frac{\alpha}{r},$$

(3.2)

where $\rho_2$ is the surface relaxivity, $\alpha$ is a shape factor accounting for pore space, $r$ is the mean pore radius, and $S/V$ is the pore surface area to volume ratio. Equation 3.2 is the basis for interpreting the $T_2$ distribution as a PSD. NMR-derived PSDs can further be used to estimate other hydraulic properties, such as the permeability or hydraulic conductivity and the water retention curves of soils [Costabel and Yaramanci, 2013; Osterman et al., 2016, 2019]. However, as stated by Costabel and Yaramanci [2013], the NMR-derived PSD is unsuitable for estimating these hydraulic parameters if the samples are not saturated. In this study, we focus on measurements made at full saturation to avoid ambiguities in interpretation.

### 3.4 Materials and methods

#### 3.4.1 Soil samples

A total of 65 agricultural soils were used for laboratory analysis. Soils were collected from 13 profiles across three agricultural field sites (five profiles at site 1; four profiles at site 2 and site 3) in northwestern (NW) Illinois, USA. The number of profiles at each site was chosen to ensure that the samples from each site represented the soil variability across the field using a bulk apparent soil electrical conductivity map to stratify sample placement. At each profile location, a soil core sample (2.54 cm diameter, 15 cm height) was collected every 15 cm using a soil probe. Five soil cores were collected at each location at depths of 0–15, 15–30, 30–45, 45–60, and 60–75 cm. Samples were collected in zip lock bags and air-dried at room temperature before any further analysis. The following name convention was used for all soil samples: the
first number refers to the site (“1”, “2”, or “3”), the following number “−1”, “−2”, “−3” etc. indicates the profile ID within that site, and the depth range in a pair of parentheses indicates top and bottom depths for soil sampling. For example, sample 1–2(0–15 cm) refers to the soil sample collected at depths of 0–15 cm from profile 2 at site 1.

The sites for this study were chosen to represent the two major soil genetic landscapes in the local area of the study, which included portions of Rock Island (site 1), Mercer (site 2), and Henderson (site 3) Counties, in NW Illinois. Sites 1 and 2 are located on alluvium from the nearby (<3 km) Mississippi River. Site 3 was located in an adjacent upland ridgetop setting formed in loess over till. The alluvial history of sites 1 and 2 produced a wide range of soil textural and morphological variability in mostly flat terrain. The upland landscape of site 3 includes some variability from local drainage incision but samples are collected entirely in loess. Table 3.1 shows the United States Department of Agriculture (USDA) soil taxonomic designations obtained from the U.S. Soil Survey Geographic Database (SSURGO) [Soil survey staff] for the 13 profiles in the study sites. Images of three soils from each site were selected to show the variation across the different sites. Samples from site 1 are shown in Figure 3.1 a–c; samples from site 2 are shown in Figure 3.1 d–f; samples from site 3 are shown in Figure 3.1 g–i.
Table 3.1: The Soil Survey Geographic Database (SSURGO) map unit and USDA taxonomic designations for soil profiles sampled in this study

<table>
<thead>
<tr>
<th>Site</th>
<th>Profile ID</th>
<th>SSURGO map unit</th>
<th>USDA soil taxonomy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>1</td>
<td>Sawmill silty clay loam, 0 to 2 percent slopes, rarely flooded</td>
<td>Fine-silty, mixed, superactive, mesic Cumulic Endoaquolls</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Sawmill silty clay loam, 0 to 2 percent slopes, rarely flooded</td>
<td>Fine-silty, mixed, superactive, mesic Cumulic Endoaquolls</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Sawmill silty clay loam, 0 to 2 percent slopes, rarely flooded</td>
<td>Fine-silty, mixed, superactive, mesic Cumulic Endoaquolls</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Wabash silty clay, 0 to 2 percent slopes, rarely flooded</td>
<td>Fine, smectitic, mesic Cumulic Vertic Endoaquolls</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>Wabash silty clay, 0 to 2 percent slopes, rarely flooded</td>
<td>Fine, smectitic, mesic Cumulic Vertic Endoaquolls</td>
</tr>
<tr>
<td>Site 2</td>
<td>1</td>
<td>Coloma sand, 1 to 7 percent slopes</td>
<td>Mixed, mesic Lamellic Udipsamments</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Crescent loam, 2 to 5 percent slopes</td>
<td>Fine-loamy, mixed, superactive, mesic Typic Argiudolls</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Crescent loam, 2 to 5 percent slopes</td>
<td>Fine-loamy, mixed, superactive, mesic Typic Argiudolls</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Sparta loamy sand, 2 to 6 percent slopes</td>
<td>Sandy, mixed, mesic Entic Haplustolls</td>
</tr>
<tr>
<td>Site 3</td>
<td>1</td>
<td>Joy silt loam, 0 to 2 percent slopes</td>
<td>Fine-silty, mixed, superactive, mesic Aquic Hapludolls</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Biggsville silt loam, 5 to 10 percent slopes, eroded</td>
<td>Fine-silty, mixed, superactive, mesic Dystric Eutrudepts</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>Seaton silt loam, 5 to 10 percent slopes, eroded</td>
<td>Fine-silty, mixed, superactive, mesic Typic Hapludalfs</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>Mannon silt loam, 2 to 5 percent slopes</td>
<td>Fine-silty, mixed, superactive, mesic Mollic Hapludalfs</td>
</tr>
</tbody>
</table>
3.4.2 Magnetic susceptibility measurements

Previous laboratory studies [Bryar et al., 2000; Keating and Knight, 2007, 2008] have shown that the presence of iron (III)-bearing minerals decreases the NMR relaxation time. We can measure the magnetic susceptibility (MS) of each soil sample to determine if iron-bearing minerals affect the NMR measurement. Measurements of the volumetric MS, which is the ratio of magnetization in a volume of material to the magnetic field strength applied to that volume, were made using a Bartington MS2 system with a MS2K sensor. To prepare the sample for the MS measurement, the

Figure 3.1: Representative disaggregated soil samples used in this study. (a–c) soils from site 1; (d–e) soils from site 2; (g–i) soils from site 3.
soil was oven-dried at 80 °C overnight and was packed into a 15 ml polypropylene plastic vial covered with parafilm. The MS measurement was repeated three times and the average was used as the MS value of each sample.

### 3.4.3 NMR measurements and analysis

NMR measurements were conducted before soil texture analysis. Soils were dried in an oven at 80 °C overnight and then were disaggregated. The NMR experiments were conducted on cylindrical containers with lids (diameter, 2.5 cm; length, 4.3 cm; volume, 21.11 ml), which were packed with the soils using the wet packing technique as detailed by Oliviera et al. [1996]. Parafilm was placed at the top of the container, under the lid, to prevent water from evaporating during the NMR measurement. The porosity of each sample, $\phi$, was then determined from:

$$\phi = \frac{V_w}{V_s}, \quad (3.3)$$

where $V_w$ is the volume of water used for saturation, determined gravimetrically, and $V_s$ is the volume of the sample holder.

NMR data were collected with a Magritek 2.0 MHz Rock Core Analyzer (Magritek Ltd., Wellington, New Zealand) using a CPMG pulse sequence with echo times $t_E = 200\mu s$ and the number of echoes $n = 15,000$ chosen so that the signal fully decayed within the time frame of the measurement. All CPMG measurements were stacked 32 times to ensure a high signal-to-noise level. To obtain the $T_2$ distributions, a nonnegative least-squares inversion algorithm with second-order Tikhonov regularization [Tikhonov, 1963] was applied using 160 predetermined log-spaced values of $T_2$ with a range from 0.1 ms to 10 s. The regularization parameter, which controls the smoothness of the distribution, was selected corresponding to the point of highest curvature in the root mean squared errors (RMSEs) versus regularization parameter curve, as described by Costabel and Yaramanci [2013].
3.4.4 Laser diffraction particle size analysis

After the NMR measurements, LDPSA was performed for each sample (without sieving before the measurements). A 500 mg to 1 g (larger amounts were used for sandier soils) subsample of each soil was weighed and dispersed using 10 ml of hexametaphosphate (40 g/L) and sodium carbonate (10 g/L) solution in a 25 ml glass bottle before testing. The LDPSA data were collected with a Beckman Coulter LS 13 320 (Brea, California, USA), which contains a 5 mW laser diode with a wavelength of 750 nm and can measure particle sizes ranging from 0.017 to 2000 µm using the polarization intensity differential scattering (PIDS) option. Further details about the LDPSA, the PIDS system, sample preparation and the instrument set up can be found in Xu [2001] and Zobeck [2004]. The effective particle size, \( D_{10} \), which corresponds to the diameter when 10% of the cumulative volume is reached based on the LDPSA-determined GSD, was calculated for each sample.

3.4.5 Sieve-pipette method

Particle size analysis using the standard sieve-pipette method was performed following the NMR and LDPSA measurements. The procedure used for the sieve-pipette method is based on that initially developed by Van Reeuwijk [2002]. First, each soil sample was dried in an oven at 80 °C overnight, ground, and then sieved to remove coarse particles larger than 2 mm. The coarse material with particle size >2 mm was less than 0.5% in all samples. A 20 g subsample of the fine material with particle size <2 mm was used for particle size analysis. Next, the samples were pretreated to enhance the separation or dispersion of the aggregates Gee and Or [2002]. Each sample was treated with hydrogen peroxide (\( \text{H}_2\text{O}_2; 30\% \text{ concentration} \)) to decompose the organic matter and then transferred to a 500ml bottle, filled to 400 ml by adding water to a 20 ml dispersing solution (sodium hexametaphosphate (\( \text{NaPO}_3 \)) 6; 40 g/L and sodium carbonate \( \text{Na}_2\text{CO}_3; 10 \text{ g/L} \)). The bottles were left on an end-over-end
shaker overnight. For more details about the particle size analysis by sieve-pipette method, readers are referred to work by Gee and Or [2002].

### 3.4.6 Determination of cut-off times

To obtain the relative fractions of each particle size from the saturated $T_2$ distribution, we determined two cut-off times, $T_{2a}$ which separates clay and silt, and $T_{2b}$, which separates silt and sand. These two cut-off times are used to partition the $T_2$ distributions into three regions, as shown in Figure 3.2. Clay is represented by short relaxation times, silt is represented by intermediate relaxation times, and sand is represented by long relaxation times. The relative portion of clay, silt, and sand can be measured by the ratio of the sum of water content under the respective portion of the $T_2$ distribution to the sum of water content under the whole $T_2$ distribution. The two cut-off values were determined by minimizing the RMSE from

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{j=1}^{N} (\hat{y}_j - y_j)^2}.$$  \hspace{1cm} (3.4)

where $\hat{y}_j$ are the clay, silt, and sand fractions derived from the NMR $T_2$ distributions and $y_j$ is the corresponding fraction measured by the sieve-pipette method. The fits were initialized with $T_{2a} = 2$ ms and $T_{2b} = 100$ ms to calculate the clay, silt, and sand fraction from $T_2$ distributions, and the optimal values of $T_{2a}$ and $T_{2b}$ were determined when the RMSE was minimized overall soil samples according to the method described by Lagarias et al. [1998], with MATLAB using the fminsearch function.
3.5 Results

3.5.1 Soil texture determined from the sieve-pipette method

A ternary diagram of the soil texture, determined using the sieve-pipette method, showed that the 65 soil samples cover a large range of soil textures (Figure 3.3). Soils from site 1 ranged from sandy-clay loam to clay and had the highest clay fraction (∼20 to 60%) of all sites. Soils from site 2 ranged from sand to silty-clay loam and had the highest sand fraction (∼20 to 90%) of all sites. Soils from site 3 ranged from silty-clay loam to silt loam and had the highest silt fraction (∼60 to 85%) of all sites.
3.5.2 Physical properties

The GSDs of all soil samples, determined using LDPSA, were plotted as volume percent versus the diameter in Figure 3.4. For site 1 soils, the GSDs were broad with a dominant peak at diameter $5 \, \mu m$ and a second peak at $\sim 200 \, \mu m$ present only in multiple depths at profiles 1, 2, and 3. The GSDs of site 2 soils showed two kinds of distributions: the GSDs of soils from profiles 1 and 4 were narrow with a peak centered at large diameter ($\sim 300 \, \mu m$), whereas for soils from profiles 2 and 3, the GSDs were broad and centered around small diameters without a dominant peak like profiles 1 and 4. For site 3 soils, the GSDs were consistent across all profiles and
depths with a peek at the diameter of $\sim 40 \mu m$.

![Figure 3.4: Grain size distributions (GSDs) of soil samples from all sites determined using laser diffraction particle size analysis (LDPSA)](image)

The MS and porosity values for all soil samples are given in Table 3.2. The averaged MS values $\pm$ standard deviation for soil samples from site 1, 2, and 3 were $1.38 \pm 0.28$, $8.67 \pm 2.92$, and $1.56 \pm 0.81 \times 10^{-4}$ SI, respectively. The soil samples from site 2 had higher mean MS values than samples from sites 1 and 3. Most soil samples from sites 1 and 3 had MS values lower than $2 \times 10^{-4}$ SI; however, there were a few samples from sites 1 and 3 (samples 1–3 [0–15 cm], 1–3 [15–30 cm], 3–4 [0–15 cm], and 3–4 [15–30 cm]) that had higher MS values ranging from $2.05 \times 10^{-4}$ to $4.69 \times 10^{-4}$ SI.

The porosity (given in Table 3.2) ranged from 0.43 to 0.66, from 0.27 to 0.56, and from 0.50 to 0.61 for site 1, 2, and 3 soils, respectively. $D_{10}$ values ranged from $\sim 1$ to 177 $\mu m$ for all soils. Soils from site 1 had $D_{10}$ values from 0.87 to 1.67 $\mu m$. Soils from site 2 had $D_{10}$ values ranging from 1.05 to 177 $\mu m$. Soils from site 3 had $D_{10}$ values ranging from 1.83 to 2.6 $\mu m$. 
Table 3.2: Physical properties, magnetic susceptibility (MS), porosity ($\phi$), and the soil particle size ($D_{10}$), for each soil sample.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Site 1</th>
<th></th>
<th>Site 2</th>
<th></th>
<th>Site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ProfileMS ID</td>
<td>$\phi$ ($10^{-4}$ SI)</td>
<td>$D_{10}$ ($\mu$m)</td>
<td>ProfileMS ID</td>
<td>$\phi$ ($10^{-4}$ SI)</td>
</tr>
<tr>
<td>0-15</td>
<td>1</td>
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<td>1.52</td>
<td>1</td>
</tr>
<tr>
<td>15-30</td>
<td>1</td>
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<td>1</td>
</tr>
<tr>
<td>30-45</td>
<td>1</td>
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<td>0.49</td>
<td>1.52</td>
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</tr>
<tr>
<td>45-60</td>
<td>1</td>
<td>1.46</td>
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<td>1.38</td>
<td>1</td>
</tr>
<tr>
<td>60-75</td>
<td>1</td>
<td>1.18</td>
<td>0.48</td>
<td>1.67</td>
<td>1</td>
</tr>
<tr>
<td>0-15</td>
<td>2</td>
<td>1.36</td>
<td>0.52</td>
<td>1.26</td>
<td>2</td>
</tr>
<tr>
<td>15-30</td>
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<td>0.98</td>
<td>0.48</td>
<td>0.87</td>
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</tr>
<tr>
<td>30-45</td>
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<td>0.47</td>
<td>1.52</td>
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</tr>
<tr>
<td>45-60</td>
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<td>2</td>
</tr>
<tr>
<td>60-75</td>
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<tr>
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<td>2.05</td>
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</tr>
<tr>
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<td>0.56</td>
<td>1.26</td>
<td>4</td>
</tr>
<tr>
<td>15-30</td>
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<td>0.59</td>
<td>1.15</td>
<td>4</td>
</tr>
<tr>
<td>30-45</td>
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<td>1.22</td>
<td>0.57</td>
<td>1.26</td>
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</tr>
<tr>
<td>45-60</td>
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<td>1.26</td>
<td>4</td>
</tr>
<tr>
<td>60-75</td>
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<td>1.49</td>
<td>0.61</td>
<td>1.26</td>
<td>4</td>
</tr>
<tr>
<td>0-15</td>
<td>5</td>
<td>1.62</td>
<td>0.61</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>15-30</td>
<td>5</td>
<td>1.57</td>
<td>0.63</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>30-45</td>
<td>5</td>
<td>1.41</td>
<td>0.63</td>
<td>1.15</td>
<td></td>
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<tr>
<td>45-60</td>
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<td>1.41</td>
<td>0.66</td>
<td>1.15</td>
<td></td>
</tr>
<tr>
<td>60-75</td>
<td>5</td>
<td>1.42</td>
<td>0.62</td>
<td>1.15</td>
<td></td>
</tr>
</tbody>
</table>
### 3.5.3 $T_2$ distribution from NMR

The $T_2$ distributions of all soils are shown in Figure 3.5. The $T_2$ distributions were normalized by the initial signal amplitude from an NMR measurement made on deionized water, thus yielding a plot of water content versus $T_2$. For soils at site 1, the $T_2$ distributions were consistent across all coring profiles and depths and showed a dominant peak at about 5 ms and a smaller peak near 1 ms. At site 2, the $T_2$ distributions were broad at all profiles. The dominant peak of $T_2$ distributions for profile 1 samples occurred approximately 100 ms later than the dominant peak of soils from the other three profiles in site 2. The $T_2$ distributions of profiles 2 and 3 were consistent, whereas the dominant peak of profile 4 was shifted towards shorter $T_2$. The $T_2$ distributions of site 3 soils were consistent across all sampled profiles and were centered around medium relaxation times, between 5 and 20 ms, and also with a smaller peak at around 1 ms. For soil samples from the same profile in site 3, the dominant peak of $T_2$ distributions shifted towards longer $T_2$ as depth increases.

![Figure 3.5: $T_2$ distributions of soil samples from all sites](image)

Figure 3.5: $T_2$ distributions of soil samples from all sites
3.5.4 **Comparison of LDPSA and sieve-pipette measurements of soil texture**

We first compared the LDPSA and sieve-pipette measurements of clay, silt, and sand content. For the comparison, we first need to determine the fractions of clay, silt, and sand from the GSDs; to do this we calculated the cumulative volume for particles with diameter $<8 \mu m$, $>8 \mu m$ and $<63 \mu m$, and $>63 \mu m$, to represent the clay, silt, and sand fractions, respectively. The grain size of 8 $\mu m$ was used to determine the clay fraction instead of the standard 2 $\mu m$, as using 2 $\mu m$ to estimate the clay fraction from LDPSA has been shown to result in an underestimation of the clay fraction due to deviations of the clay particles from the spherical shape and the heterogeneity of soil particle density [Konert and Vandenberghe, 1997; Eshel et al., 2004; Bah et al., 2009]. Konert and Vandenberghe [1997] showed that using a grain size of 8 $\mu m$ provided a more accurate determination of the clay fraction. A comparison of the clay, silt, and sand fractions determined from LDPSA and the sieve-pipette measurements is shown for all 65 soil samples in Figure 3.6a–c, respectively. Good agreement was found compared to the sieve-pipette results (RMSE = 10.74, see Table 3.3). The clay fraction was slightly overestimated with LDPSA measurements but overall compared well with the values determined from the sieve-pipette measurements (RMSE = 9.41%). The silt fraction from LDPSA also compared well with the values from the sieve-pipette method for all samples (RMSE = 8.41%). As shown in Figure 3.6b, for sites 1 and 2, the silt fraction determined from LDPSA compared well with the silt fraction from the sieve-pipette method; however, for site 3, the LDPSA-determined silt fraction was lower than the silt fraction determined with the sieve-pipette method. Considering the sand fraction comparison (Figure 3.6c), we found that there was a poor match between the values estimated from LDPSA and the sieve-pipette method (RMSE = 13.68%). For sites 1 and 2, the sand fraction determined with LDPSA was substantially smaller than the sand fraction determined with the sieve-pipette method.
method; however, for site 3, the sand fractions determined by both methods were comparable.

Figure 3.6: A comparison of clay, silt, and sand fractions obtained by laser diffraction particle size analysis (LDPSA) and the sieve-pipette method. A grain size of 8 µm is used to determine the clay fraction for LDPSA data.

Table 3.3: Root mean squared error (RMSE) values from the comparisons of particle-size fractions estimated by laser diffraction particle size analysis (LDPSA) or nuclear magnetic resonance (NMR) to that measured by sieve-pipette method.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Sites</th>
<th>RMSE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sites</td>
<td>Overall</td>
</tr>
<tr>
<td>LDPSA</td>
<td>All sites</td>
<td>10.74</td>
</tr>
<tr>
<td></td>
<td>Sites 1 and 3</td>
<td>11.88</td>
</tr>
<tr>
<td>NMR with non-site-specific $T_2$ cut-offs</td>
<td>All sites</td>
<td>23.24</td>
</tr>
<tr>
<td></td>
<td>Sites 1 and 3</td>
<td>18.77</td>
</tr>
<tr>
<td>NMR with site-specific $T_2$ cut-offs</td>
<td>All sites</td>
<td>15.37</td>
</tr>
<tr>
<td></td>
<td>Site 1 and 3</td>
<td>9.43</td>
</tr>
</tbody>
</table>

3.5.5 Comparison of NMR and sieve-pipette measurements of soil texture

We next compared estimates of the clay, silt, and sand fractions determined from the NMR measurements with the sieve-pipette measurements. To obtain the clay, silt, and sand fractions from the $T_2$ distributions, we split the $T_2$ distribution into regions separating the different grain sizes, similar to the GSD and as illustrated in Figure
3.2. A comparison of the clay, silt, and sand fraction for all sites determined by the NMR $T_2$ distributions using the non-site-specific cut-off times and the sieve-pipette method is shown in Figure 3.7a-c, respectively. The RMSE values for the NMR with non-site-specific $T_2$ cut-offs approach are given in Table 3.3. Overall, a poor agreement was found for the soil texture estimated by NMR compared to the sieve-pipette results (RMSE = 23.24%). For the clay, silt, and sand fractions estimated from NMR compared to the sieve-pipette method for all soils, poor agreement was also observed (RMSE = 20.01, 20.03, and 28.6% for clay, silt, and sand, respectively).

Closely examining the results in Figure 3.7a, there was a good agreement for the clay fraction from sites 1 and 3 with low MS values between the NMR data and the sieve-pipette measurements but poor agreement for soils from site 2 with high MS values. In the samples with high MS values, NMR yielded a consistently higher clay fraction than the sieve-pipette method. Poor agreements between the NMR and sieve-pipette data were also found for the silt and sand fractions for samples from site 2 (see Figure 3.7b and c).

We next compared the NMR-estimated clay, silt, and sand fraction with the sieve-pipette measurement without site 2; for these comparisons the $T_2$ cut-off times were determined from samples with low MS ($<4\times10^{-4}$ SI) for sites 1 and 3. Although a poor agreement was found (RMSE = 18.77%, see Table 3.3), the clay fraction from NMR compares well to the sieve-pipette method for samples with low MS (RMSE = 9.80%). Poor agreement was found in the comparison between the NMR-estimated silt and sand fraction for site 1 and 3 soils with low MS values (RMSE = 21.90% for silt fraction and RMSE = 21.94% for sand fraction).

We next examined the NMR estimates of soil texture using site-specific cut-off times. The comparisons of NMR estimates of soil texture versus measurements from the sieve-pipette method for all soils are shown in Figure 3.7d-f. Similar to when non-site-specific cut-off times were used, poor agreements were observed for the comparisons of clay, silt, and sand fractions from NMR to those from the sieve-pipette...
method for all soils (RMSE = 18.24, 11.23 and 15.82% for clay, silt, and sand fractions, respectively). For the clay fraction, as shown in Figure 3.7d, we found similar results as when non-site-specific cutoff times were used; there was a good agreement for site 1 and 3 soils and poor agreement for site 2 soils. Similarly, a poor agreement was also found for site 2 soils in silt and sand fraction comparisons between the NMR and sieve-pipette data (Figure 3.7e and f). The approach using NMR with site-specific $T_2$ cut-off times for soils with low MS provided the best result (RMSE = 9.43%). Similar to when non-site-specific cut-off times were used, the clay fraction from NMR compared well with the values from the sieve-pipette method for samples with low MS (RMSE = 9.53%). However, in contrast to when non-site-specific cut-off
times were used, good agreement was found in the comparison between the NMR-estimated silt and sand fractions for site 1 and 3 soils with low MS values (RMSE = 7.86% for silt fraction and RMSE = 10.69% for sand fraction).

3.5.6 Comparisons of the soil texture determined by sieve-pipette, LDPSA, and NMR $T_2$ measurement

Sieve-pipette texture, LDPSA texture, and NMR texture using site-specific $T_2$ cut-off times of the 65 soil samples were shown in a ternary diagram using the USDA soil texture classification in Figure 3.8a-c (A comparison including LDPSA using a grain size of 2 µm is shown in Figure A.1). The NMR data presented in Figure 3.8c was the same as that presented in Figure 3.7d-f. Based on the sieve-pipette method, the soil samples fell into multiple major texture groups: two soils from site 1 were clays and the remainder were sandy/silty clay loam and silty clay; the majority of soils from site 3 were silt loam; soils from site 2 were sand to loam. Comparatively, the LDPSA data showed: three soils from site 1 were loams and the rest were clay and silty clay; the majority of soils from site 3 were silty clay loams; soils from site 2 ranged from sand to silty clay. As for the NMR texture, one soil from site 1 was loam, two soils were silty clay, and the remainder were sandy/silty clay loam and clay; one soil from site 3 was silt and the majority of soils were silt loam; five soils from site 1 were loamy sand and the remainder were sandy clay and clay. For site 1 and 3 soils with low MS values, NMR provided better estimates of soil texture (RMSE = 9.43%) than LDPSA (RMSE = 11.88%) when compared to the sieve-pipette measurements.
3.6 Discussion

3.6.1 Influence of magnetic susceptibility on the \( T_2 \) distributions

Although \( T_2 \) distributions are often assumed to be linearly proportional to the pore-size distributions, this is only true when the diffusion relaxation time (in equation 3.1) is negligible and relaxation occurs in the fast diffusion regime [Godefroy et al., 2001]. In materials with high magnetic susceptibility, induced magnetization associated with the magnetic particles results in inhomogeneities in the magnetic field. In this case, the diffusion relaxation term is no longer negligible; laboratory and numerical studies have shown that this results in a broadening of the \( T_2 \) distribution and a shift of the \( T_2 \) distribution to shorter relaxation times [Keating and Knight, 2007; Fay et al., 2015; Grombacher et al., 2016]. When we compare the \( T_2 \) distributions to the GSDs from the LDPSA data, we see the effect of the high magnetic susceptibility minerals most clearly at profiles 2, 3, and 4 in site 2. The broadening and shift to faster relaxation times of the \( T_2 \) distributions for the soil samples with high magnetic susceptibility
explain why, for these samples, the clay fraction is overestimated. The low (< $2 \times 10^{-4}$ SI) and high (> $4 \times 10^{-4}$ SI) MS values are based on the data from this study and do not represent a universal cut-off; however, they are consistent with other studies showing that the NMR response of water-saturated materials with MS > $4 \times 10^{-4}$ SI are impacted by magnetic field inhomogeneities (Keating et al., 2020).

3.6.2 The $T_2$ cut-off times

Cut-off times that binning the NMR $T_2$ distribution into regions that characterize the pore space have been widely applied. In petroleum well logging, the cut-off times are used to determine the fraction of clay-bound fluid, capillary-bound fluid, and free fluid; these fractions yield information about the volume of extractable fluid and can be applied to estimate the permeability [Coates et al., 1999; Allen et al., 2000; Freedman, 2006]. The $T_2$ cut-off time between the free and bound fluid is typically set to 33 ms in sandstones [Straley et al., 1997] and can range from 45 to 200 ms for different types of carbonates (e.g. Westphal et al. [2005]; Maliva et al. [2009]); the $T_2$ cut-off time between the capillary-bound fluid and the clay-bound fluid is commonly set to 3 ms for sandstones [Straley et al., 1997; Allen et al., 2000]. Although in our study we use the cut-off times to define grain-size boundaries, not pore-size boundaries as is done in the petroleum industry, it is still useful to compare the cut-off times determined in this study to those used in reservoir evaluation. The $T_{2a}$ and $T_{2b}$ cut-off times determined in this study are shown in Table 3.4. We find that the cut-off times between the clay and silt fractions, $T_{2a}$, are around 3 ms for soils with low MS from sites 1 and 3 and regardless of whether a site-specific cut-off time is used. These values are similar to the oil industry standard of 3 ms used to define the capillary-bound and clay-bound fluid in sandstones. However, the value around 3 ms of $T_{2a}$ is not applicable to site 2 soils with high MS, which can cause relaxation to occur faster and cause the relaxation time distributions to be broader (Keating and Knight, 2008; Grombacher et al., 2016; Keating et al., 2020). The $T_2$
distribution of site 2 soils with high MS is not linearly proportional to the PSD as the diffusion relaxation term is no longer negligible. As shown in Figure 3.7 a and d, the NMR-derived clay content for site 2 was overestimated when compared with the clay content from the sieve-pipette method. The cut-off times between the silt and sand fractions, $T_{2a}$, vary between 4.6 and 37 ms and strongly depend on whether they were calculated using the high and low MS materials or whether a site-specific cut-off time was calculated.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Sites</th>
<th>$T_{2a}$ (ms)</th>
<th>$T_{2b}$ (ms)</th>
</tr>
</thead>
<tbody>
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<td>All sites</td>
<td>3</td>
<td>18.8</td>
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<td>Sites 1 and 3</td>
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</tr>
<tr>
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<td>Site 3</td>
<td>2.8</td>
<td>37</td>
</tr>
</tbody>
</table>

### 3.6.3 Poor estimates of the sand fraction

We observe poor estimates of the sand fraction when comparing both LDPSA and NMR measurements to the sieve-pipette method. Comparing the sand fraction determined by LDPSA and the sieve-pipette method, the RMSE = 13.68%. Analysis of site 1 and 2 soils shows that the sand fractions are underestimated by LDPSA with respect to the sieve-pipette method. For site 3, the sand fractions determined by LDPSA are comparable to those obtained by the sieve-pipette method. Poor estimates between LDPSA and the sieve-pipette method have been observed and previously been explained by the variations in particle mineralogy, shape, and other factors [Eshel et al., 2004; Makó et al., 2017].

Comparing the sand fractions measured by NMR and the sieve-pipette method, a poor agreement exists in site 2 soils regardless of whether a site-specific cut-off time is used. This difference can be explained in part because of the high MS value, $8.67 \pm 2.92$. 
\( \times 10^{-4} \) SI, of the site 2 soils. However, an additional important consideration is a regime in which relaxation occurs. The relationship between relaxation time and pore size described in equation 3.2 is only valid in the fast diffusion regime. The assumption of fast diffusion can be verified by calculating the control parameter \( \kappa = \frac{\rho r_{\text{eff}}}{D} \), where \( r_{\text{eff}} \) is the characteristic pore size [Brownstein and Tarr, 1979; Ryu, 2009; Keating and Knight, 2012]. Relaxation occurs within the fast diffusion regime if \( \kappa \ll 1 \), and in slow or intermediate diffusion regime if \( \kappa > 1 \). Following the approach of Costabel et al. [2018] and Keating and Knight [2012], we calculated \( \kappa \) for the samples in our study (see Table A.1 in the supplemental information). Although \( \kappa \) is less than 1 for soil samples from site 1 (with exception of soil profile 2 (0–15 cm) and is close to or less than 1 for site 3, for site 2, \( \kappa \gg 1 \) (as high as \( \sim 134 \)) for most soils. This indicates that relation may occur in the slow diffusion regime for the samples from site 2 and may further explain why the \( T_2 \) distributions from site 2 do not provide reliable estimates of the soil texture.

In our approach we have assumed that GSD is linearly related to the PSD; however, the specific mechanism by which the packing occurs will affect the true PSD and thus the NMR \( T_2 \) distribution. For example, Osterman et al. [2019] demonstrated that the distribution of clay (i.e., either homogeneously or as clay aggregates) within a sand/clay mixture affected the \( T_2 \) distribution. Further studies are thus needed to systematically examine the effects of packing on the soil texture estimates from NMR data.

Other factors that may complicate the interpretation of our data are the presence of organic matter or swelling clays. Schaumann et al. [2005] showed that the organic matter may cause an expansion of small pores and lead to a decrease in the micropore volume. The PSDs of soils with large organic matter content would show small water contents in the micropore and medium pore regions and thus the \( T_2 \) distributions would shift to a small area under short \( T_2 \) values, for example, \( \leq 4.5 \) ms [Meyer et al., 2018]. Similarly, the presence of swelling clay may impact our NMR results.
Specifically, swelling clays would increase pore volume, especially in the micropore region. When the swelling clay increases the micropore domain, the PSD shifts to show a larger volume in the micropore region [Meyer et al., 2018], and thus, similarly, the $T_2$ distribution will show a large water content at short $T_2$ values, for example, $\leq 1.8$ ms [Buchmann et al., 2015; Meyer et al., 2018]. We collected NMR measurements with organic matter removed from few samples; a comparison of the $T_2$-distributions from samples with organic matter and with organic matter removed are shown in Figure A.2. We see some changes in the distribution, the distributions shift slightly to shorter relaxation times with the organic matter removed. We thus expect that the OM has a small effect on the overall relaxation time distribution in our experiment.

An alternative method for determining PSD from NMR $T_2$ distribution that is independent of the surface relaxivity was presented by Hiller and Klitzsch [2018]. In their approach, NMR measurements were collected at multiple saturations and a triangular pore model was used to determine the full PSD. When measurements are available at multiple known saturations, the approach of Hiller & Klitzsch could provide an improved method for estimating soil texture.

### 3.7 Conclusions

In this study, we examined the use of low-field NMR $T_2$ distributions to estimate soil texture. Universal, non-site-specific cut-off times to separate the $T_2$ distribution into clay, silt, and sand fractions were not found to provide accurate estimates of soil texture. However, when site-specific cut-off times were used the NMR $T_2$ distributions were found to reasonably estimate the soil texture for soils with low magnetic susceptibility. Furthermore, $T_2$ distributions using site-specific cut-off times for soils with low magnetic susceptibility provided better estimates of soil texture than that determined from LDPSA.

The approach of obtaining site-specific $T_2$ cut-offs through minimizing the RMSE
between NMR-derived clay, silt, and sand fractions and those determined using the sieve-pipette method in this study has great value for advancing the application of the NMR technique in hydrogeological investigations. Standard empirical values that are commonly used in petroleum applications need to be verified if a high level of accuracy is needed when applying NMR in hydrogeological investigations.
Chapter 4

An examination of NMR logging to determine soil water content for agricultural investigations

4.1 Abstract

Monitoring soil water content is critical for irrigation management in agriculture. In this study, we evaluate nuclear magnetic resonance (NMR) measurements of soil water content at an agricultural site in the Central Valley of California. In situ NMR measurements were collected using a small-diameter NMR probe in 6 PVC-cased boreholes during two different growth stages of corn in June and September 2016. Soil water content at each well was also measured using time-domain reflectometry (TDR) as a reference comparison method. The results show that the NMR-derived soil water content is lower than the TDR-derived soil water content at all boreholes, although changes in the water content from the June and September experiments for the two methods are very close. Laboratory analysis of samples collected at the site revealed that the soils had high magnetic susceptibility (>12 × 10^{-4} SI); laboratory NMR water content estimates of the samples at full saturation were found to be low when comparing with the gravimetric porosity. A calibration equation was developed for the laboratory estimates of NMR water content and the associated gravimetric porosity using a linear regression analysis which accounted for the magnetic susceptibility. However, when applied to the field data, the calibrated NMR-derived water content was still in poor agreement with the TDR-derived water content. Our results indicate that further laboratory and field experiments are needed to study the NMR
measurements of soil water content in partially saturated settings in presence of soils with magnetic minerals.

4.2 Introduction

Reliable and robust techniques for the measurements of soil water content are extremely useful for irrigation management, especially in regions under long-term pressures to reduce the quantities of irrigation water used in agriculture. A wide range of automated techniques for in situ measurement of the soil water content have been developed [Robinson et al., 2008a]. Soil moisture sensors based on the time-domain reflectometry (TDR) measurements of the dielectric constant of soils are widely accepted to estimate the soil water content [Robinson et al., 2003; Walker et al., 2004; Jia et al., 2020]. However, TDR measurements at the point scale may not be suitable for monitoring soil water content in a large area as a number of TDR sensors are required, and the accuracy of the estimated soil water content highly depends on the applied calibration models.

Nuclear magnetic resonance (NMR) is a geophysical method that is directly sensitive to hydrogen protons in water and recently has been widely used for groundwater evaluation and the volumetric soil water content estimates in permafrost [Kass et al., 2017; Niu et al., 2019; Ren et al., 2019]. The NMR logging technique has been accepted as a mature method in the oil and gas industry to estimate the hydraulic properties of reservoirs. The recent advances in the development of low-field, slimhole NMR tools [Sucre et al., 2011; Walsh et al., 2013] for near-surface application has aided in the enhanced use of NMR in measuring the soil water content [Claes et al., 2019; Wu et al., 2019; Crow et al., 2020]. The NMR measurement can be used to determine the porosity of water-saturated materials [Keating and Falzone, 2013; Behroozmand et al., 2017]. For a geologic material with high magnetic susceptibility, however, the NMR estimated porosity will be underestimated when compared to gravimetric porosity [Keating and Knight, 2008; Keating et al., 2020]. While NMR has
now been widely used to characterize saturated systems, its use in partially saturated systems is still being developed.

This work aims to evaluate NMR measurements of estimating soil water content in the shallow soils of the subsurface. Two NMR experiments were conducted in June and September 2016 during two different growth stages of corn at an agricultural site in Woodland, California. In situ NMR measurements were collected using a small-diameter NMR probe [Walsh et al., 2013] in 6 PVC-cased boreholes, and at each borehole, soil water content was also measured using time-domain reflectometry (TDR) as a reference method for comparison. In this study, we propose a calibration method for obtaining reliable NMR measurements when in presence of magnetic minerals, which was evaluated through comparison between the calibrated NMR water content and the TDR-derived water content.

4.3 Background and theory

The NMR phenomenon arises because of the precession of the hydrogen nucleus with a certain magnetic moment placed in an external magnetic field, $B_0$. The rate of precession of the magnetic moment around $B_0$ is called Larmor frequency, which is related to the strength of $B_0$. An alternating current is applied with a frequency equal to the Larmor frequency of hydrogen protons; this applied alternating current induces an alternating magnetic field that excited the nuclear spins. The spins of the hydrogen nuclei in water will then produce a bulk magnetization, which is represented as a sum of the individual magnetic moments. By measuring the electromagnetic signal generated by the precession of the bulk magnetization, one can detect the presence of the water within the sample. In borehole and laboratory NMR measurements, a typical energizing pulse called Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [Carr and Purcell, 1954; Meiboom and Gill, 1958; Behroozmand et al., 2015] is used. The CPMG pulse sequence consists of a $90^\circ$ pulse, which is used to excite the spinning protons and move them away from the direction of the static magnetic field, and a
series of 180° pluses divided by a fixed time called echo time, $t_E$. In a downhole NMR measurement usually, the transverse component of a decaying signal $A_{xy}(t)$ is measured inductively between the 180° pluses. $A_{xy}(t)$ can be represented as a multiexponential decay with an initial signal amplitude $A_0$ that is proportional to the volume of water in the detective zone, and with multiple time constants that represent the transverse ($T_2$) relaxation time, which is related to the pore size.

4.4 Methods and materials

4.4.1 Field study design

Our study site is located on a managed-environment station in woodland, CA. The station was committed to drought research on maize, where a diverse range of water regimes can be generated from drought to fully irrigated [Cooper et al., 2014]. The field experiment is a strip-plot design (Figure 4.1) with three blocks (length: 5 m, width: 11 m). The available amount of water is controlled by a drip irrigation system, and water is delivered to each strip through drip tape buried in the soil. We conducted two NMR experiments to measure the soil water content of maize strips during vegetative stages in June 2016 and during reproductive stages in September 2016. NMR data were collected through PVC-cased boreholes with a depth of about 3 m, which were installed to monitor water uptake. The NMR experiment was conducted on 6 boreholes across the three blocks (one borehole at block A and B; four boreholes at block C). At each borehole, right after the NMR measurements, time-domain reflectometry (TDR) data were collected to measure the soil water content for comparison. A total of 15 soil samples were collected at an interval depth of 20 cm from one logger station for laboratory analysis of the soil properties.
4.4.2 Magnetic susceptibility and grain size distribution

To determine if iron-bearing minerals affect the NMR-derived porosity, we can measure the apparent volumetric magnetic susceptibility (MS), which is the ratio of magnetization in a volume of a soil sample to the strength of the applied magnetic field. To prepare an MS sample, the soil was oven-dried at 80 °C and was then packed into a cylindrical sample holder (diameter, 38.1 mm; length, 100 mm). The MS measurement was made using a Bartington MS3 system with an MS2C core logging sensor and was repeated three times for each soil sample. The average was used as the MS value for each soil.

To characterize the grain sizes of each soil, we use a Beckman Coulter LS 13320 (Brea, California, USA) laser diffraction particle size analyzer that can measure grain sizes in the range of 0.04–2000 µm. For each soil sample, three subsamples were prepared and used for the grain-size analysis. Further details about the instrument set up, the author is referred to [Zobeck, 2004]. The effective particle size $D_{10}$, which
is the grain diameter when 10% of the cumulative volume is reached based on the grain-size distributions, was calculated for each soil.

4.4.3 Nuclear magnetic resonance measurements

To create samples for NMR laboratory measurements, soil samples were first oven-dried and then packed into cylindrical Teflon sample holders (inner height 56.3 mm, inner diameter 31.0 mm). Further details about the NMR sample preparation are described in Keating [2014]. The gravimetric porosity, $\phi_{grav}$, was calculated from the volume of water used for saturation normalized by the volume of the sample holder. NMR data were collected using a 2.0 MHz Rock Core Analyzer (Magritek Ltd., Wellington, New Zealand). A CPMG pulse sequence with echo time $t_E = 200 \mu s$ was used for data collection. The NMR-derived porosity, $\phi_{NMR}$, was determined from the initial signal amplitude of an NMR measurement made on a sample calibrated by that of a measurement made on a sample holder filled with water.

The downhole NMR measurements were collected with the dart probe JP175 [Walsh et al., 2013], which is 4.45 cm in diameter and has a vertical resolution of 25 cm. Dual-frequency measurements were made with the dart probe at frequencies range from 425 to 475 kHz, which relate to a cylindrical sensitive zone with two cylindrical shells of 7.5 and 6.7 cm radially from the center of the probe. For this study, we only analyze results from measurements at low frequency, 425 kHz, which images farther from the disturbed zone around the well. In the field, the NMR data were collected in 25 cm depth increments starting from the top of the PVC-cased borehole. The Dart uses two CPMG pulses for each frequency, specifically, a short recovery time (Tr) of 100 ms record and a long recovery time of 1000 ms record. To improve the signal-to-noise ratio, the short Tr was stacked 1000 times and the long Tr was stacked 10 times. It takes $\sim4$ minutes to complete the measurement for each depth using these settings and $\sim1$ hour to finish measurements of one borehole.
The NMR data are originally recorded as voltages by the Dart tool and subsequently, a time-varying percent water content was given after normalized by a calibration factor set by the manufacturer. Data were processed using the post-processing software provided by the manufacturer (Vista Clara Inc. Javelin Processor version 3.4.3). During the data processing process, to reduce the data noise over the early time decay of 100 ms, the recorded data of short and long Tr were combined for each depth increment. After removing the impulse noise, data were fit with a multiexponential decay curve and inverted to produce a $T_2$ distribution, using a non-negative least squares algorithm with second-order Tikhonov regularization [Tikhonov, 1963; Aster et al., 2013]. The obtained $T_2$ distribution was further used to quantify water content.

4.4.4 Time-domain reflectometry measurements

Time-domain reflectometry (TDR) has become a standard method for measuring soil moisture. TDR is an electromagnetic method that measures the dielectric constant of soil layers based on the difference of propagation velocity of electromagnetic waves on soil layers. The dielectric constant can then be used to estimate the water content of different soil types using the standard Topp et al. [1980] calibration equation. For a thorough review of TDR theory and applications, readers are referred to Jones et al. [2002]. The TDR measurements were made at all boreholes following the path of the NMR borehole experiment conducted at the same time. TDR data were collected at an interval of 20 cm.
4.5 Results and Discussion

4.5.1 Downhole NMR $T_2$ distribution

Figure 4.2 shows the inverted relaxation time distributions for three representative wells (well WO-1 at block A; well WO-2 at block B; and well WO-3 at block C) in the NMR in June (4.2a-c) and September (Figure 4.2d-f) 2016 experiments. For the $T_2$ distributions from NMR measurements collected in June (Figure 4.2a-c) 2016, we notice a similar pattern in all three wells and the $T_2$ relaxation times in all wells are <0.01 s. Within 1 m depth, the $T_2$ distributions gradually increase with depth. Between 1.0 and 2.0 m depth, the $T_2$ distributions are continuous and the $T_2$ relaxation times within this region are between 0.001 and 0.01 s (except for well WO-1 between 1.0 and 1.5 m depth). For well WO-1 (Figure 4.2a) and well WO-2 (Figure 4.2b), at depth below 2 m, the $T_2$ decay times gradually decrease with depth, whereas for well WO-3 (Figure 4.2c), at a depth around 2 m, the $T_2$ distributions transition from longer to shorter (∼0.001 s) relaxation times. For the $T_2$ distributions obtained in the September (Figure 4.2d-f) 2016 experiment, the majority of the $T_2$ relaxation times are around short relaxation times (∼0.001 s). Same as the results in June, the $T_2$ relaxation times in all wells are <0.01 s. However, unlike the $T_2$ distributions obtained in June 2016 experiment, $T_2$ distributions from the September 2016 experiment for all wells contain fewer $T_2$ relaxation times between 0.001 and 0.01 s.

4.5.2 Soil water content

The comparisons between the volumetric water contents derived from borehole NMR measurements and those converted from the dielectric constants with the TDR method in June and September 2016 experiments are shown in Figure 4.3a-c for wells WO-1, WO-2, and WO-3, respectively. The absolute values of NMR-derived water contents

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Footnote:

The results of downhole NMR measurements for the wells WO-4, WO-5, and WO-6 can be found in Appendix B from Figure B.1 to B.3.
Figure 4.2: $T_2$ distribution color maps of NMR downhole measurements: (a) well WO-1, June 2016; (b) well WO-2, June 2016; (c) well WO-3, June 2016; (d) well WO-1, September 2016; (e) well WO-2, September 2016; (f) well WO-3, September 2016.
\( (\theta_{NMR}) \) are lower than TDR-estimated water contents \( (\theta_{grav}) \). For \( \theta_{NMR} \) in the June 2016 experiment, a similar pattern in water content and \( T_2 \) relaxation times (Figure 4.3) occurs within 1 m depth for all wells: the water contents increase with the depth just like the \( T_2 \) values increase with the depth. Between 1.0 and 2.0 m depth, the water contents are higher than 10%. For wells WO-1 (Figure 4.3a) and WO-2 (Figure 4.3b), the water content gradually decreased at depths below 2 m, whereas for well WO-3 (Figure 4.3c), the water content abruptly decreased to \( \sim 5\% \) at a depth around 2 m. The absolute values of \( \theta_{NMR} \) in September 2016 experiment are less than 10% for all wells.

![Figure 4.3: The water content profile derived from borehole NMR and TDR experiments conducted in June and September 2016 for (a) well WO-1; (b) well WO-2; (c) well WO-3.](image)

The absolute values of \( \theta_{grav} \) in both June and September experiments are higher than 10%. The \( \theta_{grav} \) at each well in June 2016 experiment showed similar behavior as observed in \( \theta_{NMR} \) from the NMR measurements (Figure 4.3). For \( \theta_{grav} \) at the top 1 m in all wells, the absolute values are around 20% from the experiment in June.
2016 and are close to those from the experiment in September 2016. Between 1.0 and 2.0 m depth, the TDR-derived water contents (> 20%) in June 2016 are higher than those in September 2016. However, in the depth below 2.0 m, the TDR-derived water contents (<20%) in June 2016 are lower than those from the experiment in September 2016.

Figure 4.4 shows the recorded changes in water content between the experiments in June and September 2016 by both TDR and NMR methods. For all wells, the largest changes in the water contents (~10%) from TDR measurements occur in depths between 2.5 and 3.0 m, whereas the largest changes in the water content (~10%) with the borehole NMR method occur between 1.0 and 2.0 m depth. Between 1.0 and 2.5 m depth, although the water contents derived from the borehole NMR method were lower than those converted from TDR measurements (Figure 4.3), the same magnitude of the changes in water content was detected by both the NMR and TDR methods at each well.

Figure 4.4: Changes in water content from June to September 2016 for (a) well WO-1; (b) well WO-2; (c) well WO-3.
4.5.3 Physical properties of soil samples

The causes of the discrepancy between $\theta_{\text{grav}}$ and $\theta_{\text{NMR}}$ were studied through some laboratory analysis on soil samples collected from one well and conducted. Grain-size distributions (GSDs) for all soils, measured by the laser diffraction particle size analyzer, are shown in Figure 4.5. Soils at depth $\leq 2.8$ m have broad and unimodal GSDs with a dominant peak at diameter between 50 and 100 $\mu$m and a smaller diameter around 8 $\mu$m for soil at depth of 2.8 m, whereas the soil at a depth of 3.0 m has a bimodal GSD with one peak at diameter around 80 $\mu$m and a second peak at around 10 $\mu$m. The $D_{10}$ values are shown in Table 4.1 and are 1.1 $\mu$m and 1.5 $\mu$m for the finer-grained soils at depths of 2.8 and 3.0 m respectively. The $D_{10}$ values for the remaining soils range from 2.0 to 3.9 $\mu$m.

Table 4.1: Physical properties and NMR-derived porosity $\phi_{\text{NMR}}$, for all soils used in this study

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>MS $10^{-4}$ SI</th>
<th>$\phi_{\text{grav}}$ (-)</th>
<th>$\phi_{\text{NMR}}$ (-)</th>
<th>$D_{10}$ $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>16.67±0.38</td>
<td>0.50</td>
<td>0.43</td>
<td>2.2</td>
</tr>
<tr>
<td>0.4</td>
<td>16.35±0.43</td>
<td>0.52</td>
<td>0.44</td>
<td>2.0</td>
</tr>
<tr>
<td>0.6</td>
<td>16.02±0.55</td>
<td>0.52</td>
<td>0.44</td>
<td>2.9</td>
</tr>
<tr>
<td>0.8</td>
<td>14.52±0.52</td>
<td>0.50</td>
<td>0.47</td>
<td>2.4</td>
</tr>
<tr>
<td>1.0</td>
<td>14.89±0.11</td>
<td>0.46</td>
<td>0.41</td>
<td>3.2</td>
</tr>
<tr>
<td>1.2</td>
<td>14.72±0.03</td>
<td>0.47</td>
<td>0.42</td>
<td>2.4</td>
</tr>
<tr>
<td>1.4</td>
<td>14.46±0.52</td>
<td>0.51</td>
<td>0.47</td>
<td>2.0</td>
</tr>
<tr>
<td>1.6</td>
<td>12.83±0.42</td>
<td>0.50</td>
<td>0.44</td>
<td>2.0</td>
</tr>
<tr>
<td>1.8</td>
<td>15.40±0.37</td>
<td>0.49</td>
<td>0.44</td>
<td>2.4</td>
</tr>
<tr>
<td>2.0</td>
<td>14.09±0.17</td>
<td>0.52</td>
<td>0.46</td>
<td>3.2</td>
</tr>
<tr>
<td>2.2</td>
<td>15.58±0.49</td>
<td>0.46</td>
<td>0.42</td>
<td>3.9</td>
</tr>
<tr>
<td>2.4</td>
<td>16.49±0.21</td>
<td>0.50</td>
<td>0.44</td>
<td>3.5</td>
</tr>
<tr>
<td>2.6</td>
<td>18.42±0.03</td>
<td>0.50</td>
<td>0.46</td>
<td>2.9</td>
</tr>
<tr>
<td>2.8</td>
<td>12.32±0.03</td>
<td>0.56</td>
<td>0.50</td>
<td>1.1</td>
</tr>
<tr>
<td>3.0</td>
<td>13.04±0.18</td>
<td>0.60</td>
<td>0.55</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The physical properties including the MS values and gravimetric porosity $\phi_{\text{grav}}$, and NMR-derived porosity $\phi_{\text{NMR}}$ for all soils are shown in Table 4.1. All soil samples have high MS values $>12 \times 10^{-4}$ SI. The MS values ± standard deviation range from
12.32±0.03 to 18.42±0.03×10⁻⁴ SI for soil at a depth of 2.8 m, 2.6 m, respectively.

Figure 4.5: Grain-size distributions (GSDs) of all soils measured using a laser particle size analyzer.

For all soils, as shown in Table 4.1, the gravimetric porosity $\phi_{grav}$ values are higher than the NMR-estimated porosity $\phi_{NMR}$: $\phi_{grav}$ varies between 0.46 and 0.60, whereas $\phi_{NMR}$ varies between 0.42 and 0.55. Figure 4.6 shows a comparison of the $\phi_{NMR}$ and the $\phi_{grav}$. There is a poor agreement between $\phi_{NMR}$ and $\phi_{grav}$ for all soils: the gravimetric porosity is underestimated by the NMR porosity. An approach using a linear model which accounts the MS of each soil sample was proposed to calibrate the saturated water content $\phi_{NMR}$. The linear regression equation is given by

$$\phi_{NMR\_calibrated} = \phi_{NMR} + \alpha \times \log_{10}(MS) ,$$  \hspace{1cm} (4.1)
the parameter $\alpha$ is determined by a least-squares method which minimizes the cost function (or the residual sum of squares) of the expression:

$$cost(m) = \sum_{i=1}^{n} |\phi_{grav} - [\phi_{NMR} + \alpha \times \log_{10}(MS)]|^2,$$

As shown in Figure 4.6, $\phi_{NMR}$ was calibrated via the decimal logarithm of the magnetic susceptibility value for each soil. The calibrated $\phi_{NMR}$ can accurately predict the gravimetric porosity $\phi_{grav}$ for all soils with a high $R^2$ near 1 when the value of $\alpha$ is 0.0465.

Figure 4.6: NMR-derived porosity $\phi_{NMR}$ versus gravimetric porosity $\phi_{grav}$ in the laboratory. The black circles indicate the original $\phi_{NMR}$ versus the true $\phi_{grav}$. The red squares indicate the comparison of the calibrated $\phi_{NMR}$ to the true $\phi_{grav}$. The dashed line represents the one-to-one curve.
4.5.4 Soil water content calibration

For all wells in the June and September 2016 experiments, the water content estimated from the NMR data is lower than those converted from TDR measurements. To make the absolute values of water contents from both methods favorably agreed with each other, the linear regression analysis result of the relationship between $\phi_{NMR}$ and $\phi_{grav}$ in the laboratory are applied to calibrate the water content $\theta_{NMR}$ measured in the field. In both June and September experiments, the $\theta_{NMR}$ from all boreholes were calibrated by using equation 4.1 with $\alpha = 0.0465$ and was given by:

$$\theta_{NMR_{\text{calibrated}}} = \theta_{NMR} + \alpha \times \log_{10}(MS),$$  

(4.3)

where the log values of magnetic susceptibility are from the sampling soil profile and $\alpha = 4.65$ because the unit of water content $\theta_{NMR}$ is % m$^3$/m$^3$. Figure 4.7 shows the calibrated NMR-derived water contents for well WO-1 and compared with the TDR measurements of water contents. It is still challenging to directly compare the absolute values of water contents from borehole NMR data and TDR measurements, although the absolute values of calibrated NMR-derived water contents are increased but still less than those of TDR estimated water contents (Figure 4.7).

The shortening $T_2$ relaxations time of water in the regions with magnetic minerals will lead to an underestimate of water content by the NMR method [Keating et al., 2020], as showed in Figure 4.3, borehole NMR estimated water content is lower than the water content converted from TDR data. The reported difference in the absolute values of estimated water contents from TDR measurements and NMR data may be caused by the difference in the size and shape of the sampled volume from each method. The borehole NMR measures a small cylindrical shell at a depth of 7.5 cm to the probe surface around the well every 25 cm [Walsh et al., 2013]. The size of this shell does not change with depth during the NMR experiment. For the TDR measurements, the soil water content is derived from the bulk dielectric constants and
provides the water content over a volume surrounding the borehole. The difference in the scale of the measurements from the two methods may contribute to the discrepancy in the estimates of water content. Furthermore, the accuracy of the measure of soil water content depends strongly on the calibration curve being used. Although the universal calibration equation proposed by Topp et al. [1980] was commonly used, numerous studies and gravimetric analysis on soil samples have indicated the need for particular calibrations for different soils to make accurate calibrations [Rajkai and Rydén, 1992; Quinones et al., 2003; Logsdon, 2009; Sikora et al., 2019; Jia et al., 2020]. To make accurate use of the TDR measurements, further investigations and improvements on TDR data such as an improved calibration procedure or a different sensor are needed.

Figure 4.7: Calibrated NMR-derived water contents and TDR-estimated water contents for well WO-1

The internal gradient magnitudes are influenced by both the pore sizes and the
distributions of the magnetic grains and the magnetic susceptibility of the sample [Fay et al., 2015]. Although many studies have examined the impact of the internal gradient magnetic field on the shape of relaxation time distributions from the NMR responses [Hürlimann, 1998; Grombacher et al., 2016] or even measured the magnitude of internal gradients in sediments [Fay et al., 2015], it is still difficult to quantify the influences of magnetic susceptibility on the NMR relaxation times and thus on the estimated water contents. Song et al. [2000] proposed a new technique, which is called Decay due to Diffusion in the Internal Field (DDIF) method, to directly obtain the pore size distributions of porous media using the internal magnetic fields. The capabilities of this method already demonstrated in carbonate and sandstone rocks [Song et al., 2000; Song, 2001, 2003] are also of great potential for the characterization of unconsolidated soils and sediments.

4.6 Conclusion

We examined the estimates of soil water content from NMR logging data during two different growth stages of corn. The NMR estimated soil water content was found in poor agreement with the soil water content derived from TDR measurements: NMR estimated soil water content, because of the presence of soils with high magnetic susceptibility, was relatively lower than TDR-derived soil water content. The calibration method, which takes into account the magnetic susceptibility, was capable of calibrating the NMR estimated porosity but was discouraging in the calibration of the NMR estimated water content. These results suggest that a robust calibration method is required to calibrate the NMR estimated water content in the presence of magnetic minerals.
Chapter 5

Conclusions

5.1 Summary and significance of findings

This thesis focuses on estimating soil texture and water content using nuclear magnetic resonance (NMR) measurements for agricultural applications. The experiment from Chapter 2 examined the effect of clay, silt, and sand content in synthetic clay-silt-sand mixtures on NMR relaxation time distributions. When applying NMR measurements in the laboratory with various clay, silt, and sand contents, the shape of the transverse ($T_2$) relaxation time distribution strongly depends on the clay content. Silt and sand were shown to affect the $T_2$ relaxation times only for mixtures with clay contents <10\% by mass. The focus of Chapter 3 was exploring the use of NMR $T_2$ distributions as an alternative method to estimate the texture of soils collected from three agriculture sites. The results of this laboratory experiment suggest that NMR can offer better estimates of clay, silt, and sand fractions for soils with low magnetic susceptibility than the laser diffraction method. In Chapter 4, two borehole NMR experiments were conducted to estimate the soil water content for partially saturated material. At each experiment, the soil water estimated from NMR data was lower than that derived from time-domain reflectometry (TDR) measurements; however, changes in water content from the NMR experiments were in close agreement with the changes from the TDR experiments. The proposed approach, which was successful in calibrating the NMR estimated porosity in the laboratory, failed to calibrate the NMR estimated water content in the field as the calibrated soil water content
estimated from NMR data was lower than that estimated from TDR measurements.

The laboratory experiments in Chapters 2 and 3 improve our understanding of the relationship between NMR $T_2$ relaxation time distribution and soil texture. The results from the clay-silt-sand mixture study in Chapter 2 suggest that the $T_2$ relaxation times are dependent on clay, silt, and sand contents, and the strong effect of the clay on the $T_2$ relaxation times is due to the high specific area. In the study of soil texture analysis in Chapter 3, NMR $T_2$ distributions of soils with low magnetic susceptibility, which can be partitioned using two $T_2$ cutoff times, were used to determine the pore size distributions quantitatively and demonstrated to provide a reasonable estimate of soil texture. For soils with high magnetic susceptibility, however, the soil texture was poorly predicted from NMR measurements because: (1) the broad $T_2$ distributions caused by high magnetic susceptibility cannot be applied to represent the pore size distributions; (2) the condition of fast diffusion is not strictly satisfied thus $T_2$ cutoff times are no longer linearly related to the pore size distributions.

In chapter 4, the estimate of soil water content from borehole NMR measurements was influenced by soils with high magnetic susceptibility. An approach that takes into account the effect of magnetic susceptibility on NMR measurements, was proposed to calibrate the estimates of water content that was poorly estimated from NMR data for soils with high magnetic susceptibility. Although this approach did not provide perfect calibration of the NMR estimated water content, it is considered to be the start of looking for robust solutions for accurately estimating the water content of soils with high magnetic susceptibilities from NMR measurements in the field.

In conclusion, the studies in this thesis fulfilled the main objectives and determined the relationship between NMR $T_2$ relaxation times and soil texture. The strong influence of clay content in soils on the NMR responses was demonstrated. The approach using NMR $T_2$ relaxation times to estimate the soil texture of water-saturated soil samples was described, extending the application of NMR in soil science. Finally, a simple method that takes into account the magnetic susceptibility was proposed to
calibrate the estimate of water content from NMR data. The findings demonstrate
NMR as a promising tool will help to gain a valuable understanding of soil properties.

5.2 Future directions

This thesis has demonstrated the relations between soil texture and NMR relaxation
times; an approach to calibrate the estimates of water content from NMR data is also
introduced. Some potential future research that builds on the results of this thesis
can include:

(I) The experiment in Chapter 2 used relatively simple materials that allow us
to focus on investigating the effect of particle size on the NMR response of
water-saturated soils with controlled variations of clay, silt, and sand con-
tents. Specifically, the clay mineral selected for testing in Chapter 2 is a well-
characterized non-swelling kaolinite. Future research should focus on testing
clay minerals with moderate to high swelling, such as illite and montmoril-
lonite, as clay mineralogy may have additional impacts on the soil texture
analysis from NMR measurements. The swelling of clay increases pore volume
in the micropore domain, as reported in [Meyer et al., 2018], the NMR relax-
ation time distributions will show a large water content at short relaxation
times (e.g., ≤1.8 ms) in the presence of swelling clays.

(II) In the clay-silt-sand mixture study in Chapter 2, all NMR samples are prepared
homogeneously. Therefore, the clay is homogeneously distributed throughout
the mixture, which is not usually encountered in realistic geological situations.
According to Osterman et al. [2019], the packing structure also has a strong
effect on the NMR responses of water-saturated soil samples. The potential
study of particular interest is to test the NMR response of geologically realistic
clay distributions, e.g., clustered or laminated distributed clay.
(III) To support in situ investigations of agricultural applications, future research is needs to take into account the effect of organic matter (OM) on the NMR responses. In contrast to the swelling of clay, swelling of OM will reduce the pore volumes in the micropore domain, which will further affect the pore size distributions determined from NMR. In the research presented in Chapter 3, the OM content across all soil samples is <4.5%, which has a small effect on the $T_2$ relaxation time distributions. However, for soils that contain large amounts of swelling OM, e.g., >10% in the study by Meyer et al. [2018], the effects of swelling OM on NMR relaxation time distributions and thus the pore size distributions should be examined further.

(IV) To test alternate methods for taking into account the influence of magnetic susceptibility on NMR responses. The internal magnetic field gradients were produced by the susceptibility contrast between the pore fluid and the solid materials. New experiment technique such as the Decay due to Diffusion in the Internal Field (DDIF) method, was used to exploit the internal gradients and has been successfully applied to obtain pore size information in fluid-filled consolidated rocks such as carbonate and sandstone [Song et al., 2000; Song, 2001, 2003]. This method directly addresses the pore geometry that might be of great value for the in situ characterization of unconsolidated soils and sediments.
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Appendices

A Chapter 3 Supplemental Information

Relaxation occurs within the fast diffusion regime when the control parameter, $\kappa = \frac{\rho a}{D} \ll 1$ [Brownstein and Tarr, 1979; Ryu, 2009; Keating and Knight, 2012]. To test the assumption of fast diffusion, we calculate the control parameter for all samples. Assuming a spherical grain, we can determine a characteristic grain size, $d_{GSD}$, using $D_{50}$ from the GSD. Assuming a cylindrical capillary pore model, we can then estimate an effective pore radius $r_{eff} = \frac{\phi}{3(1-\phi)}$ [Costabel et al., 2018]. We determine the value of $\rho_2$ using $\frac{1}{\rho_2} = T_{\text{ML}} \frac{S}{V} = T_{\text{ML}} \frac{2}{r_{eff}}$, which results from rearranging equation 1.8 in Chapter 1. Substituting this equation for $\rho_2$, the control parameter is given by

$$\kappa = \frac{r_{eff}^2}{2T_{\text{ML}} D}.$$

For the samples in this study, the calculated $\kappa$ values are shown in Table A.1. For site 1, $\kappa$ is less than 1 for most samples except for soil 1–2 (0–15 cm), and for site 3, $\kappa$ less than, or close to 1 (between 1.07 and 3.01). These calculations provide evidence that relaxation occurs within, or close to the fast diffusion regime for the samples in sites 1 and 3. However, for the samples from site 2, $\kappa > 1$ for most soils. This indicates that relaxation may occur in the slow diffusion regime for these samples and may further explain why the $T_2$-distributions from site 2 do not provide reliable estimates of the soil texture. We note that we use a simplified geometric model to calculate $r_{eff}$; we have chosen this approach such that we overestimate the value of $r_{eff}$ and thus provide an upper limit on the value of $\kappa$. 
Table A.1: NMR properties: the control parameter $\kappa$ for all soil samples.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Site 1</th>
<th>Site 2</th>
<th>Site 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Profile ID</td>
<td>$\kappa$</td>
<td>Profile ID</td>
</tr>
<tr>
<td>0-15</td>
<td>1</td>
<td>0.36</td>
<td>1</td>
</tr>
<tr>
<td>15-30</td>
<td>1</td>
<td>0.19</td>
<td>1</td>
</tr>
<tr>
<td>30-45</td>
<td>1</td>
<td>0.26</td>
<td>1</td>
</tr>
<tr>
<td>45-60</td>
<td>1</td>
<td>0.24</td>
<td>1</td>
</tr>
<tr>
<td>60-75</td>
<td>1</td>
<td>0.48</td>
<td>1</td>
</tr>
<tr>
<td>0-15</td>
<td>2</td>
<td>3.91</td>
<td>2</td>
</tr>
<tr>
<td>15-30</td>
<td>2</td>
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<td>2</td>
</tr>
<tr>
<td>30-45</td>
<td>2</td>
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<td>2</td>
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<td>2</td>
</tr>
<tr>
<td>60-75</td>
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<td>0.81</td>
<td>2</td>
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<td>3</td>
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<tr>
<td>15-30</td>
<td>3</td>
<td>0.36</td>
<td>3</td>
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<tr>
<td>30-45</td>
<td>3</td>
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<tr>
<td>45-60</td>
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<td>60-75</td>
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<tr>
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</tr>
<tr>
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<tr>
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<td>30-45</td>
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</tr>
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</tr>
<tr>
<td>60-75</td>
<td>5</td>
<td>0.48</td>
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</table>
The results of LDPSA estimated soil texture were improved when 8 µm was chosen as the cut off between silt and clay particles. In Figure A.1, LDPSA results with 2 µm (b) and 8 µm(c) are plotted on the ternary diagram and compared to the results of the sieve-pipette method (a) and NMR with non-site-specific (d) and site-specific (e) cutoffs applied. The clay content was underestimated by LDPSA using 2 µm for silt and clay when comparing to results of the sieve-pipette method. This is the reason that 8 µm was chosen for the separation of silt and clay in Chapter 3. The sand content was underestimated by NMR with non-site-specific $T_2$ cutoff times when comparing to results of the sieve-pipette method.
Figure A.1: Distribution of USDA soil texture classification using percentage of clay, silt, and sand determined by the sieve-pipette method (a), by LDPSA using a grain size of 2 μm (b) and 8 μm (c), and by NMR data using non-site-specific (d) and site-specific cutoff values (e) to separate the clay and silt fractions.
The organic matter (OM) in a representative soil sample from each profile was measured for the study in Chapter 3. The OM content across all samples ranges from 0.7 to 4.4% with an average of 2.8±0.9%. NMR measurements were collected for soil samples with OM removed, and a comparison of the $T_2$ distributions from samples with OM and with OM removed are shown in Figure A.2. We noticed some changes in the $T_2$ distributions, such as for soil 2-3(0–15 cm), the $T_2$ distributions shift slightly to shorter relaxation times with the OM removed. We thus expect that the OM has a small effect on the overall relaxation time distribution.

Figure A.2: A comparison of NMR $T_2$ distributions from samples with OM (black line) and with OM removed (dash line)
Figure B.1 shows the $T_2$ distributions for wells WO-4, WO-5, and WO-6 at block C in the June and September NMR experiments. For the $T_2$ distributions from NMR measurements collected in June 2016 (Figure B.1a-c), the $T_2$ relaxation times in all wells are $< 0.01$ s except in well WO-5 where there are continuous $T_2$ distributions with the value of $T_2$ ranges from 0.01 and 0.1 s at depth from 0.5-2.25 m. For all three wells, there are isolated high water content with low relaxations ($<0.001$ s). Similar to the results of wells WO-1, WO-2, and WO-3 in the June 2016 NMR experiment, the $T_2$ distributions are continuous with the $T_2$ relaxation times range from 0.001-0.01 s at depth between 0.5 and 2.0 m (from 0.5-2.75 m for well WO-5). At depth below 2 m, for well WO-4 (Figure B.1a) $T_2$ distributions are continuous at around 0.001 s, while for well WO-6 (Figure B.1c), $T_2$ is distributed isolated at low relaxation times around (or shorter than) 0.001 s. For the $T_2$ distributions obtained in the September (Figure B.1d-f) 2016 experiment, $T_2$ relaxation times are discontinuously distributed at all wells. For all wells, when compared to the the $T_2$ distributions obtained in the June experiment, $T_2$ distributions color maps from the September experiment contain fewer water content at long relaxation times between 0.001 and 0.01 s.
Figure B.1: $T_2$ distribution color maps of NMR downhole measurements: (a) well WO-4, June 2016; (b) well WO-5, June 2016; (c) well WO-6, June 2016; (d) well WO-4, September 2016; (e) well WO-5, September 2016; (f) well WO-5, September 2016
The comparisons of the volumetric water contents derived from borehole NMR measurements and those converted from the dielectric constants with the TDR method in June and September 2016 experiments are shown in Figure B.2a-c for wells WO-4, WO-5, and WO-6, respectively. Same to the results of wells WO-1, WO-2, and WO-3, the absolute values of NMR-derived water contents ($\theta_{NMR}$) are lower than TDR-estimated water contents ($\theta_{TDR}$). For $\theta_{NMR}$ in the June 2016 experiment at all wells WO-4, WO-5, and WO-6 the water contents are higher than 10% at the depth <2.0 m but lower than 10% at the depth >2.0m. At all wells WO-4, WO-5, and WO-6, same to the results of wells WO-1, WO-2, and WO-3, the absolute values of $\theta_{NMR}$ in September 2016 experiment are less than 10%.

The absolute values of $\theta_{TDR}$ in both June and September experiments are higher than 10%. At depth between 1.5 and 2.25 m, $\theta_{TDR}$ measured in September is in transition from higher than $\theta_{TDR}$ measured in June to lower than $\theta_{TDR}$ measured in June.

Figure B.2: The water content profile derived from borehole NMR and TDR experiments conducted in June and September 2016 for (a) well WO-4; (b) well WO-5; (c) well WO-6
Figure B.3 shows the comparisons of the changes in water content from the June and September experiments by TDR and NMR methods. For all wells, the largest change in the water contents (∼10%) from TDR measurements occurs at a depth between 2.0 and 3.0 m, whereas the largest change in the water content (∼10%) with the borehole NMR method occurs at a depth <2.0 m.

Figure B.3: Changes in water content from June to September 2016 for (a) well WO-4; (b) well WO-5; (c) well WO-6