2011

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Recommended Citation

Chighladze, Giorgi, "Estimation of change in soil water nitrate-nitrogen concentration using impedance spectra" (2011). *Graduate Theses and Dissertations*. 10174.
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Estimation of change in soil water nitrate-nitrogen concentration using impedance spectra

by

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A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Co-majors: Agricultural Engineering and Environmental Science

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Ames, Iowa

2011

In memory of my grandfather Vakhtang Chitadze

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ABSTRACT

A fast and reliable method for *in situ* monitoring of soil nitrate-nitrogen (NO_3-N) concentration is vital for evaluation of N management practices focused on reduction of NO_3-N losses to ground and surface waters from agricultural systems. Conductive behavior of soil has been successfully used by a time domain reflectometry (TDR) technique to estimate pore water NO_3-N concentration, but due to a high cost of a TDR system and inconveniences associated with its field deployment *in situ* application of this method has been limited. Capacitance type probes are a relatively cheap and easy-to-deploy alternative to TDR probes for continuous monitoring of soil water content and salinity (depending on the probe), but capacitance probes have never been used to estimate change in soil solution NO_3-N concentration. Furthermore, most of the commercially available capacitance sensors measure soil permittivity at a single frequency, which can be adequate to estimate a single soil property. Using dielectric measurements at multiple frequencies can help to estimate several physical and chemical soil properties simultaneously. Hence the goal of this study is to examine the feasibility to estimate changes in pore water NO_3-N concentration together with volumetric water content (VWC) from the dielectric measurements obtained at multiple frequencies below several MHz where conductive behavior of soil dominates.

An initial experiment with two off-the-shelf capacitance probes showed that at a relatively high frequency response of the probe was primarily correlated with VWC, while measurements at a lower frequency made by the second probe also incorporated the effect induced by changes in pore water ionic concentration. These results confirmed that using measurements at multiple frequencies can provide information about several soil properties, including NO_3-N concentration. Consequently two follow-up laboratory experiments used impedance spectroscopy to estimate changes in NO_3-N concentration in pure solutions and bulk soil, respectively, using a multivariate chemometric analysis, particularly partial least squares (PLS) regression. The results showed that change in NO_3-N concentration could be estimated with sufficient accuracy when its concentration was greater than concentration of other anions (chloride (Cl) in our case). In addition, estimation of NO_3-N in pore water improved significantly with increasing VWC. A good agreement was found between actual and estimated NO_3-N concentration when the PLS model was built using the imaginary permittivity data obtained at VWC ≥ 0.20 m^3 m^{-3}. R^2 and the root mean square error (RMSE) of NO_3-N estimation for the best model (VWC $\geq$ 0.20 m^3 m^{-3} and concentration of Cl < 500 mg L^{-1}) were 0.84 and 28 mg L^{-1}, respectively. In general, the study demonstrated that PLS regression method coupled with the dielectric measurements obtained at multiple frequencies below several MHz can be used to indirectly estimate VWC and NO_3-N concentration, but after a proper calibration equally covering the expected variations in VWC and NO_3-N. For *in situ* application other environmental variables such as temperature should also be incorporated into the calibration process.

CHAPTER 1. GENERAL INTRODUCTION

Introduction

Nitrate Management

Nitrogen (N) is among the most important elements required in agricultural systems, central to the production of all crop plants, and required for the survival of all living things (Addiscott et al., 1991). To sustain and maximize agricultural production in order to supply the nutritional needs of a continually growing world population, agriculture systems will need adequate N inputs. But the extensive use of N in agriculture can significantly increase a risk of the N losses to the environment causing degradation of the water, air, and soil in many regions of the world (Skiba et al., 1992; Addiscot, 2005). Since N inputs are necessary for maintaining the viability of intensive agricultural systems, it is essential to understand how management impacts the transport and fate of N and the environment as a whole. Traditional methods for determining soil N concentration involve time-consuming and tedious procedures, which are impractical for a large scale monitoring (Carter and Gregorich, 2007). Therefore a fast real-time monitoring system is needed that will help us to comprehend effectiveness of different strategies to minimize N loss while preserving agricultural productivity.

Nitrate (NO_3^-) is one of the most mobile ionic forms of N in agricultural systems and its leaching is a primary source of the contamination in drinking water (Follett and

Delgado, 2002). NO_3, which is a water-soluble byproduct of nitrogen-rich agricultural fertilizers, is a main environmental concern in the contemporary world that stems largely from potential health effects on humans and animals. High levels of NO_3 in drinking water (the WHO permissible limit of NO_3-N in drinking water is 50 mg L^{-1}, while the US drinking water standard is 10 mg L^{-1}) are dangerous for human health and can increase risk of specific cancers (gastric, oespphageal, etc) or induce methemoglobinemia (blue-baby syndrome) in infants under 6 months old (Bruningfann and Kaneene, 1993; Gupta et al., 2000; Ward et al., 2005; Grosse et al., 2006). Furthermore in surface waters, medium to high NO_3 levels can cause eutrophication of the aquatic environment (NRCS, 1997). This condition produces excessive growth of algae and macrophytes to levels that can choke navigable waterways, increase turbidity, and depress dissolved oxygen concentrations (hypoxia). When a large mass of algae dies and begins to decay, it depletes the oxygen dissolved in water and produces certain toxins, which can kill fish. As a result excess algae growth can create aesthetically unpleasant and obnoxious conditions in water bodies, cause serious taste and odor problems, and increase water treatment costs by clogging screens and requiring more chemicals.

Ion exchange, reverse osmosis, biological denitrification and chemical reduction have been commonly used in water treatment processes to achieve safe NO_3 levels with varying efficiencies, but relatively little have been done to address non-point sources of NO_3 leaching. Lagging behind of preventive measures results in increased costs associated with NO_3 pollution. Recently, the largest NO_3 removal facility in the world was installed in Des Moines, IA to cleanup NO_3 in water obtained from the Raccoon

River, which has the highest average NO_3 concentration among the 42 largest tributaries in the Mississippi River Basin (Hatfield et al., 2009).

In the US, NO_3 transported from row crop agriculture to the Gulf of Mexico, leading to an increase in hypoxia, has become a major environmental problem over the last several decade (Alexander et al., 2008). Average annual export of NO_3 from surface water in Iowa was estimated to range from approximately 204,000 to 222,000 Mg, or about 25% of the NO_3 that the Mississippi river delivers to the Gulf of Mexico, despite the fact that Iowa occupies less than 5% of its drainage basin (Libra et al., 1999; Schilling and Libra, 2000). Water quality issues like this arising from heavy agricultural production make Iowa and much of the Midwest the major source of environmental concerns.

Currently, N is applied uniformly across corn fields in most of Iowa. However corn demand for N is highly spatially and temporally variable, evidenced by the fact that N uptake is highly correlated to corn yield (90% of nitrogen uptake appears in the corn kernels), which varies in space and time. Variability in plant population, N mineralization from organic matter, water stress, soil properties, and pests within a field create variability in kernel number per unit land area and this leads to spatial and temporal variation in N uptake within a field. Thus traditional uniform N applications result in over- and under-application of N in different parts of the field due to this spatial variation. Any portion of the unused N can leach from the fields to ground water through natural and artificial drainage systems in the form of NO_3. Furthermore, high concentration of NO_3 is soil water can increase its osmotic potential making the water less available to the plants. This presents a challenge to apply N according to a “prescription” to match the spatial needs within the field (Hoskinson et al., 1999; Roberts et al., 2002). Recent studies confirm that adaptation of site-specific management of N fertilizer will reduce total N applications to optimal levels and increase grain yields, crop quality, and net dollar returns while decreasing nutrient loadings to the environment. Koch et al. (2004) reported a 6-46% reduction of in total N fertilizer use through variable-rate N application, compared with uniform N management. However he also underscored the importance of developing cost-effective approaches to prepare “prescription application maps”.

Over the last decade, technological advances such as the emergence of global positioning systems (GPS), geographical information system (GIS), and variable-rate technology (VRT) on agricultural equipment have led to increased interest and adoption of the concept of precision agriculture, which implies applying of the right level of inputs at the right place in the field at the right time with the goals of improving production efficiency, environmental impact, and food security (Dobermann et al., 2004). By using precision farming techniques to match N application rates to plant demands at a high resolution in a field, reduced NO_3 losses to the environment are expected. For this, one needs methods to evaluate applied N rates to match their spatial and temporal crop demand. Therefore it is necessary to monitor and understand the spatial and temporal loss pathways for N. This information would then provide the basis for the development of site-specific N management strategies to maximize N utilization efficiency and minimize the environmental impacts by: (a) understanding which areas are transporting the most NO_3 to target different strategies to different locations, and (b) better managing fertilizer application to avoid using excess N.

Soil Dielectric Measurements

Rapid technological development in the microelectronics industry in the past decades have enabled the measurement of the electromagnetic (EM) properties of mediums more accessible then before attracting increasing attention to applications in different areas. Studying electromagnetic wave interaction with materials advanced our knowledge and ability to characterize materials, including solids (Vendik et al., 1998; Weber, 2006), liquids (Kaatze, 1995; Buchner et al., 1999; Buchner, 2008; Hunger et al., 2009), polymers (Dominguez-Espinosa et al., 2006; Sanchis et al., 2010), glass-forming systems (Angell et al., 2000) and biological tissues (Gabriel et al., 1996a; Gabriel et al., 1996b; Chelidze, 2002; Asami, 2002), using their dielectric properties. Monitoring water content of materials by measuring their dielectric permittivity has drawn considerable interest finding its application in different realms of human activity including civil engineering (Hager and Domszy, 2004; Volgyi, 2007), crude oil exploration and processing (de la Beernardie et al., 2008), meteorology (Robinson et al., 2008), forestry and timber industry (Tomppo et al., 2009), food production (Clerjon and Damez, 2007; Nelson et al., 2007) and agriculture (Topp et al., 1980; Nelson, 2005; Bogena et al., 2007).

Possibility to continuously estimate moisture content in a same sample made the dielectric measurements the most practical indirect method for soil water monitoring. As a result, various techniques, ranging from sample scale electrical sensors to active microwave remote sensing, were developed using EM response to estimate soil moisture content (Robinson et al., 2008). These advancements in moisture sensing technology allowed automated collection of important soil information on appropriate spatial and temporal scale with no or little disturbance of the medium. A sampling intensity of the developed dielectric sensors is several orders of magnitude greater than what is attainable with the conventional thermo-gravimetric method, which is destructive, slow, time-consuming, labor-intensive and does not allow for making repetitions in the same location. Success of the dielectric sensors, however, depends on their ability to accurately measure the bulk soil dielectric permittivity, which is commonly used to estimate soil moisture content.

Time domain reflectometry (TDR) and time domain transmission (TDT) techniques have proved to be reliable methods for determining soil water content. Topp et al. (1980) was the first to use the TDR probe for measuring the volumetric water content (WVC) using four mineral soils. They developed a calibration model relating VWC to a polynomial function of the apparent soil permittivity. Since then, TDR probes have been successfully used in soil water monitoring.

The quality and the volume of the TDR measurement, however, depend on the design and construction of the probe (Ferre et al., 1998; Robinson et al., 2003). There are several commercially available TDR systems for soil moisture monitoring including the TRASE (Soil Moisture Equipment Corps, Santa Barbara, CA), Trime (IMKO, Ettlingen, Germany), the Acclima (Acclima Inc, Meridian, ID) and CS-TDR100 (Campbell Scientific, Logan, UT). In general, TDR and TDT systems measure the propagation velocity of a step voltage pulse with a bandwidth of around 20 kHz to 1.5 GHz along a pair of electrodes to determine the permittivity of the material through which it travels (Heimovaara, 1994; Heimovaara et al., 1994). Shorter the rise time of the step pulse more accurate is the soil water estimations. A longer rise time (>2000ps) results in susceptibility to changes in other soil properties, such as bulk soil salinity. More details about operational principals of the TDR can be found in a number of review literatures (Noborio, 2001; Robinson et al., 2003).

Dalton et al. (1984) first demonstrated the utility of TDR probes to measure bulk soil electrical conductivity from the amplitude of the reflected waveform. This unique ability to simultaneously measure the apparent permittivity (hence, the VWC) and the bulk soil electrical conductivity using the same instrumentation and probes, and in the same soil volumes, provided new opportunities to investigate solute movement in soil both in field and laboratory experiments. As a result, numerous studies have been conducted during the last couple of decades using TDR probes to monitor solute mass in soil column (Vanclooster et al., 1993; Ward et al., 1994; Vanclooster et al., 1995; Vogeler et al., 1996; Risler et al., 1996; Persson, 1997; Nissen et al., 2000; Bouksila et al., 2008). Vogeler et al. (2000) successfully tested the method for measuring anion retardation in unsaturated leaching experiments carried in the laboratory using two soil columns. The results obtained based on TDR measurements of soil water content and bulk soil electrical conductivity with time were similar to those obtained from the collected effluent. Vogeler et al. (2000) concluded that TDR could be a valuable *in situ* technique for monitoring solute transport through soil. Several studies have been conducted to monitor solute transport under steady state conditions in the field using TDR probes (Kachanoski et al., 1992; Noborio et al., 1994).

For its part the bulk soil electrical conductivity is influenced by several soil parameters, including the pore water conductivity, the water content, the surface conductivity of the surface particles, and the tortuosity of the electrical flow paths. As a result several models have been developed relating the soil moisture content and the bulk soil conductivity to the pore water conductivity, which is primarily influenced by soil solution ionic concentration (Rhoades et al., 1976; Nadler, 1982; Mualem and Friedman, 1991; Heimovaara et al., 1995). But these models required determination of one or more physical parameters by measuring soil properties. Later Hilhorst (2000) presented a linear model relating the simultaneously measured dielectric permittivity and conductivity of the bulk soil to the pore water conductivity without use of the soil specific parameters. Amente et al. (2000) compared several different models relating the soil solution electrical conductivity to the bulk soil conductivity for sandy soil, and concluded that there is no advantage to the use models based on soil hydraulic properties compared to the simpler models that do not require them.

Rhoades and Oster (1986) pointed out that total ionic concentration of the soil solution can be determined from the measurement of the bulk soil conductivity. However to estimate ionic concentration soil- and solution-specific calibrations are needed. In general, there are two calibration approaches. The first approach assumes an empirical linear relationship between the concentration of solutes and the bulk conductivity measurement (Kachanoski et al., 1992), while the second approach incorporates intermediate step of secondary calibration so that the solution concentration is determined from the soil solution conductivity. For its part, the last is obtained from the bulk soil conductivity using a functional relationship between these two. The second approach is relatively simple and has been used both in the field and laboratory (Noborio et al., 1994; Heimovaara et al., 1995; Persson , 1997; Das et al., 1999; Krishnapillai and Sri Ranjan, 2009).

Later several studies have been conducted to estimate NO_3 concentration of soil solution from the bulk soil electrical conductivity measurement using the TDR probe both in the laboratory and field experiments (Nissen et al., 1998; Das et al., 1999; Payero et al., 2006; Krishnapillai and Ranjan, 2009). They found a good agreement between NO_3-N concentration and the bulk electrical conductivity sensed by the TDR probe after the proper calibration. It should be emphasized that no electrolytes were applied to the soil during these experiments, other than the NO_3-N, hence any change in the solution conductivity was mostly resulting from the changes on the NO_3-N concentration.

Das et al. (1999) evaluated the potential to use TDR to simultaneously estimate volumetric soil water content, soil solution electrical conductivity, and soil NO_3-N concentration in an irrigated peppermint field using simple models and calibration methods. They compared TDR-estimated NO_3-N concentration with those obtained from direct soil measurements (soil cores and soil solution samples) and found that estimates from all methods were comparable, having similar pattern, magnitude and variance. Payero et al., (2006) also evaluated the feasibility of using TDR to monitor changes in NO_3-N concentration in an irrigated agricultural soil and concluded that TDR probes could be used to measure NO_3-N in non-saline soils and water after the proper calibration over a long enough period of time to include the expected variations in VWC, temperature and NO_3-N. De Neve et al. (2000) showed that mineralization of soil organic N resulted in a measureable increase in the measured electrical conductivity and concluded that it could be monitored using the TDR probe, which they confirmed in their later work (De Neve et al., 2003).

But the *in situ* application of this method is hampered by a high cost of a TDR system and inconveniences associated with its field deployment. Additional drawbacks associated with TDR method are: problems with extracting accurate parameters from the received waveforms, difficulties in detecting the reflected signal in saline soils, and measurement dependence on the coaxial cable and probe lengths (Robinson et al., 2003).

Frequency domain reflectometry (FDR) and capacitance-type probes are an alternative to TDR probes offering less expensive measurement of soil moisture content. Furthermore, the geometry of capacitance probes is more adaptable than TDR for short electrodes making them particularly suitable for *in situ* monitoring. Most of the commercially available probes operate at a single frequency (generally above a few MHz) and measure the apparent dielectric constant of the medium which can be correlated with VWC using factory-provided regression models. The operating frequencies of these sensors generally range between 5 and 150 MHz (Robinson et al., 2003). For example the Theta Probe operates at about 100 MHz (Delta-T Devices, Ltd., Cambridge, UK), ECH$_2$O EC-10 probe (Decagon Devices, Pullman, WA) at 5 MHz, while ECH$_2$O EC-5 at 70 MHz.

The frequency domain technique, which is exploited by both FDR and capacitance-type probes, measures the electrical capacitance of a capacitor that uses soil as a dielectric. An oscillator connected to this capacitor in a circuit generates repetitive electric waveforms at a characteristic frequency. Soil moisture content of the capacitor affects the circuit operating frequency making it possible to detect changes in VWC. In capacitance-type sensors the dielectric permittivity of a medium is determined by measuring the charge time of a capacitor made with that medium. While, in FDR the oscillator frequency is swept under control within a certain frequency range to find the resonant frequency, which can be used to measure soil water content.

Different studies have demonstrated that the electrical conductivity of soil has a negligible effect on the permittivity measurement at frequencies above 50 MHz making most of the capacitance-type sensors insensitive to soil salinity, but with decreasing measurement frequency, the effect of the soil electrical conductivity becomes stronger (Knoll et al., 1994; Campbell, 1990; Andrade et al., 2001; Kelleners et al., 2004; Regalado et al., 2007; Thompson et al., 2007; Kizito et al., 2008). In general, dielectric sensors operating at an effective frequency above 500 MHz benefit from the relatively stable permittivity region (Kelleners at al., 2005), while at frequencies below 50 MHz dielectric permittivity measurements are biased by the electrical conductivity and require calibration (Roth et al., 1990; Campbell, 1990). Baumhardt et al. (2000) tested the accuracy of multisensory capacitance probes in soil columns and demonstrated sensitivity of estimated VWC to both temperature and soil water salinity, which were attributed to changes in the soil permittivity. Kizito et al. (2008) and Bogena et al. (2007) pointed out that these errors in water content estimate can be corrected if the bulk soil electrical conductivity and temperature are taken into account. Results of studies have also shown that besides water content, soil salinity and temperature, capacitance-type probes are sensitive to soil type, bulk density, clay and organic matter content (Baumhardt et al., 2000; Chandler et al., 2004; Logsdon and Laird, 2004; Zhang et al., 2004; Kelleners et al., 2005).

One of the reasons of being susceptible to variability in soil environment is related to the fact that the most of dielectric probes determine the apparent permittivity rather than the real permittivity (Topp et al., 1980). Unlike the real part of permittivity, the apparent permittivity is also influenced by the imaginary part of permittivity, which affects accuracy and reliability of soil moisture estimates (Logsdon et al., 2010). It should be noted that the real (capacitive) part of the permittivity is mainly related to the soil water content, while the imaginary (conductive) part is related to the soil bulk electrical conductivity and the dielectric relaxation.

At lower frequencies the contribution of the conductive part becomes stronger than of the capacitive part of permittivity (Logsdon and Hornbuckle, 2006; Seyfried and Grant, 2007). As a result the apparent permittivity determined by capacitance probes becomes increasingly related to the changes in the dielectric loss, including changes in the bulk soil conductivity. Several studies have shown that the capacitive behavior of soil at relatively low frequencies is affected by the conductive behavior of medium causing an increase in the dielectric permittivity measurement (Thompson et al., 2007; Regalado et al., 2007; Baumhardt et al., 2000). Carr et al. (2007) studied the effect of dissolved ions in soil moisture on the permittivity measurements using ECH$_2$O EC-5 and EC-10 probes operating at fixed-frequencies of 70 and 5 MHz, respectively. They found that the EC-10 probe was more sensitive to ionic conductivity than EC-5, hence illustrating a potential to estimate soil salinity using the low frequency capacitance probe.

Only a handful of capacitance sensors have been developed that can estimate both VWC and the soil bulk electrical conductivity by independent measurement of the conductive and capacitive components of dielectric permittivity of a porous material. The Hydra Probes II (Stevens, Beaverton, OR) operating at about 50 MHz and ECH$_2$O 5TE (Decagon Devices, Pullman, WA) operating at 70 MHz belong to these new generation of capacitance probes that can measure VWC, the bulk electrical conductivity and temperature in the same volume. Despite this valuable feature of measuring several parameters simultaneously, no study has been done to estimate change in NO_3-N concentration in bulk soil using any of the abovementioned capacitance probes.

One of the most important limitations associated with the commercially available capacitance probes is that soil permittivity measurements are usually done at a single frequency, which can be adequate for estimation of a single soil property. But, as was mentioned above, the bulk soil permittivity measured using capacitance type probes is sensitive to multiple physical and chemical properties of soil, thus the permittivity measured at a single frequency represents an integrated dielectric response of multiple soil properties at that particular frequency. Furthermore, interaction between these properties is complex involving several physical and chemical processes that are not well understood. Therefore separation of individual effects using a single-frequency measurement is difficult. But measuring dielectric response at multiple frequencies covering relatively large frequency range (from low kHz to couple of hundreds MHz) can help to separate these effects and, thus, estimate several physical and chemical soil properties simultaneously.

Zhang et al. (2004) developed a capacitance-type sensor with a Wenner array configuration capable of making multi-frequency measurements ranging from 1 Hz to 15 MHz, hence covering most of the conductive part of the permittivity spectra. Later it was modified to extend the frequency range to 100 MHz, so the capacitive part of the dielectric spectra was also included (Lee et al., 2007; Lee and Zhang, 2007). They successfully established calibration models relating VWC and soil salinity with frequency-response data using a multivariate chemometric analysis, particularly partial least squares (PLS) regression. The results of these laboratory studies demonstrated the potential to estimate multiple soil properties by analyzing the patterns of the spectral data using PLS regression method; however no experimental work has been conducted to determine the feasibility of this method for estimating a specific ionic concentration of pore water.

The overall goal of this dissertation is to evaluate the feasibility of estimating changes in pore water NO_3-N concentration from the dielectric spectra obtained at frequencies below several MHz using a multivariate chemometric analysis, particularly PLS regression.

Theory

Dielectric Permittivity of Soils

Application of an electric field to a material causes its polarization, which is a dynamic effect produced by forces and torques acting on atoms and molecules of the material. Internal and viscous forces oppose the changes induced by the applied electric field, thus making the EM properties of the material frequency dependent (Santamarina, 2001). Permittivity (ε) is a frequency dependent parameter that describes the ability of the material to polarize in response to the electric field and it is a complex quantity. Hence, the dielectric permittivity (ε^*) of the material can be presented as:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \quad [1]$$

where ε' is the dielectric constant (or real part) describing energy storage, ε'' is the imaginary part describing dielectric losses, and $j^2 = -1$. But for practical reasons, the

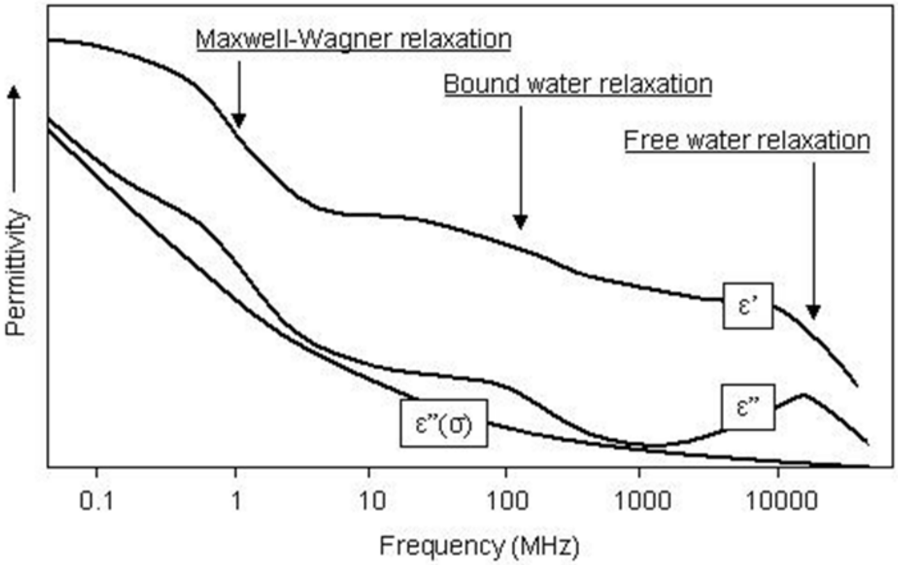

Figure 1. Frequency-dependent dielectric response and major relaxation phenomena of wet soils. ε' and ε'' refer to the real and imaginary parts of relative permittivity, respectively, while $\varepsilon''(\sigma)$ represents conductive part of the dielectric loss.

dielectric permittivity of a given material is normalized with respect to the permittivity of vacuum or "free space" (ε_0). Therefore, the relative complex permittivity (κ^*) can be expressed as:

$$\kappa^* = \frac{\varepsilon^*}{\varepsilon_0} = \kappa' - j\kappa'' \quad [2]$$

For its part, the relative dielectric loss is a function of the relative relaxation loss (κ''_d), the ionic conductivity (σ), and frequency (f):

$$\kappa'' = \kappa''_d + \frac{\sigma}{2\pi f \varepsilon_0} \quad [3]$$

Soil consists of three basic phases: soil particles, air, and water. So the bulk relative dielectric permittivity of soil (κ_b) is dependent on such factors as: (i) total volumetric water content and the relative fractions of free and bound water (which are relative to the soil surface area per unit volume), (ii) soil salinity, and (iii) soil type and texture (Jones et al., 2002). At relatively high frequencies (100 MHz – 1 GHz) dielectric losses are generally low and κ_b is primarily correlated with VWC (Topp et al., 1980). At lower frequencies κ' and κ'' are very sensitive to changes in soil water conductivity above 10 mS/m (Knoll et al., 1994). When frequency is below 50 MHz soil salinity, soil type and texture have a significant effect on κ_b and dielectric sensors operating at this frequency generally require calibration (Roth et al., 1990). The effect of ionic conductivity and clay-water-ion interactions on the permittivity reading was also reported by Kelleners et al. (2005). Explaining significance of these processes as a function of the measured frequency, they suggested raising the effective frequency of dielectric sensors above 500 MHz to benefit from the relatively stable permittivity region.

For the estimation of water content, the relationship between κ_b and the volumetric water content (θ_v) must be determined. This relationship can be described using dielectric mixing, or empirical models. Dielectric mixing, a.k.a. volumetric models describe the dielectric properties of a soil based on the relative amounts of the different soil constituents and their individual dielectric characteristics (Roth et al., 1990; Heimovaara et al., 1994). Drawback of these models is that they require determination of several input parameters (e.g. solid matter, pore space), which are not always available. Empirical models mathematically describe the relationship between dielectric properties of a soil and θ_v. The classic empirical model developed by Topp (1980) for mineral soils is expressed as:

$$\theta_v = 10^{-4}(-530 + 292\kappa_b' - 5.5(\kappa_b')^2 + 0.43(\kappa_b')^3) \quad [4]$$

However at very low water contents the Topp-model does not perform well, especially for soils with large clay content (Heimovaara et al., 1994). Similar empirical models have been developed by other researchers, including the models incorporating the effect of bulk density and soil sand/clay content (Roth et al., 1990; Malicki et al., 1996).

Rhoades et al. (1997) demonstrated that conductivity measurements at field capacity can be used to assess soil salinity. In soils that are not at field capacity the conductivity is a function of the soil structure and geometry, tortuosity of the current pathways, soil moisture content, and ionic concentration of the soil. For soil that is not at field capacity Rhoades et al. (1997) developed an empirical functional relationship between the soil bulk electrical conductivity (σ_b), soil water content (θ_v), ionic conductivity of the pore water (σ_p), and the soil surface conductivity (σ_s) related to exchangeable ions at the soil/liquid interface:

$$\sigma_b = \sigma_p \theta_v (\alpha \theta_v + \beta) + \sigma_s \quad [5]$$

where α and β are constants for a given soil depending on the amounts of the free and bound water. Application of this equation requires the constants be determined.

Recently, Hilhorst (2000) developed the method for measuring ionic conductivity of pore water by simultaneous measuring permittivity and conductivity of the bulk soil independently of soil water content. The functional relationship for the ionic conductivity of the pore water σ_p has the following form:

$$\sigma_p = \frac{\kappa_p' \sigma_b}{\left(\kappa_b' - \kappa_b'|_{\sigma_b=0}\right)} \quad [6]$$

where κ_p' is the dielectric constant of the pore water, κ_b' is the soil bulk dielectric constant, and $\kappa_b'|_{\sigma_b=0}$ is the dielectric constant of the dry soil. A significant advantage of this approach is that the term $\kappa_b'|_{\sigma_b=0}$ can be determined from soil bulk permittivity measurements at two arbitrary free water content levels.

Frequency- Dependent Electrical Conductivity of Solutions

Concentration and composition of ions in soil aqueous phase can influence the pore water conductivity (σ_p). Thus, understanding changes in σ_p can provide an opportunity to investigate behavior and movement of ionic solutes in soil. Generally, conductivity of an electrolytic solution can be expressed as (Oldham and Myland, 1994):

$$\sigma_p = F \sum_i u_i c_i |z_i| \quad [7]$$

where $F = N_A Q_e$ is the Faraday's constant describing the charge carried by one mole of univalent ions (96485 C mol^{-1}), and for each ionic species i, u_i is the ionic mobility, c_i is the ionic concentration, and z_i is the ion charge number; N_A and Q_e are the Avogadro's constant (6.0220×10^{23} mol^{-1}) and the elementary charge (1.6022×10^{-19} C), respectively. According to eq. 7 any significant change in the ionic concentration would result in corresponding change in the pore water conductivity. Wraith and Das (1998) observed a linear correlation between NO_3 concentrations and σ_p of soil solutions extracted from field sample cores ($r^2 = 0.98$), and in field studies concluded that estimated NO_3 levels based on σ_p measurements exhibited trends similar as those measured from soil cores.

The fraction of the total current carried by the given ionic species when electrical current is passed through the aqueous electrolytic solution is known as the transport number or transference number of that species, and can be expressed by (Horvath, 1985)

$$t_i = \frac{u_i c_i |z_i|}{\sum_i u_i c_i |z_i|} \quad [8]$$

The sum of the transport numbers of all ion species present in a solution is 1. However, contribution of an individual ion species to the total current, hence its transport number, should change with frequency due to Debye-Falkenhagen effect that relates frequency-dependent conductivity of the aqueous solution to the dynamic effect of the relaxation of the ion atmosphere on the motion of that ion species (Koryta et al., 1993). Before explaining the Debye-Falkenhagen theory in more details, it is important to underscore the influence of the ionic atmosphere on its electrostatic behavior.

Consider a solution of moderate ionic strength containing a variety of ions of different charges, and focus attention on a particular ion called the “central ion” (Koryta et al., 1993; Oldham and Myland, 1994; Barrow, 1996). The vicinity of this ion, if it is cation, will be at a more positive potential than the average potential of the solution. Due to Brownian movement different ions, both cations and anions, will periodically wander into this region. According to the Boltzmann distribution law ions of opposite sign (counter ions) will tend to linger longer than those of same sign. The time-averaged effect will be to create a spherically symmetric zone of opposite charge around the central ion. This zone, known as the ionic atmosphere of the central ion, first was quantified by Debye and Huckel. The electrical potential created by the ionic atmosphere (φ_{atm}) resembles a shallow well of opposite sign, which stabilizes the central ion by reducing its activity (Fig. 2). When no external EM field is applied to the solution the central ion is located in the centre of the spherically symmetric atmosphere where the electrical potential is reaching minimum, but if an external alternating field is applied to the solution this equilibrium is disturbed.

Electromigration or simply migration is a transport mechanism describing movement of ions in the presence of an electrical field: anions flow towards the anode while cations flow towards the cathode. An ion’s ability to move under the influence of an electrical field in solution is measured by the ionic mobility (u), which is defined as the terminal velocity of an ion subjected to a unit electric field (Santamarina, 2001):

$$u_i = \frac{v_i}{E} = \frac{|z_i| Q_e}{6\pi\eta r_h} \quad [9]$$

where v_i is the velocity of the i ion, E is the strength of the electric field, η is the viscosity of the solution, and r_h is Stokes' radius for the hydrated ion (rather than of the crystal ion).

Hydration is the ions' tendency to surround themselves by water molecules, mainly because of the electrostatic attraction between the charged ion and the dipole of water. A few of these water molecules are more or less strongly attached to the ion and move together with it during electromigration (Robinson and Stokes, 1968). This hydration effect increases with increasing ionic potential (the ratio of the electric charge to the non-hydrated radius of an ion) and makes dissolved ions larger than the corresponding crystal ions. The number of hydrated water molecules, however, is not very exactly defined since its value may depend on the measurement technique.

In general, smaller the hydrated radius of an ion is faster it moves through solution under the influence of an electrical field and larger is its ionic mobility. But the mobility of an ion in the presence of an alternating electrical field at low frequencies is somewhat decreased by the presence of the ionic atmosphere, because predominantly oppositely charged ions surrounding the central ion tend to hold it back (Falkenhagen, 1934; Hasted, 1973; Oldham and Myland, 1994). This effect is included in the normally measured ionic mobility. However, when the ion is exposed to a very high frequency electrical field, it is displaced so little relative to its central position that there is no retardation by its

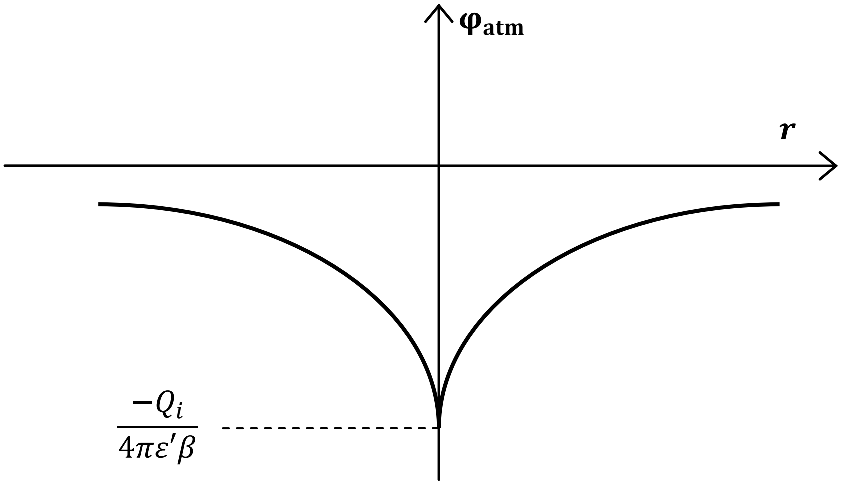

Figure 2. Potential well created by the ionic atmosphere of a cation. β is the Debye length, Q_i is the charge of the central ion, and r is a distance from the center of the ionic atmosphere. The central ion is located at $r = 0$ when there is no external electromagnetic disturbance.

atmosphere and the mobility of the ion (consequently the electrical conductivity of the solution) increases.

According to the Debye-Falkenhagen theory, when the time for one oscillation of an external alternating field ($1/2\pi f$) is larger compared with the relaxation time (τ_{rel}) of the ionic atmosphere the latter will be in its asymmetric state causing a retarding effect on the ion motion. When $1/2\pi f$ and τ_{rel} are of the same order the buildup of the ionic atmosphere to the asymmetric state cannot occur fast enough resulting in a less asymmetric atmosphere. At characteristic frequencies the relaxation effect can totally disappear due to inability of ionic atmosphere to reach the asymmetric state. At these frequencies the velocity of ions and their individual ionic conductivities are significantly higher than at ordinary frequencies. As a result contribution to the total ionic conductivity of the ion species and, hence, their transportation number will change with frequency of the applied electric field. Chandra and Bagchi (2000) predicted the Debye-Falkenhagen effect in low-concentration solutions to occur in the MHz to GHz region that includes operating frequency range of most capacitance probes.

Furthermore, as in other dynamic phenomena, characteristic frequency of an ion is inversely proportional to its mass (Santamarina, 2001). In other words, ions with larger mass will exhibit the Debye-Falkenhagen effect at lower frequencies than lighter ions assuming that their hydration numbers are similar. This will cause an ion-specific increase in σ_p at the characteristic frequency of that particular ion species. Hence the macro-scale response of the medium can reveal micro-scale information about the composition of a material. As a result analyzing dielectric response of pore water (directly, using soil solution extracts or indirectly, from bulk soil samples) measured at multiple frequencies should be capable of providing an information about concentrations of specific ions.

Organization of the Dissertation

This dissertation adopted the manuscript format as defined by the Graduate College of Iowa State University. Three technical papers, including one paper published in the Soil Science Society of America Journal and two papers to be submitted to other peer-reviewed journals, are presented in three separate chapters. The first paper (chapter 2), “Sensitivity of capacitance soil moisture sensors to nitrate ions in soil solution”, describes a qualitative study that evaluated sensitivity of two commercially-available capacitance probes operating at fixed frequencies of 5 and 70 MHz to changes in soil solution nitrate concentration in a laboratory setting. The second paper (chapter 3), “Estimation of solution nitrate-nitrogen concentration from spectral response using PLS regression", demonstrates using of multivariate chemometric techniques to estimate aqueous NO_3-N concentration from the dielectric spectra measurement obtained at 48 frequencies ranging from 200 Hz to 13 MHz. The third paper (chapter 4), "Estimation of nitrate-nitrogen concentration in soil solution from dielectric spectra using PLS analysis", explores feasibility to simultaneously estimate change in VWC and pore water NO_3-N concentration in soil sample from frequency response data obtained from 5 Hz to 13 MHz range using the same chemometric analysis.

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CHAPTER 2. SENSITIVITY OF CAPACITANCE SOIL MOISTURE SENSORS TO NITRATE IONS IN SOIL SOLUTION

A paper published in *the Soil Science Society of America Journal*

G. Chighladze, A. Kaleita, S. Birrell

Abstract

Capacitance type sensors have been widely used to monitor soil water content and salinity. But little is known about their response to specific ions in soil solution. The goal of this laboratory study was to investigate the sensitivity of two capacitance probes ECH$_2$O EC-5 and EC-10, to NO$_3$ concentration in soil solutions, as well as to understand the differences in sensor response to presence of other ions in the solutions. Uniformly packed 45 soil samples were prepared using a homogenized loam soil wetted to 5 volumetric water contents (VWC) with 9 solutions containing different concentrations of NO_3^-, Cl^-, or both. A two-stage analysis of the normalized data revealed that ion type and concentration had a significant effect ($P \sim 0.01$) only on the response of the EC-10 probes operating at a frequency of 5 MHz. The response of the EC-5 probes, operating at 70 MHz, was mainly explained by changes in VWC. Multiple linear regression models fitted to the EC-10 response to individual solutions showed that concentration had a statistically significant predictive value only for samples wetted with NO$_3$ solutions when temperature was incorporated in the model. The study confirmed that capacitance probes

operating at a relatively low frequency of 5 MHz are more sensitive to change in NO_3 concentration than in Cl. We attributed this effect to difference in ion mass that manifest through increase in conductivity at ion-specific frequency. Additional experimental work is needed, however, to accurately define optimal frequencies for measuring ion-induced effects on dielectric measurement and to quantify interrelations between them.

Abbreviations: EC, electrical conductivity; VWC, volumetric water content.

Introduction

Extensive use of chemical fertilizers has significantly increased agricultural production worldwide during the last several decades (Addiscott, 2005). Nitrogen is among the most important elements required to sustain this thriving crop production; however, the extensive use of N in agriculture can significantly increase the risk of N loss to the environment, largely through leaching to the groundwater of NO_3 that was not used by the crop. High level of NO_3 in surface and subsurface waters can cause human health problems such as methemoglobinemia or increase the risk for specific cancers such as gastric cancer (Bruning-Fann and Kaneene, 1993; Gupta et al., 2000; Grosse et al., 2006; Ward et al., 2005), as well as environmental problems such as eutrophication and hypoxia in aquatic environments (NRCS, 1997). Redundant NO_3 leached out of the farm represents wasted money in fertilizer for the producers, which decreases their net profit. To minimize NO_3 loss from agricultural land, a balance should be achieved between maximized crop production and N application by matching spatial and temporal needs within the field (Hoskinson et al., 1999; Roberts et al., 2002). The traditional method for determining the existing soil NO_3 concentration involves time-consuming and tedious procedures of extracting pore water from soil samples and its subsequent laboratory chemical analysis (Carter and Gregorich, 2007), which is impractical for large-scale or high-resolution monitoring. Furthermore, this conventional method of soil sampling is destructive while the results of analysis are inconsistent, varying with different techniques and equipment used. Plant tissue tests have also frequently been used by crop producers to improve N management practices, but like soil tests, these do not allow farmers to monitor the dynamic nature of NO_3 in a timely manner (Balkcom et al., 2003). Therefore, real-time *in situ* measurement techniques are needed that will allow the evaluation of changes in NO_3 concentrations with sufficient resolution in space and time.

Intensive development of precision farming techniques has stimulated an increased interest in the use of new, energy-efficient dielectric soil probes for continuous monitoring of field variables such as soil moisture content (Robinson et al., 2008; Andrade-Sánchez et al., 2004). These commercially available soil moisture probes use a variety of techniques to measure the dielectric constant of the soil medium, which is correlated with the volumetric soil moisture content by various empirical or theoretical models (e.g., Topp et al., 1980; Dalton et al., 1984). Numerous studies have shown, however, that at relatively low frequencies, the dielectric permittivity of the soil is sensitive not only to soil water content but also particularly to soil temperature and soluble salt content (Kizito et al., 2008; Thompson et al., 2007; Regalado et al., 2007; Kelleners et al., 2004; Baumhardt et al., 2000; Andrade et al., 2001). Dielectric sensors operating at an effective frequency above 500 MHz benefit from the relatively stable permittivity region (Kelleners et al., 2005), while at a frequency below 50 MHz, dielectric permittivity measurements are biased by the soil bulk electrical conductivity

(Gardner et al., 1998; Campbell, 1990). The resulting error in water content estimation using low-frequency dielectric sensors can be corrected if the soil electrical conductivity (EC) and temperature are taken into account (Kizito et al., 2008; Bogena et al., 2007; Saito et al., 2008; Saito et al., 2009).

Only a handful of capacitance-type sensors have been developed that can measure both the VWC and soil bulk EC by independent measurement of the conductive and capacitive components of the complex dielectric permittivity of a porous material. While the real (capacitive) part of the permittivity is mainly influenced by the soil water content, the imaginary (conductive) part is related to the soil bulk EC. Most of the commercially available dielectric sensors, however, respond to the soil bulk permittivity, also called the apparent permittivity, which incorporates both real and imaginary parts in the measurement (Logsdon et al., 2010). As a result, at relatively low frequencies the apparent permittivity is noticeably affected by the conductive behavior, causing a corresponding overestimation of the VWC. Carr et al. (2007) studied the effect of dissolved ions in the soil water on the permittivity measurements using the capacitance-type probes ECH$_2$O EC-5 and EC-10 (Decagon Devices, Pullman, WA) operating at fixed frequencies of 70 and 5 MHz, respectively. They found that the EC-10 probe was more sensitive to ionic conductivity than the EC-5, hence illustrating the potential to estimate soil salinity by taking permittivity measurements at two frequencies, one relatively high and one relatively low.

The ionic conductivity of an electrolyte is frequency dependent, however, and the manner in which it changes is governed by the chemical composition and solute concentration of the aqueous solution (Chandra and Bagchi, 2000). Furthermore, the velocity of an individual ion species, and hence its contribution to the total ionic conductivity of the aqueous solution, can significantly increase at the ion-specific characteristic frequency (<1 GHz) due to relaxation of the ionic atmosphere.

Based on the discussion above, we hypothesized that the cumulative effect of soil moisture and frequency-dependent ionic conductivity on the soil bulk permittivity measurement could be utilized to estimate the change in individual ion concentrations during continuous monitoring of agricultural fields through the use of multifrequency measurements. Specifically, combining measurements at several frequencies rather than using a single frequency would allow us to partition the dielectric response into components associated with the VWC, salinity, and concentrations of individual ions (NO_3 in our case). The goal of this study was to test the validity of this conceptually new approach of measuring the effect of ion-specific conductivity on the dielectric response of bulk soil using off-the-shelf technology, particularly ECH_2O EC-5 and EC-10 probes. The potential for obtaining additional information from ECH_2O sensors can be increasingly valuable, taking into account the relatively low cost and operational simplicity of the probes. The specific objective of this study was to evaluate the sensitivity of these capacitance probes to changes in the soil solution NO_3 concentration at environmentally relevant levels at two fixed measurement frequencies (70 and 5 MHz) for a range of soil moisture contents. Furthermore, to determine the effect of other soil solutes on capacitance probes, we examined the differences in sensor response between soil samples wetted with NO_3, Cl, and NO_3–Cl solutions at both measurement frequencies.

Theory

Soil as a multi-phase system consists of three components: the solid matrix (soil particles), air, and the liquid water phase. The dielectric constant of water is 78.5 at 25°C, while those of air and most soil minerals are about 1 and in the range of 2 to 8, respectively. Hence, the bulk permittivity measurement of the soil is strongly influenced by its water content. By applying an alternating electrical field to the soil the molecules of water will overcome their random thermal motion and align with the field, thus storing the energy. Soil water is never pure, however, and contains some ions, which can cause energy loss through ionic conductivity. Depending on the applied frequency (f), some energy can also be dissipated through molecular relaxation. Hence, the frequency-dependent dielectric properties of the soil can be represented by the following complex dielectric response function:

$$\varepsilon = \varepsilon' - j\left(\varepsilon_{\mathrm{rel}}'' + \frac{\sigma}{2\pi f \varepsilon_0}\right) \quad [1]$$

where ε is the complex dielectric permittivity, ε' is the real part of the permittivity that measures the polarization of the soil, ε_{rel}'' is a relaxation component of the imaginary part of the permittivity, σ is the bulk conductivity (which is usually approximated by direct current conductivity), and ε_0 is the permittivity for free space (8.854×10^{-12} F m^{-1}).

The bulk soil EC consists of the surface (σ_S) and the liquid-phase (σ_W) conductivities and can be written as (Rhoades et al., 1976):

$$\sigma = \theta\tau\sigma_W + \sigma_S \quad [2]$$

where θ is the volumetric water content and τ is the tortuosity factor. For soils with small specific surface σ is directly proportional to σ_W (Santamarina et al. 2001, p.329-364).

Like the complex permittivity, conductivity is also a frequency dependent complex variable consisting of real and imaginary parts. For ionic solutions (electrolytes), the conductivity can be expressed using a multiple Debye form:

$$\sigma_W(\omega) = \frac{1}{k_B T}\sum_i \frac{\rho_i q_i^2 D_i}{1 - i\omega D_i\, m_i/k_B T} \quad [3]$$

where q_i, m_i, ρ_i and D_i are the charge, mass, bulk number density, and self-diffusion coefficient, respectively, of an ion of ith species, $\omega = 2\pi f$ is the angular frequency, k_B is the Boltzmann constant, and T is the absolute temperature.

In solutions, $\sigma_W(\omega)$ is related to the dynamic effect of the relaxation of the ion atmosphere on the motion of an ion, which manifest through Debye-Falkenhagen effect (Chandra and Bagchi, 2000). According to Debye-Falkenhagen theory, when the time for one oscillation of an external alternating field $(1/f)$ is larger compared with the relaxation time (τ_{rel}) of the ionic atmosphere the latter will be in its asymmetric state causing a retarding effect on the ion motion. When $1/f$ and τ_{rel} are of the same order the buildup of the ionic atmosphere to the asymmetric state cannot occur fast enough resulting in a less asymmetric atmosphere. At characteristic frequencies the relaxation effect can totally disappears due to inability of ionic atmosphere to reach the asymmetric state. At this frequencies the velocity of the ions and their individual ionic molar conductivities are significantly higher than for ordinary frequencies.

As in other dynamic phenomena, characteristic frequency of an ion is inversely proportional to its mass. In other words, ions with larger mass will exhibit the Debye-Falkenhagen effect at lower frequencies than lighter ions, causing an ion-specific increase in σ_W at the characteristic frequency of that particular ion species. Hence the macro-scale response of the medium can reveal micro-scale information about the composition of material.

The Debye-Falkenhagen effect in low-concentration solutions is predicted to occur in the megahertz to gigahertz region that includes operating frequency range of most capacitance probes (Chandra and Bagchi, 2000). Many of these sensors, including ECH_2O EC-5 and EC-10, response to apparent permittivity (ε_a), which integrate both the real and the imaginary part of the complex permittivity, thus incorporating σ_W in their measurements (Logsdon et al., 2000). Different operational frequencies of geometrically similar EC-5 (70 MHz) and EC-10 (5 MHz) probes can provide a valuable insight into applicability of multi-frequency measurement method for detecting ion-specific response of capacitance sensors.

Methods

The soil used for the laboratory-scale experiment was collected from a depth of 0.20m in the Iowa State University Agronomy Research Farm located in Boone County, IA. The soil was air-dried, grinded and sieved to approximately ≤ 2 mm. The particle size distribution was determined using the hydrometer method (43% sand, 33% silt) and was classified as a loam based on the USDA textural triangle, although it was mapped as Webster silty clay loam (a fine-loamy, mixed, superactive, mesic Typic Endoaquoll) according to the NRCS soil survey. The soil bulk density was found to be 1.15 g cm-3 and was later maintained for all soil samples prepared for the experiment. Air-dry soil samples were analyzed for soluble salt by Ward Laboratory (Kearney, NE) using 1:1

soil/water suspension. The average soil salinity was determined as 0.36 dS m^{-1} with standard deviation of 0.06 dS m^{-1}.

Six identical 22-cm-long, cylindrical sample holders were constructed using 10-cm-diameter polyvinyl chloride (PVC) pipe. A removable threaded plug and a PVC cap were attached to the top and bottom, respectively, of the sample holder to prevent soil water from leaking or evaporating and the soil particles from falling out during an experiment. Each cylindrical container was marked at volumetric intervals of 300 cm^3 to facilitate homogenizing of the bulk density throughout the soil sample during packing.

Three KNO_3 and three KCl solutions were prepared with concentrations of 6, 25 and 60 mg L^{-1} of NO_3-N and Cl, respectively. The NO_3 concentration reflects the actual range of NO_3-N in Iowa fields, which changes from < 10 to > 100 mg L^{-1} during dry years, and during wet years hardly exceeds 60 mg L^{-1} (Balkcom et al., 2003; Killorn, 1990). The 25 mg L^{-1} corresponds to the optimal soil NO_3-N concentration for maximum yields (Blackmer et al., 1989). Electrical conductivities of the six wetting solutions were measured. Values ranged from 0.05 to 0.51 dS m^{-1} for the KNO_3 solutions and from 0.02 to 0.22 dS m^{-1} for the KCl solutions. Three additional solutions were prepared by mixing equal parts of the NO_3 and Cl solutions of the same concentration. The EC of these solutions were in the range of 0.04 to 0.37 dS m^{-1}.

The air-dried soil, with an initial volumetric water content of 0.04 m^3 m^{-3}, was uniformly moistened with each solution to prepare individual soil samples. Each sample was thoroughly mixed on a tray by gradually adding the required amount of specific solution to arrive at the designed VWC. A total of five VWC levels were used during experiment ranging from 0.10 to 0.30 m^3 m^{-3} by increments of 0.05 m^3 m^{-3}. As a result, 45 samples were prepared, one for each solution and moisture content combination. The actual VWC of each soil mixture was defined by oven drying two subsamples collected from individual samples. One subsample was taken right after wetting, the other right after taking the sensor measurement.

The mixed soil was transferred to the cylindrical container and packed to the homogeneous bulk density in sections corresponding to the marked volumetric intervals. The sample holder was sealed at both ends and placed on a rotator device for at least 12 h to allow the sample to reach equilibrium. The rotator device, similar to one described by Logsdon et al. (1993), held six cylindrical containers at a time in a horizontal position, while rotating them back and forth nearly 360° about their cylindrical axis at 2 rpm to avoid accumulation of the added solution at the bottom of the sample.

After 12 h, the sample holders were removed from the rotating device, the lids were unscrewed, and readings were taken from each soil sample using four EC-5 and four EC-10 probes separately inserted. Both sensor types have a flat design for simple insertion and use specialized circuitry to measure the dielectric of the medium surrounding a thin, fiberglass-enclosed probe. The EC-5 probe (8.9-cm length, 1.8-cm width, 0.7-cm depth) operates at a frequency of 70 MHz, while the EC-10 probe (14.5-cm length, 1.8-cm width, 1.5-cm depth) has an excitation frequency of 5 MHz, which makes it more sensitive to soil salinity. According to the manual measurement accuracy of EC-10 is ±0.04 $m^3 m^{-3}$ in soil with an EC < 0.5 dS m^{-1} and ±0.03 $m^3 m^{-3}$ for EC-5 in soil with an EC up to 8 dS m^{-1} (Decagon Devices, 2009). Further information on operational and measurement principals of both probes can be found in Bogena et al. (2007) and Decagon Devices (2006a,b).

A DaqBook100 datalogger (IOtech, Cleveland, OH) with a screw-terminal expansion card DBK11A was used to supply a constant 2.5 V of direct current excitation to each probe and to measure the sensor response as an analog signal in millivolts. The raw probe outputs were recorded for 10 minutes at 10 readings per minute in each test. The averaged output of each probe was used for further analysis. In addition, soil temperature readings were taken simultaneously in each sample using the temperature sensor AD22100 (Analog Device, Norwood, MA). After taking the measurements, the soil samples were wetted with the corresponding solution to reach next VWC, repacked in the same cylindrical container and left in the rotator to equilibrate for 12 h until new measurements were taken. The whole process, starting from the lowest end of the moisture content to the highest, took from 5 to 7 d.

Statistical Analysis

Linear regression models were developed for each probe using the raw data set to evaluate sensor performances. Although the data showed slight nonlinearity, particularly at low water content, models with higher order (except of fourth order) did not perform better. As a result, linear models were used to fit the data points for the rest of the analysis, which agrees with the manufacturer's recommendation for the VWC range used in the experiment (Decagon Devices, 2006b). Responses of individual sensors were normalized to remove biases originated from sensor-to-sensor variability. The normalized data of the four sensors were averaged for each probe type and used for the statistical analysis.

A two-stage analysis was employed to understand the sensitivity of EC-5 and EC-10 probes to change in soil solution type and concentration. The analysis incorporated nine experimental units, defined as a unique combination of individual solution type and concentration (3 solution types × 3 concentrations = 9 combinations). In the first stage, simple linear regression models were fitted to each unit so that repeated measurements on the same experimental unit were reduced to a single response slope of the linear regression model ($dx/d\theta$, where x is a probe response in mV and θ is VWC in cubic meters per cubic meter), which is influenced by the soil water ionic conductivity. In the second step, the effect of the experimental factors (solution type and concentration) on the new response was examined by regressing the slopes of the experimental units on solution type (nominal variable) and concentration (continuous variable).

Results

Sensor Calibration

Models fitted to four EC-5 and four EC-10 sensors for all wetting solutions combined are shown in Fig. 1. The raw voltage output of both the EC-5 and EC-10 probes increased with increasing soil water content for all nine wetting solutions within the studied range of 0.10 to 0.30 m^3 m^{-3}. Furthermore, with an increase in moisture content, the difference between sensor readings in the same medium increased for both types of probe. As a result, the measurements at higher water content were more scattered than at lower end. These variations were mostly within the 95% prediction interval (±3.5 and ±2.5% for EC-5 and EC-10, respectively), however, and were very close to the sensor accuracies provided by the manufacturer for all mineral soils (±3 and ±4% for EC-5 and EC-10

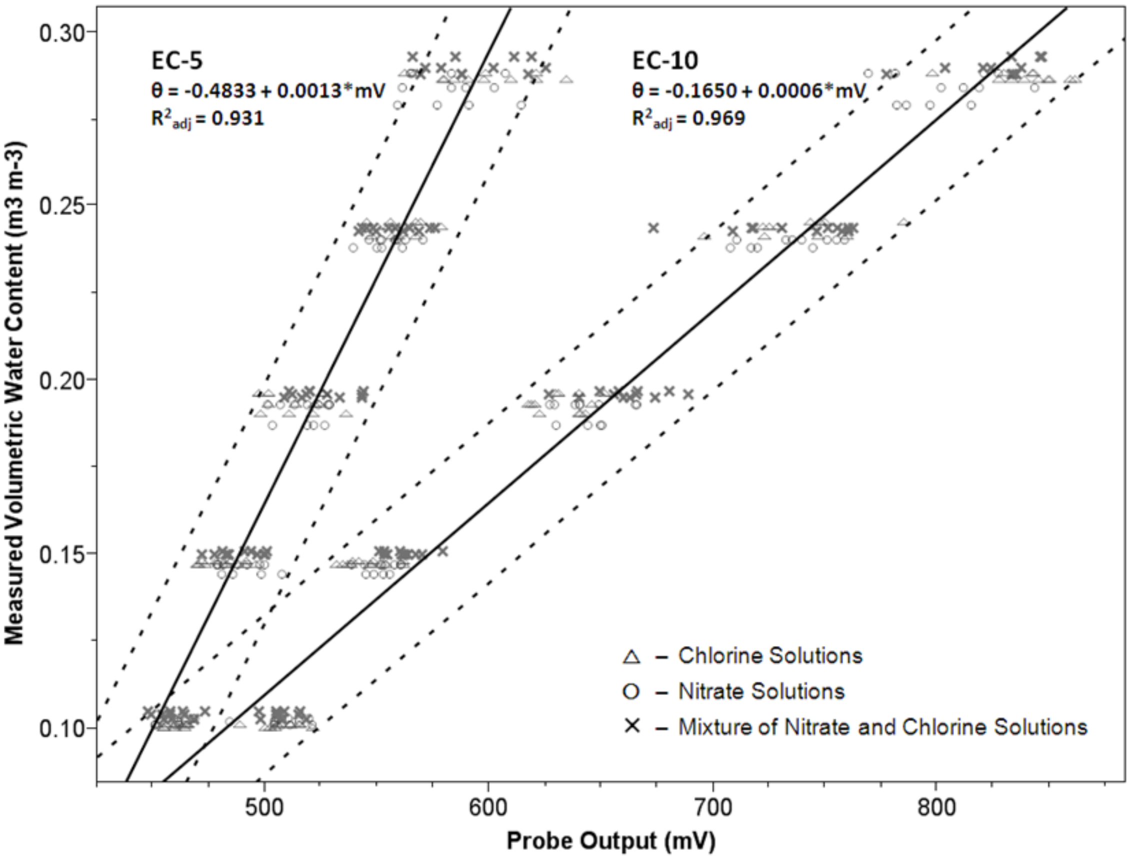

Figure 1. Calibration curves of the EC-5 and EC-10 sensors for soil samples wetted with nine different solutions

probes, respectively). The fitted linear regression models yielded R^2 values of 0.931 and 0.969 for EC-5 and EC-10 probes, respectively.

These results showed that both sensors could sufficiently estimate the VWC but also indicated that there were variations in sensor response for each sensor type. The observed scattering of the data points was not just a random error, however, and some portion of it stemmed from the conductive losses sensed by both probes to different degree (as discussed below). Furthermore, the increasing variation in sensor output with increasing VWC (observed in Fig. 1) was also attributed to conductive losses resulting from the rise in soil bulk EC with increasing VWC as predicted by Eq. [2].

Sensor-to-Sensor Variability

Statistical analysis indicated significant sensor-to-sensor variation for both sensor types. Our results showed that this variation was more prominent among the EC-5 probes than the EC-10 (Fig. 2). Normalization of the EC-5 response by bringing the data from individual probes onto a common scale improved the model performance and decreased the RMSE by 35% (Table 1). By comparison RMSE of the EC-10 model improved only 5% after similar normalization. Hence, the following statistical analyses were conducted using only normalized data averaged over the four sensors for each probe type.

A sensor-to-sensor variation was also confirmed by Rosenbaum et al. (2010) based on tests of ECH$_2$O EC-5, TE and 5TE probes in dielectric liquids, but it was not reported by other studies using soil as measurement medium (Nemali et al., 2007; Kizito et al., 2008). One of the problems in detecting this variation, particularly in field studies, is the heterogeneity or local variation in soil properties that can readily confound differences between individual sensors. In laboratory studies, however, soil samples are often purposefully homogenized, thus the main masking factor can be associated with insertion bias, which defines how good or poor the contact is between the ECH$_2$O sensor and the surrounding medium. We assumed that during our laboratory study, this error was relatively small compared with others, which allowed us to detect sensor-to-sensor variation and correct it. However to obtain higher precision, it would be more effective to use the method described by Rosenbaum et al. (2010), which can completely eliminate insertion bias during sensor-to-sensor calibration. This would be particularly beneficial for large-scale monitoring that uses a sensor network consisting of different or individual ECH$_2$O probes.

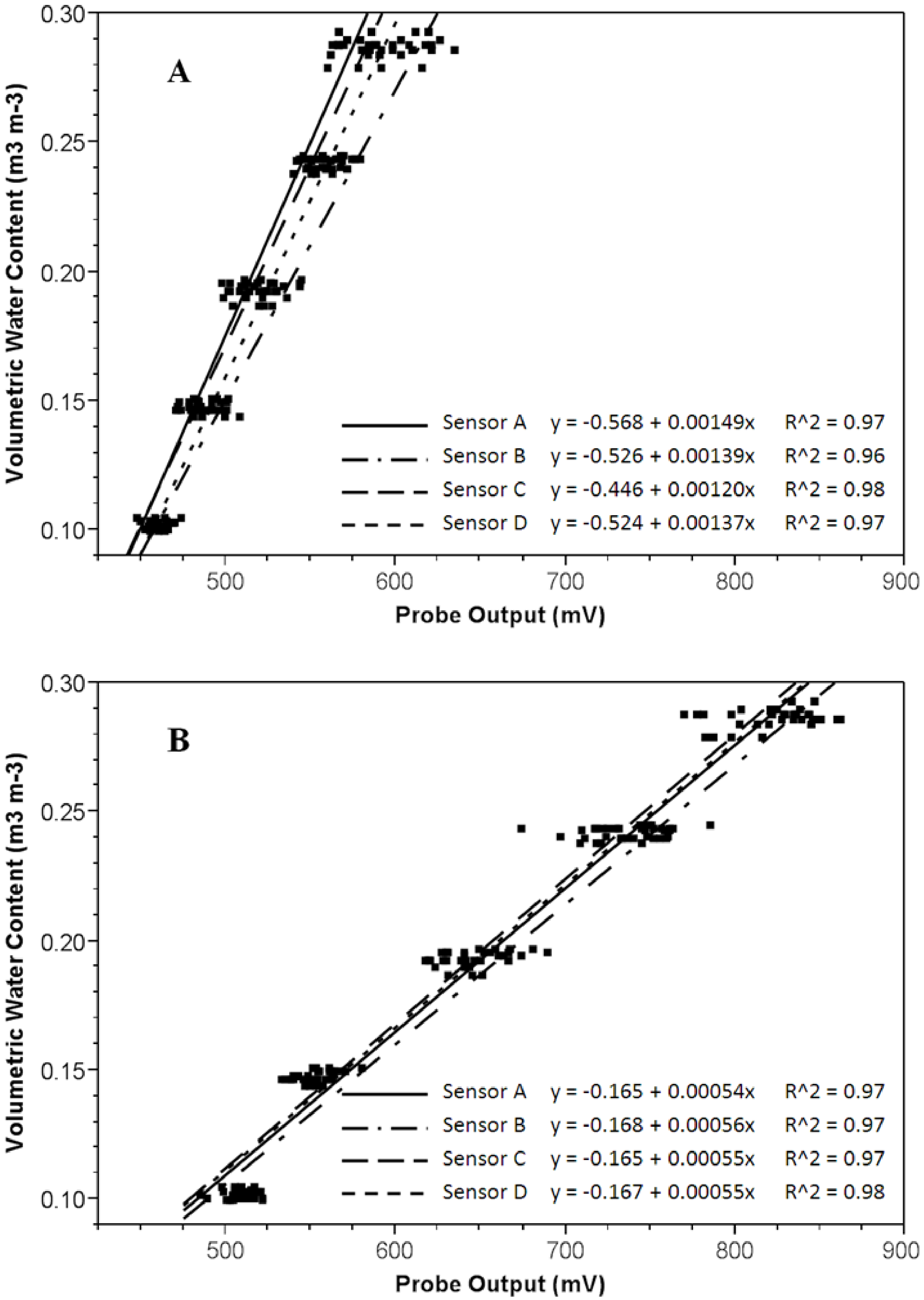

Figure 2. Response of individual probes to changes in volumetric water content for the (A) EC-5 and (B) EC-10 sensors

Table 1. Summary of model fit for non-normalized and normalized data of the EC-5 and EC-10 probes

Model Parameters	EC-5		EC-10	
	not normalized	normalized	not normalized	normalized
R^2_{adj} †	0.931	0.971	0.969	0.972
RMSE (VWC, $m^3\ m^{-3}$)	0.017	0.011	0.012	0.011

†R^2_{adj}, adjusted R^2

Effects of Solution Concentration

The two-stage analysis of the normalized data showed that the slopes of the final regression models increased with increasing concentration for all three solution types (Fig. 3). For both probe types, the slope of the Cl solution was always greater than the slope of the NO_3 solution, while the slope of the mixed solution was between these two. No interaction was revealed, however, between the solution type and concentration during the analyses. Furthermore, the solution type and concentration had significant effects ($P < 0.05$) only on the EC-10 response, while they had no statistically significant predictive value for the EC-5 (Table 2).

This behavior of the EC-5 and EC-10 probes was anticipated and stemmed from their operating frequencies. A higher frequency of 70 MHz makes the EC-5 probes less sensitive to increased ionic concentration in the soil solution, while output of the EC-10 probes operating at 5 MHz is more affected by changes in dielectric loss. Figure 4 illustrates this slight difference in sensor response between the EC-5 and EC-10 probes for all solutions together. The concentration-induced changes in the dielectric response were greater for the EC-10 sensors than for the EC-5, which demonstrates that the EC-10

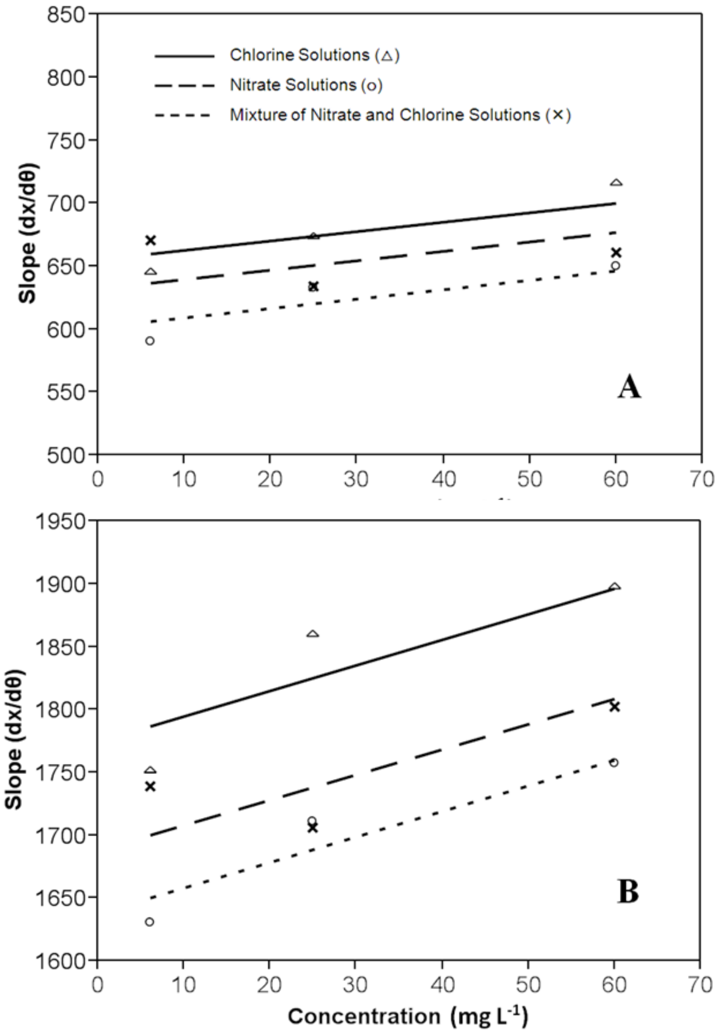

Figure 3. Sensitivity of the (A) EC-5 and (B) EC-10 sensors to individual solution concentrations (results of the two-stage analysis)

probe is more vulnerable than its counterpart to increased dielectric losses within the ionic concentration range tested. This agrees with the results of other studies (Bogena et al., 2007; Carr et al., 2007; Kizito et al., 2008; Saito et al., 2008), however conductivity levels tested here (< 1 dS m^{-1}) were lower than the levels used in those studies (mostly 1-32 dS m^{-1}). Furthermore, the results of the two-stage analysis indicated that the sensitivity of the low-frequency-capacitance probe to soil solution salinity is also solution specific (Fig. 3B).

Table 2. Significance (*P*) of the parameters of the three different models using data from the EC-5 and EC-10 probes and determined by two-step analysis of the slopes

Model Parameters	*P* value	
	EC-5	EC-10
Slope = *f* (solution type, ionic concentration)		
Solution type	0.0876	0.0125
Concentration (mg L^{-1})	0.0798	0.0113
Slope = *f* (solution EC)		
Solution EC (dS m^{-1})	0.6913	0.5927
Slope = *f* (solution type, solution EC)		
Solution type	0.0678	0.0122
Solution EC (dS m^{-1})	0.1352	0.0302

A two-stage regression model was also applied to the solution conductivity data to analyze the effect of the pure solution EC on the $dx/d\theta$ slope for both sensors. The assumption was made that changes in the soil bulk EC at fixed soil water content was intimately connected with change in the wetting solution EC; in other words, changes in the pore water EC was approximated by the differences in the solution EC. Taking into account the relatively low soil salinity (0.36 dS m^{-1}) and the range of VWC tested (> 0.10 m^3 m^{-3}), this assumption can be a very accurate approximation, implying that the level of additionally dissolved ions in the solution after mixing with the soil was relatively low and constant throughout the range of VWCs and solutions tested. The result of this

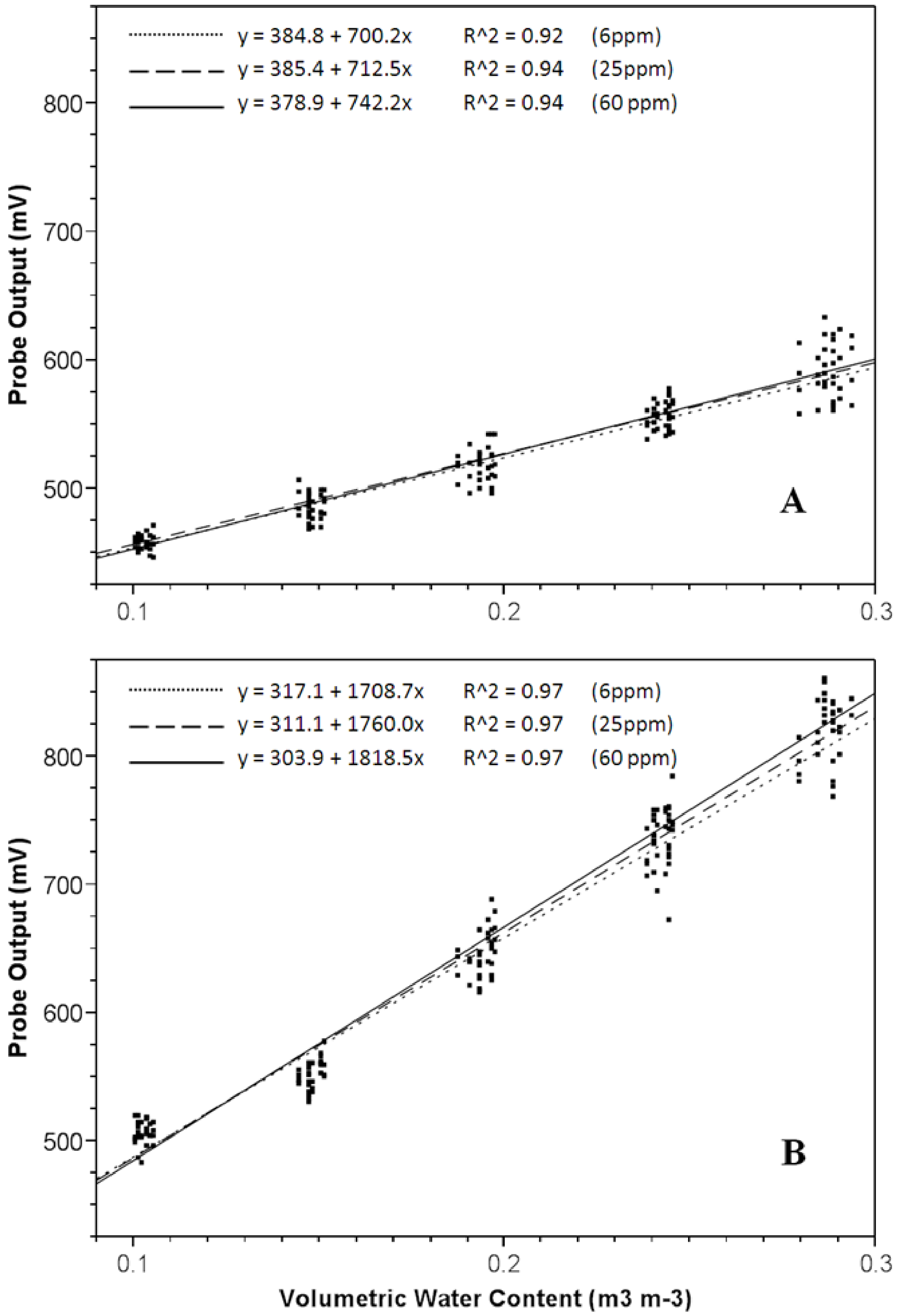

Figure 4. Sensor response to solution concentration for the (A) EC-5 and (B) EC-10 probes

analysis revealed that the solution EC could not solely explain variation in the slope for either sensor type (Fig. 5); *P* values were very high in both cases (Table 2). Including the solution type as an additional model parameter greatly improved EC's predictive value

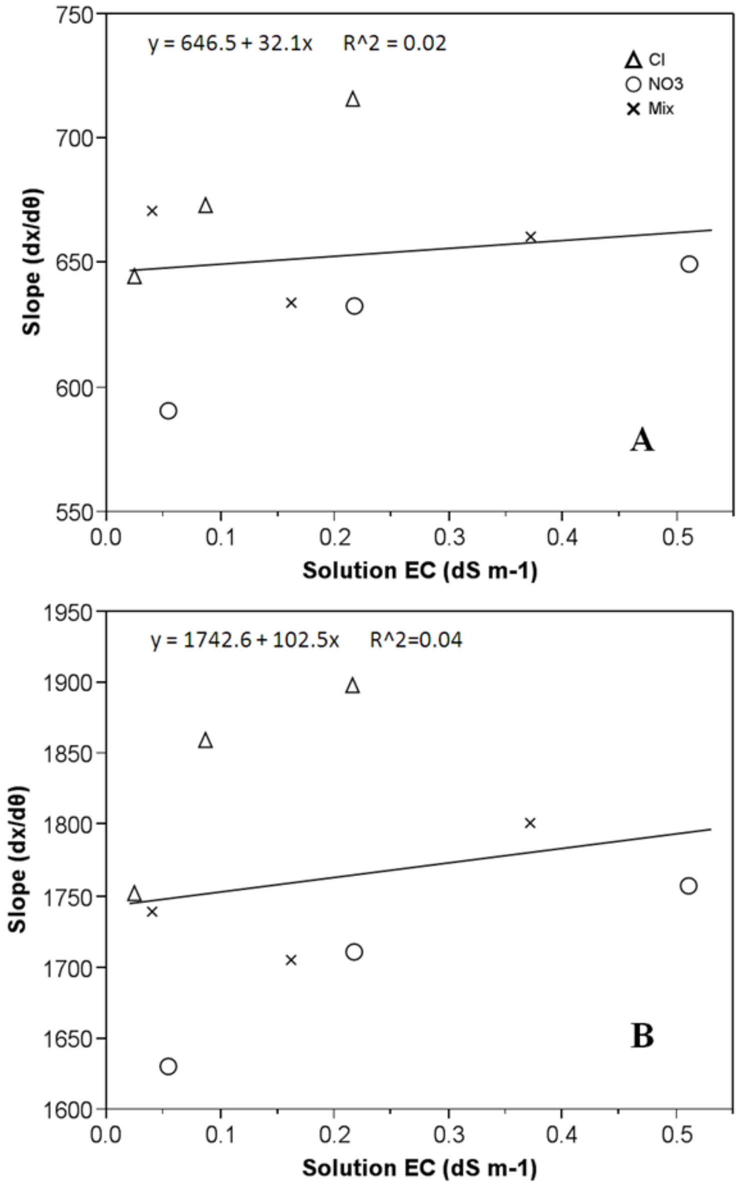

Figure 5. Sensitivity of the (A) EC-5 and (B) EC-10 sensors to solution electrical conductivity (EC) based on dx/dθ, where x is the probe response and θ is volumetric water contents (results of the two-stage analysis)

for the EC-10, making its effect statistically significant (*P* value improved from 0.59 to 0.03). The results of the last model were similar to the results of the two-stage model that used the solution concentration in milligrams per liter (rather than EC), although the model fitted with the concentration had a higher R^2 value (0.82 vs. 0.74) and the lower RMSE (0.35 vs 0.42), indicating that the ionic concentration expressed in milligrams per liter can predict better than the one expressed in decisiemens per meter. This slight preference can be related to the fact that the solution conductivity sensed by EC-10 is different than one reported due to difference in measurement frequency (5 MHz vs. near-direct current). As can be deduced from Eq. [3], the conductivity of individual solution types changes differently due to their ionic composition. These unproportional changes in EC with frequency contributed to the slight increase in random error, while the concentration expressed in milligrams per liter remained constant at all frequencies, making it the more relevant variable for inferring the effect of ionic conductivity for a frequency spectrum. This supports the results of the statistical analysis that sensor response is solution specific.

Effects of Solution Type

Three models were fitted to the EC-10 data to understand the probe's sensitivity to individual ion species. In one case, concentration was represented as the total ion concentration of the solution, while in the other two cases, concentration was expressed as a level of only NO_3 or Cl ions in the solution. Interestingly, concentration was not a significant predictor for any of the models (Table 3), but incorporation of the temperature as an additional variable made the effect of both NO_3 and total ion concentration statistically significant, while concentration of Cl remained insignificant. Furthermore, the concentration of NO_3 had a greater effect on the EC-10 response than total ion concentration. These results suggest that the NO_3 concentration dominated the change in EC-10 response compared with Cl and can independently explain the effect of ionic losses on the apparent permittivity at 5 MHz even when a comparable amount of Cl was present. Such supremacy should be related to the combined effects of (i) an increase in NO_3-induced solution conductivity at the measurement frequency compared with the reported EC value, and (ii) a relative stationarity of Cl-induced EC. This explanation of macroscopic behavior is in line with the Debye–Falkenhagen effect and consequently it follows that the characteristic frequency of NO_3 should be in vicinity of 5 MHz. Hence Cl, which is lighter that NO_3, should experience the same effect at a higher frequency and therefore at 5 MHz, its movement is still retarded by an asymmetric ionic atmosphere.

Table 3. Results of the effect test of the regression models developed for the EC-10 response based on total ions, NO_3^- only, and Cl^- only, with and without incorporating temperature (temp.) into the model

Source	Total Concentration		NO_3^- Concentration		Cl^- Concentration	
	Without temp.	With temp.	Without temp.	With temp.	Without temp.	With temp.
Volumetric water content	<0.0001***	<0.0001***	<0.0001***	<0.0001***	<0.0001***	<0.0001***
Solution type	0.9384	0.0657	0.5361	0.0230*	0.9180	0.1136
Concentration	0.1738	0.0342*	0.1628	0.0242*	0.4800	0.3133
Temperature	-	0.0018**	-	0.0013**	-	0.0058**

* Significant at $P < 0.05$.
** Significant at $P < 0.01$.
*** Significant at $P < 0.001$.

Table 4. Results of a *t*-test of the simple linear regression models fitted to the response of the EC-10 probe to individual solutions separately and globally, with and without temperature (temp.) incorporated into the model

Source	Global		NO_3		Cl		Mix	
	Without temp.	With temp.	Without temp.	With temp.	Without temp.	With temp.	Without temp.	With temp.
Volumetric water content	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Concentration	0.1639	0.0765	0.0978	0.0504	0.6602	0.6355	0.5949	0.1267
Temperature		0.0291		0.2235		0.1104		0.0083

Similar results were obtained when regression models were fitted to the response of the EC-10 probe to individual solutions (Table 4). Again, concentration was not statistically significant in all three cases but incorporation of the temperature enhanced its predictive value for the NO_3 model (P reaching the 5% threshold), while the effect of concentration still remained insignificant for the Cl and mixed samples. Although these results provide limited explanation to quantitatively differentiate the effects of the individual ions studied, nevertheless they suggest that the EC-10 sensor is more sensitive to the presence of NO_3 ions in the solution than to Cl within the concentration and soil moisture levels tested in the experiment.

It is worth mentioning that changes in temperature during the experiments, caused by room temperature variation, were relatively small (±2°C) but had a significant effect on the prediction models. An increase in the concentration effect due to incorporation of temperature as an additional term can be attributed to the fact that the change in response of the EC-10 probes to temperature variation was on the same order as the change in response caused by the variation in concentration used in the experiments. Furthermore, the EC-5 probes, which were less sensitive to soil water ionic conductivity, were also less sensitive to temperature variation (data not shown) compared with the EC-10 probes operating at a relatively lower frequency. Saito et al. (2009), in their detailed study of the temperature effect on ECH_2O probes, reported the same tendency and attributed this kind of behavior to the fact that temperature is mainly manifested through increased EC of the soil liquid phase, to which the EC-5 probe is less sensitive.

Conclusions

In the present study, the EC-5 and EC-10 capacitance-type soil probes were calibrated for measuring the VWC at different salinity levels. The responses of each sensor type were compared in soil samples wetted with different solutions. The effect of each solute concentration on the probe sensitivity was examined and the following conclusions were drawn.

- The response of the EC-5 sensor, operating at a frequency of 70 MHz, was primarily explained by moisture content. Solution concentration and type were shown to have no effect on the probe output within the range of concentration used in the experiments. Hence, the EC-5 probes are suitable for precise measurement of VWC. To improve the accuracy and eliminate sensor-to-sensor bias, however, particularly in distributed sensor networks, a probe-specific calibration is suggested.
- The EC-10 sensors operating at a relatively low frequency predicted the VWC within the accuracy provided by manufacturer. While soil moisture content was a dominant factor, the variation in probe response was also significantly affected by

soil temperature and the ionic concentration of wetting solution (hence the EC of the pore water) depending on the solution type. Although we could not distinguish the sensor response to individual solute types, yet the EC-10 probe showed a higher sensitivity to the change in NO_3 concentration in the wetting solution than to the change in Cl concentration within the water content and salinity ranges tested. The results of our study suggest that there is a potential to use EC-10 probes for estimating changes in NO_3 concentrations in pore water when the actual soil moisture content is known and the variation in soil salinity is mostly attributed to the change in soil NO_3 concentration. This is consistent with the results of Carr et al. (2007), who pointed out the usefulness of the EC-10 probes for determining soil salinity over EC-5 probes. Moreover, our analysis indicated the importance of temperature adjustment (even during minor thermal variations) to estimate relatively small changes in pore water ion concentration.

This study supports the proposed new concept that capitalizes on the drawbacks of low-frequency dielectric measurement, particularly its susceptibility to conductive losses. Unlike other studies that tried to eliminate unwanted biases in probe readings through calibration, our study demonstrated the feasibility of a completely novel approach to extract useful information by using current technology—specifically combining soil dielectric measurements at multiple frequencies to estimate several field parameters of interest. While high-frequency dielectric measurement is a good predictor of soil water content, low-frequency measurements can be used to estimate several soil solution properties, such as salinity (at very low frequency) and the concentration of individual ion species (at ion-specific characteristic frequencies). Additional studies are required, however, to quantify the nature of the capacitance sensor response to changes in the pore water ion concentration and its interaction with other field variables such as soil moisture, temperature, soil texture, and pH at different operating frequencies. Further laboratory experiments using higher concentration solutions of various ions across a large frequency spectrum can provide valuable information for development of a multifrequency dielectric probe capable of measuring several field parameters of interest in the same sensing volume.

Acknowledgements

This research was supported in part by the National Science Foundation under Grants NSF-ECCS-0601570 and NSF-ECCS-0926029. We acknowledge Loren Shiers for assistance with the solution preparation and Adam Pintar for providing statistical consultation. We are also grateful to Sally Logsdon for sharing her equipment and for constructive comments on an earlier version of the manuscript.

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CHAPTER 3. ESTIMATION OF SOLUTION NITRATE-NITROGEN CONCENTRATION FROM SPECTRAL RESPONSE USING PLS REGRESSION METHOD

A paper to be submitted to *Transactions of ASABE*

G. Chighladze, A. Kaleita, S. Birrell

Abstract

Dielectric measurements are widely used in agricultural and environmental monitoring to estimate soil moisture content, which is affected by conductive nature of the soil aqueous phase depending on measurement frequency, temperature, ion type, and concentrations present in the solution. Hence analyzing the dielectric footprint of electrolytic solutions at multiple frequencies can yield important information which can be used in dielectric sensing to evaluate ionic concentration of a soil solution.

The goal of the study was to investigate the potential to estimate nitrate-nitrogen (NO_3-N) concentration in aqueous solutions from the dielectric spectra measurement using a multivariate chemometric technique. Thirty solutions with different concentration of potassium nitrate (KNO_3) and potassium chloride (KCl) were studied in a laboratory condition at 20°C. Partial least squares (PLS) regression method was used to relate the NO_3-N concentration of the solutions with the real and imaginary parts of permittivity measured at 48 frequencies ranging from 200 Hz to 13 MHz. The results revealed that

precise estimation of the NO_3-N concentration (RMSE = 9 ppm) was possible using the dielectric loss data if the concentration of KNO_3 in the solutions was greater than the concentration of KCl. When the solutions with very high concentration of KCl were added to the rest of the data the PLS model was able to explain only 75% of the NO_3-N variation (RMSE = 34 ppm).

Introduction

Widespread application of fertilizers and pesticides in modern agricultural systems has lead to elevated environmental and health problems, which stretch beyond agricultural fields (NRCS, 1997; Gupta et al., 2000; Ward et al., 2005). In order to increase production nitrogen-reach fertilizers have been intensively applied to the fields, where the unused portion of nitrogen leaches out in a form of nitrate (NO_3) to ground and surface water bodies (Addiscott, 2005). Current developments in precision agriculture can allow farmers to apply fertilizers with high precision in space and time, however technologies for *in situ* measurement of existing levels of nutrients in soil or water is lagging behind. The conventional method for soil sampling is destructive and requires laboratory analysis of a soil solution, which can be time consuming and expensive (Carter and Gregorich, 2007). Hence, there is a need for reliable technology that can allow *in situ* monitoring of surface and soil water.

During the last several decade, sensors that measure the dielectric response of a medium have been widely adopted to characterize the medium’s physical or chemical properties. Bulk soil permittivity measurement has been used in environmental monitoring to estimate volumetric water content (VWC) and soil salinity (Andrade-

Sanchez et al., 2004; Robinson et al., 2008). Furthermore, several studies used time domain reflectometry (TDR) techniques to estimate change in nitrate-nitrogen (NO_3-N) concentration in pore water both in field and laboratory experiments (Das et al., 1999; Payeri at al., 2006; Krishnapillai and Sri Ranjan, 2009). They found a good agreement between NO_3-N concentration and the bulk electrical conductivity (EC) sensed by TDR probe after the proper calibration. It should be emphasized that change in the solution conductivity used in these experiments was achieved solely by change of a single NO_3-N containing salt content in the applied water. But the *in situ* application of this technique is hampered by a high cost of a TDR system and unsuitability for a field deployment. Additional drawbacks associated with TDR method is an accuracy of measurement, which is influenced by the coaxial cable and probe lengths, contact between the probe and soil, and waveform analysis applied to the collected data (Robinson et al., 2003).

Capacitance type probes that operate at fixed frequencies are a relatively cheap and easy-to-deploy alternative. They have gained increasing popularity in recent years as a reliable tool for soil moisture monitoring (Bogena et al., 2007; Paige and Keefer, 2008; Saito et al., 2008). Although most of the off-the-shelf capacitance type probes measure only apparent permittivity of the medium limiting their application for quantitative estimation of ionic concentration of the soil solution, a recent qualitative study of two capacitance type probes operating at fixed frequencies of 5 and 70 MHz demonstrated sensitivity to the change in soil solution NO_3 concentration for the sensor operating at a lower frequency (Chighladze et al., 2010). It should be noticed that this study was limited to only two frequencies and the dielectric measurement was integrating both capacitive and conductive part of the complex permittivity, which diminished nitrate-induced response. Hence, scrutinizing the complex (rather than integrated) dielectric response of solutions at multiple frequencies can provide more meaningful information that could be used to predict ionic concentration and composition of soil solutions. This new feature can add an enormous value to capacitance type soil probes, particularly in agricultural applications where *in situ* measurement of NO_3 remains an unsolved problem. It should be noted that there are few commercially available capacitance type sensors (like Theta probe) that measure both real (capacitive) and imaginary (conductive) party of the complex permittivity separately.

Dielectric spectroscopy is a powerful tool for investigating molecular dynamics in various materials allowing direct correlation of electrochemical and spectroscopic data. Its application varies from assessing simple characteristics of materials to obtaining physiological parameters in medicine (Prodan et al., 2004; Guerra et al., 2006). Different spectra have been used in studies to identify factors that affect the general properties and performance of the electrolytic systems. Most of these studies have been done using very high (>> GHz) frequency ranges to characterize ionic solutions (Behrends et al., 2006; Gulich et al., 2009; Hunger et al., 2009), while fewer experiments have been conducted to study spectral response in the MHz range. Bardos et al. (2005) investigated the frequency dependence of the conductance of several electrolytes contained inside a capillary from 1 kHz to 10 MHz range and found the response to be characteristic of the electrolyte concentration and composition.

Dielectric spectroscopy studies of solutions to estimate nitrate concentration have been conducted on ultraviolet spectra with some success (Karlsson et al., 1995; Dahlen et al., 2000; Tuli et al., 2009). Yet, no attempts have been made to analyze spectroscopic fingerprints of nitrate-containing solutions in the lower frequency range at which the majority of commercially available capacitance type sensors operate (below 100 MHz). Therefore, the goal of this work was to investigate the effect of NO_3-N concentration on the dielectric properties of solution, at frequencies below several MHz, and to evaluate feasibility to estimate NO_3-N concentration from the spectral footprint using a multivariate chemometric method, particularly partial least squares (PLS) analysis. Furthermore, we examined the manner in which dielectric parameters of the solutions behave as a function of ionic concentration and frequency.

PLS Analysis

PLS and other multivariate chemometric methods have been widely used to extract qualitative or quantitative information from different spectroscopy data. This “soft modeling” approach is particularly applicable for developing calibration models using high dimensional, strongly collinear data, like that observed in spectral measurements. These calibration models relate linear combinations of spectral bands to known independent physical variables of interest. Therefore during construction of the model it is recommended to avoid non-linearities in the dependence of the response on the independent variable. An advantage of the PLS method compared to other multivariate methods (such as principal components regression and multiple linear regression) is that it can handle more than one response. Furthermore PLS does not require a priori knowledge of the studied system and develops a calibration model based only on the supplied data. As a result, the generated model is only valid within the experimental domain for which it was constructed and cannot be extrapolated beyond it. Detailed description of the PLS regression method can be found in literature (Geladi and Kowalski, 1986; Varmuza and Filzmoser, 2008).

PLS has been successfully used in different fields of study to analyze the results from electrochemical spectra to, for example: predict a state of charge of a battery (Bundy et al., 1998), control composition of potted minced pork (Chanet et al., 1999), and determine frying oil degradation (Ng et al., 2007). Karlsson et al. (1995) and later Dahlen et al. (2000) used PLS analysis with success to measure nitrate concentration in municipal waste water and ground water, respectively, from UV spectra. Yet, to the best of our knowledge, this statistical tool has not been employed for estimation of aqueous solution NO_3 concentration from impedance spectra.

Materials and Methods

Experimental Setup

Dielectric properties of aqueous electrolyte samples were measured using an HP 4192A LF Impedance Analyzer (Hewlett-Packard, Palo Alto, CA, USA) connected to a 16452A Liquid Dielectric Test Fixture (Agilent Technologies Japan, Ltd., Hyogo, Japan) (Fig. 1). The HP 4162A is capable of measuring the dielectric properties of sample from 5 Hz to 13 MHz, while the operating frequency range for the test fixture is between 100 Hz and 15 MHz. Two electrical parameters, conductance and susceptance, of the aqueous electrolytes were measured at 63 frequencies covering the whole spectra of the impedance analyzer, but only 48 frequencies were used during statistical analysis due to the electrode polarization effect observed below 200 Hz.

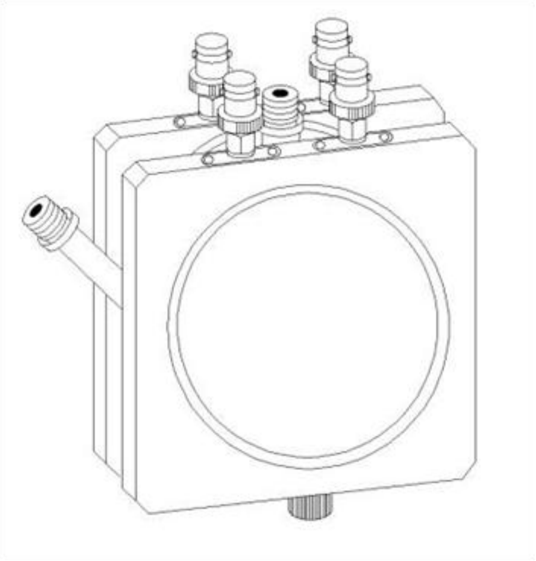

Figure 1. The Agilent 16452A Liquid Dielectric Test Fixture.

Thirty solutions with six different concentrations of potassium nitrate (KNO_3) and five concentrations of potassium chloride (KCl) were tested at constant temperature of 20 ± 1.5°C. Temperature of the samples was controlled using a RTE-5 Refrigerated Bath Circulator (NESLAB Instruments, Inc., Portsmouth, NH). Concentration of NO_3-N was limited to the maximum levels found in groundwater in agricultural ecosystems in the Corn Belt region and was varying in our experiment from 0 to 200 ppm (Balkcom et al., 2003; Killorn, 1990). Concentration of chloride in the solutions varied from 0 to 2000 ppm, with an intention to approximately represent total concentration of other anions found in Iowa waters (Iowa DNR, 2009).

Split-block experimental design was used with three spectral scans of the nitrate treatments, which was blocked by the chloride levels. This experiment was duplicated with a randomized order of NO_3 and Cl concentrations. Between each test, the system was flushed twice with the next solution to remove residual solution from previous test.

Before starting a new block of chloride concentration, the whole system was additionally flushed with distilled water.

Data collection was accomplished via a USB-based data acquisition module, USB-1208LS (Measurement Computing Corp., Norton, MA) interfaced with a personal computer. A program was written in Visual Basic for Application (VBA) language with Microsoft Excel (Microsoft Corp., Redmond, WA) to automate the flushing and data acquisition processes.

The open/short compensation technique was applied to the collected data to remove the measurement error induced by the test fixture (Santamarina et al., 2001). Before calculating dielectric parameters (real and imaginary parts of the complex permittivity) of the solutions a stray capacitance contained in the compensated data was canceled by multiplying it with the correction coefficient, which was calculated according to the liquid dielectric test fixture manual (Agilent 16452A Liquid Test Fixture: Operation and Service Manual, 2000).

Data Analysis

Each solution was scanned 3 times across the whole spectra, hence representing a matrix of impedance measurements. Before performing the statistical analysis, data from these 3 scans were averaged for all solutions, thus reducing the matrices of spectrum into a vector. Partial least squares (PLS) analysis was applied to that mean spectral response using JMP software. PLS models relating NO_3-N concentration to dielectric spectra were developed using the full spectrum of data. One-at-a-time cross validation was carried out to choose the number of extracted factors, a.k.a. latent variables, in order to test the model's performance. The determination of the number of latent variables is crucial, since using only few components in the model can result in omission of relevant information, while using too many will incorporate noise into the model through overfitting the data. The root mean square error of cross validation (RMSE-CV) was used as a measure of model performance.

Results and Discussion

General Behavior of the Solutions

Dielectric properties of the solutions showed little variation of dispersion shape with changes in both NO_3-N and Cl content of the solutions. Figures 2 and 3 demonstrate the influence of solute concentration on the dielectric response of the electrolytes, where the

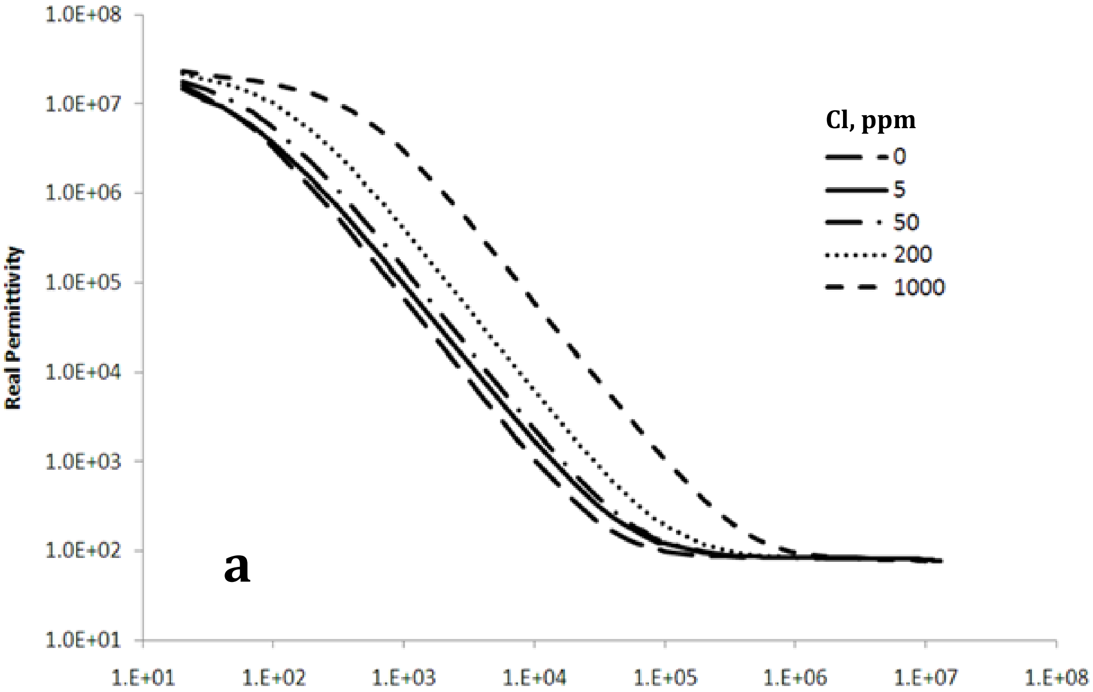

Figure 2. (a) the real permittivity, (b) the imaginary permittivity and (c) the real part of conductivity as a function of frequency for solutions with 50 ppm NO_3-N concentration at 20°C by Cl level.

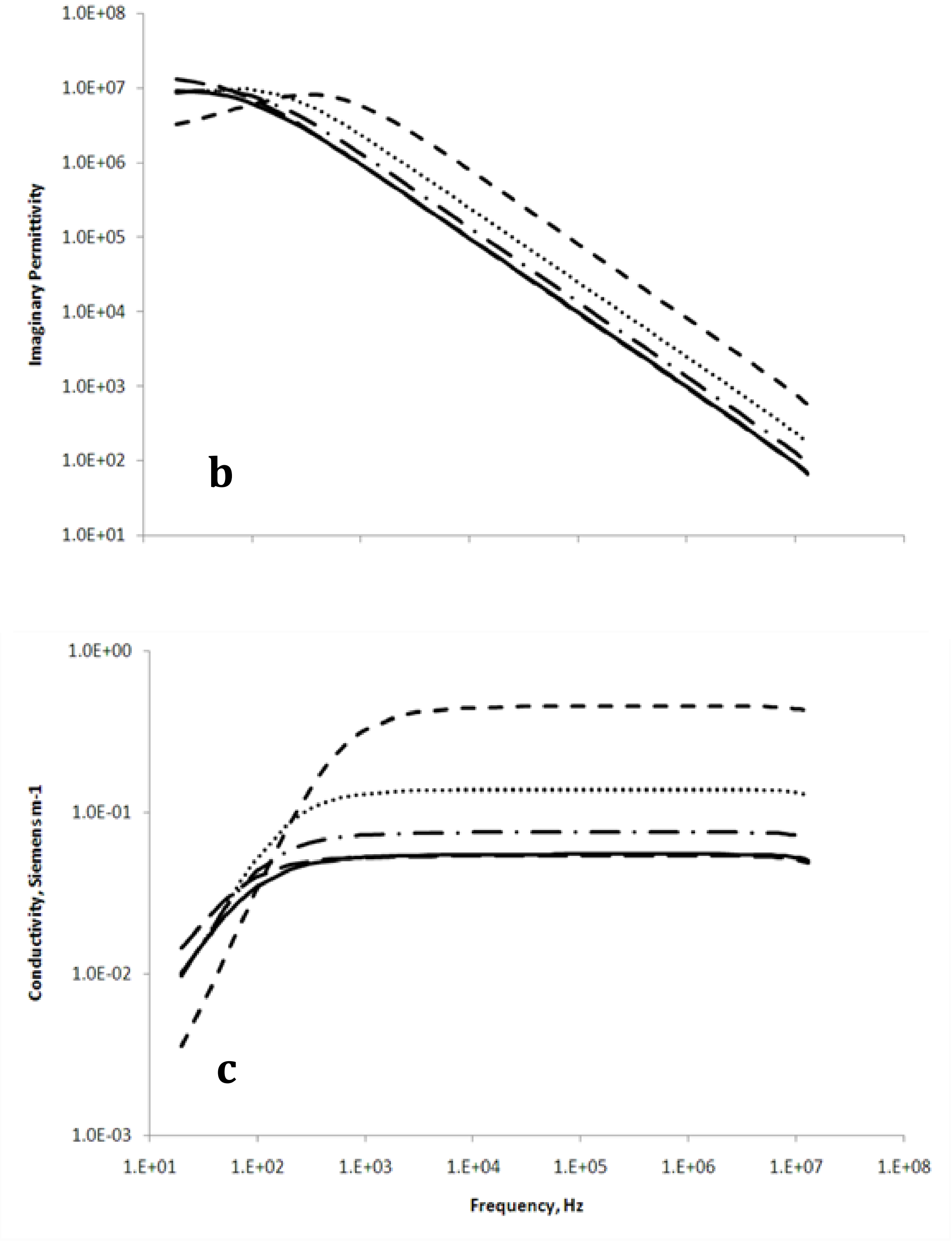

Figure 2. (continued) (a) the real permittivity, (b) the imaginary permittivity and (c) the real part of conductivity as a function of frequency for solutions with 50 ppm NO_3-N concentration at 20°C by Cl level.

real permittivity (a), the imaginary permittivity (b) and the real part of conductivity (c) are plotted as a function of frequency at a temperature of 20°C. Figure 2 shows the effect of change of Cl concentration from 0 to 1000 ppm on the spectral measurement for solutions with 50 ppm NO_3-N, while Figure 3 shows the similar effect of NO_3-N concentration ranging from 0 to 200 ppm for solutions with 50 ppm Cl. In both cases the dielectric constant of the solutions increased with increasing solute concentration below MHz frequency merging into a plateau at the lowest frequency corresponding to a static dielectric constant.

The imaginary part of permittivity of the solutions also showed an increase in magnitude with increasing concentration in the kHz range for both anions (Fig. 2b and 3b). In this frequency range the dielectric loss was inversely proportional to the frequency having a slope of a negative 1 on the double-logarithmic scale, which indicates a constant real conductivity. Figures 2c and 3c reveal the corresponding frequency-independent plateaus of the direct current (DC) conductivity with clear separations between responses at different solute concentration levels. The DC conductivity increased by a factor of 8 when Cl concentration was raised from 0 to 1000 ppm compared to a 9-fold increase associated with the change of NO_3-N concentration from 0 to 200 ppm.

In low frequencies (<200 Hz) the slope of the dielectric loss deviates from the inverse frequency relationship and the real part of conductivity is no longer constant starting decreasing at higher frequencies with increasing ionic concentration. This dielectric dispersion was related to the electrode polarization phenomenon, which occurs due to blocking of charges at the electrode interface (Klein and Santamarina, 1996). Electrode polarization is one of the most common unwanted effects in low frequency dielectric

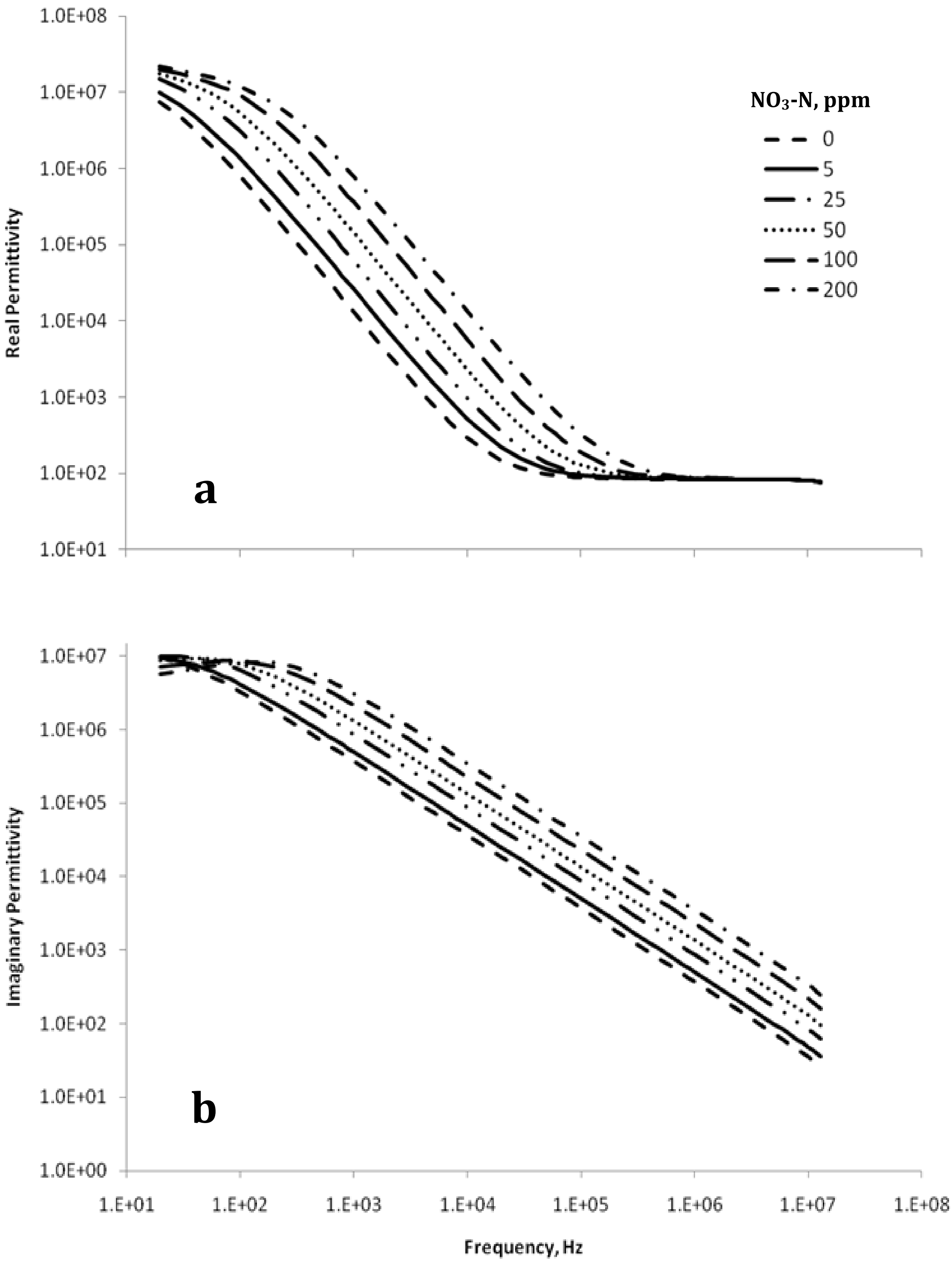

Figure 3. (a) the real permittivity, (b) the imaginary permittivity and (c) the real part of conductivity as a function of frequency for solutions with 50 ppm Cl concentration at 20°C by NO_3-N level.

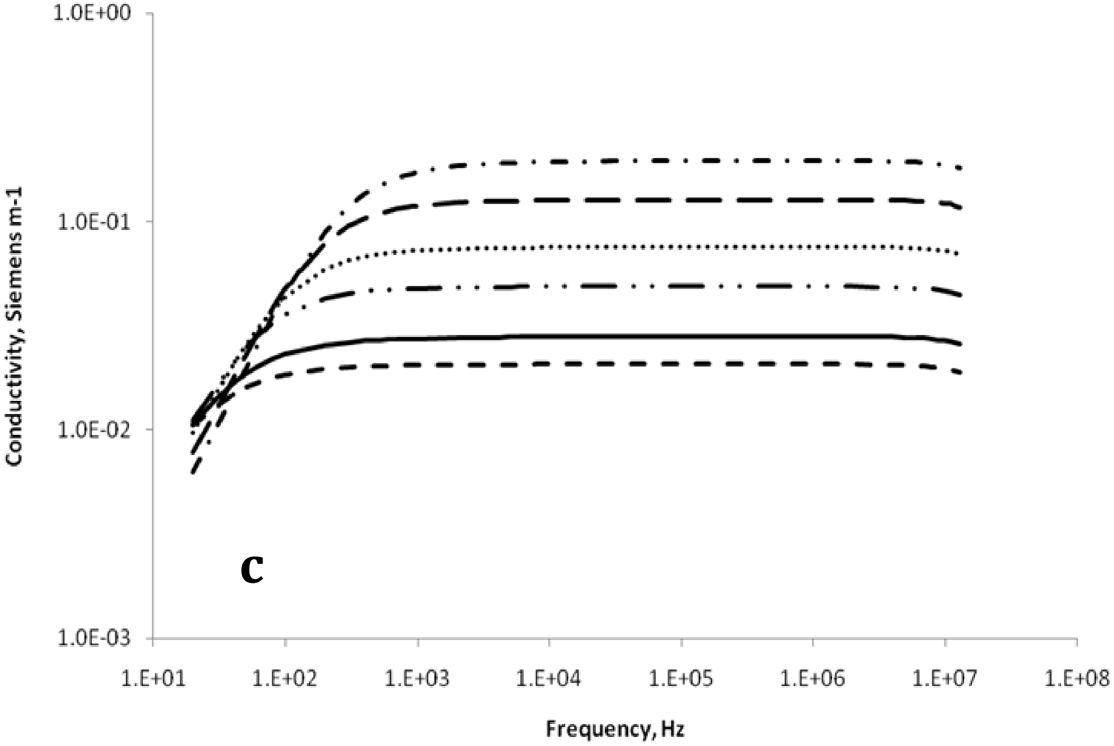

Figure 3. (continued) (a) the real permittivity, (b) the imaginary permittivity and (c) the real part of conductivity as a function of frequency for solutions with 50 ppm Cl concentration at 20°C by NO_3-N level.

spectroscopy. Based on the results the limiting lower frequency for the system, which is the minimum frequency at which electrode polarization does not significantly affect the permittivity measurements, was determined to be 200 Hz. Consequently, statistical analyses were based only on the measurements made at frequencies ≥ 200 Hz.

Little difference in magnitude of the spectral measurement was observed between identical solutions from one replicate to another due to a slight temperature variation (the temperature was determined and stabilized with 2°C precision) causing a little drift of the curves along frequency axis, but the shape and interrelation between the measurements were the same throughout all replicates. Hence the spectral response from the duplicate looked identical to the spectra in Fig. 2 and 3 for all solutions.

DC Conductivity Dependence upon Temperature and Solute Concentration

In order to better understand concentration dependences of the dielectric response for different ion species we examined changes in DC conductivity for all solutions under investigation. Figures 4 and 5 illustrate the dependences of the DC conductivity on NO_3-N and Cl concentrations, respectively. The frequency-independent conductivity of the solutions increased with increasing NO_3-N concentration in a similar manner at all Cl levels, which indicated that an effect of NO_3-N concentration on the DC conductivity remained relatively constant over the Cl concentration investigated. Analogically, Fig. 5 shows the increase of the DC conductivity with increasing Cl content at different NO_3-N levels.

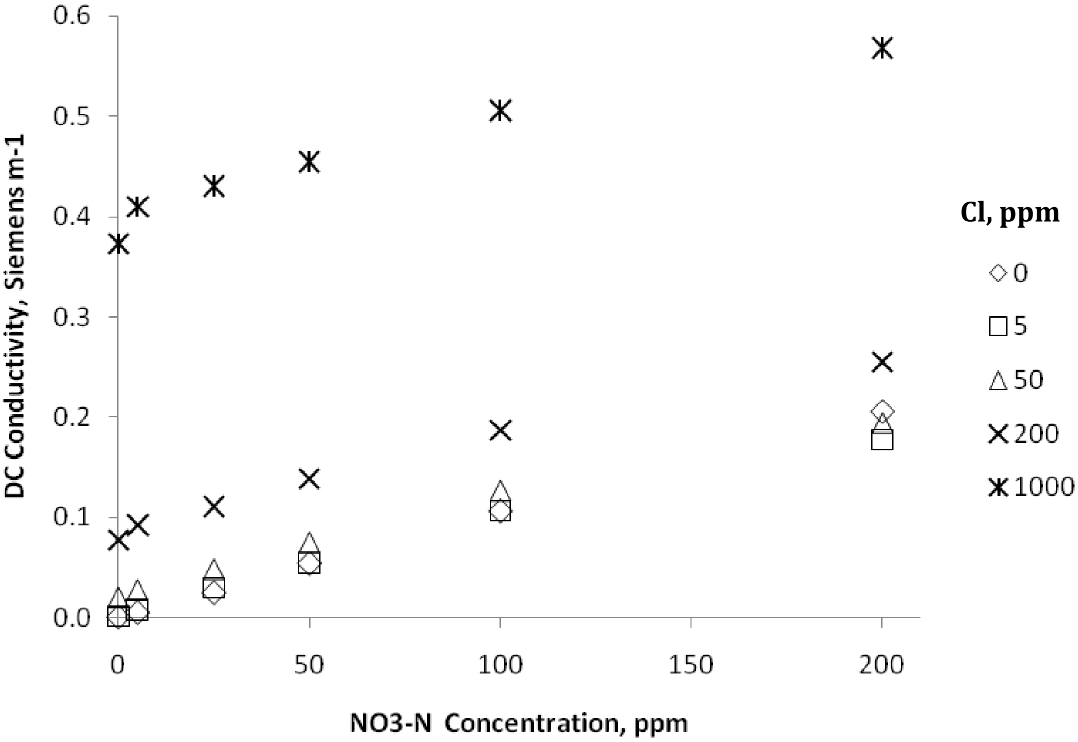

Figure 4. NO_3-N concentration dependence of the DC conductivity for solutions across different Cl levels.

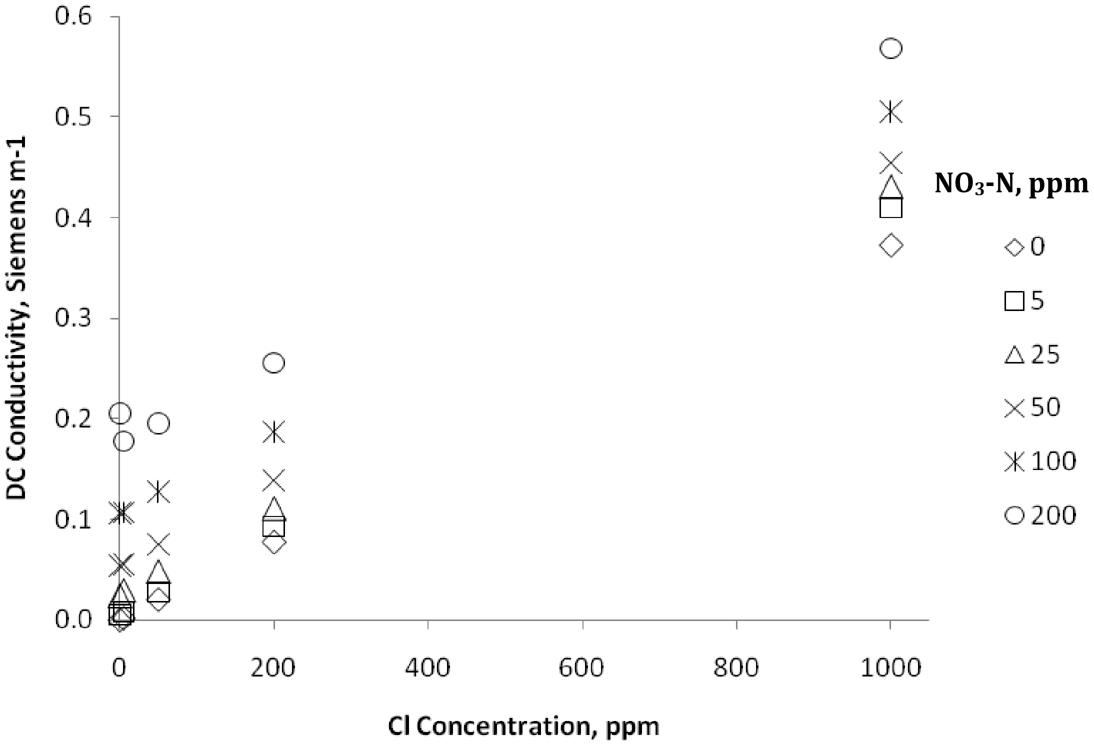

Figure 5. Cl concentration dependence of the DC conductivity for solutions across different NO_3-N levels.

PLS Analysis

In this work, the mean real and imaginary permittivity data (generated by the averaging of the three scans) obtained at a temperature of 20°C was used to evaluate the accuracy of the PLS method for estimating NO_3-N concentration of the tested electrolyte solutions. It is worth mentioning that we did not present the results of the PLS regression analysis based on the real conductivity data since they were identical to the ones constructed using the loss factor. In order to improve performance of the method the data were centered and scaled so that both independent and dependent variables had means of 0 and standard deviations of 1. As a result RSME-CV had no units and should not be interpreted in terms of NO_3-N concentration. Also, it should be noted that to estimate NO_3-N concentration in the electrolytic solutions no information about Cl content was used during construction of the models. Hence, the performance of the PLS regression method to estimate NO_3-N concentration was solely related to the measured dielectric spectra.

Outcomes (number of latent variable, RMSE of cross validation, percentage of variation of NO_3-N concentration explained by the model) of the PLS regression analysis

Table 1. Results obtained by PLS regression analysis

Model Description	**# LV***	**RMSE-CV†**	**% of NO_3-N Variation**
based on Imaginary Permittivity (ε'')			
global (using all data)	6	0.595	75.55
0 ppm of Cl	2	0.017	99.98
5 ppm of Cl	2	0.059	99.84
50 ppm of Cl	2	0.075	99.76
200 ppm of Cl	2	0.223	97.72
1000 ppm of Cl	1	0.302	94.12
based on Real Permittivity (ε')			
global (using all data)	5	0.713	65.44
0 ppm of Cl	7	0.124	99.93
5 ppm of Cl	3	0.103	99.55
50 ppm of Cl	5	0.108	99.93
200 ppm of Cl	5	0.073	99.90
1000 ppm of Cl	2	0.335	94.21

* # LV, number of latent variables
† RMSE-CV, root mean square of error for cross-validation

for different models are summarized in Table 1. In general the models using the dielectric loss performed better (having lower RMSE-CV) than the models based on the dielectric constant. Number of latent variables determined through cross validation process for the models based on the imaginary part of permittivity was smaller (except for the global model) than for the identical models constructed using the real part of permittivity. It should be emphasized that normally it is regarded as a good sign if the number of latent variables selected by cross-validation process is close or equal to the number of major factors, two in our case (concentration of KNO_3 and KCl), influencing the variation pattern in the spectral response.

Figure 6 shows the results of the actual vs. estimated concentration when the imaginary permittivity spectra from all solutions were used to estimate NO_3-N level.

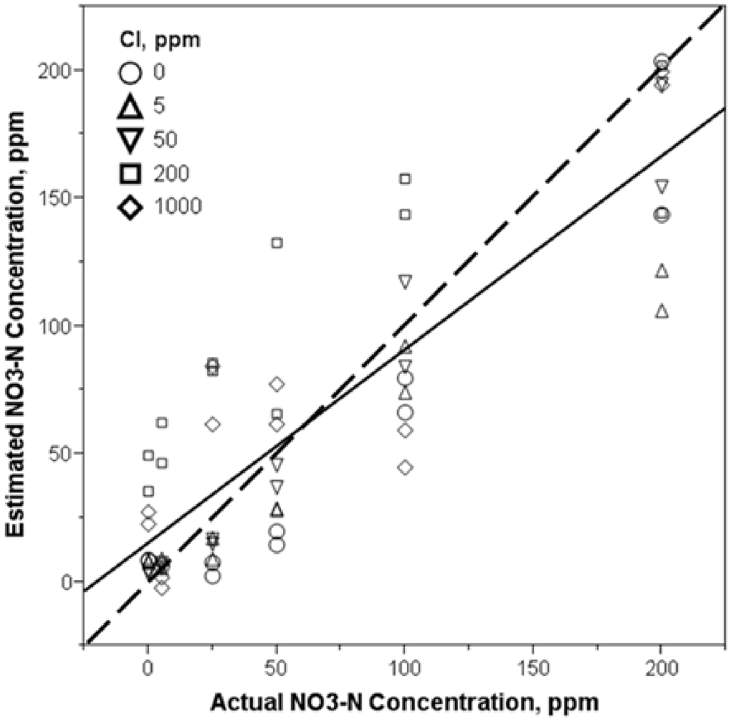

Figure 6. Actual vs. estimated NO_3-N concentration based on the imaginary part of permittivity of all solutions (R^2 = 0.76).

The solid line is a linear regression model fitted to the estimated data, and the dashed line is a 1:1 fit corresponding to the ideal fit. The RMSE between measured and estimated values was found to be 34 ppm. It can be easily seen that the PLS model underestimates NO_3-N concentration at the high end and overestimates it at the low end. One of the reasons for such a behavior can be related to the fact that concentrations of NO_3-N are unequally distributed that hampers calibration capabilities of PLS. Most of the data are located at the lower concentrations, while samples with the highest NO_3-N content are somewhat isolated resulting in a particularly poor estimation at 200 ppm (majority of estimated NO_3-N values at 200 ppm are below the 1:1 line). Similar results were obtained when a PLS model was developed using the imaginary permittivity data with NO_3-N concentration below 200 ppm (Fig. 7). Like in the previous case, most of the data were

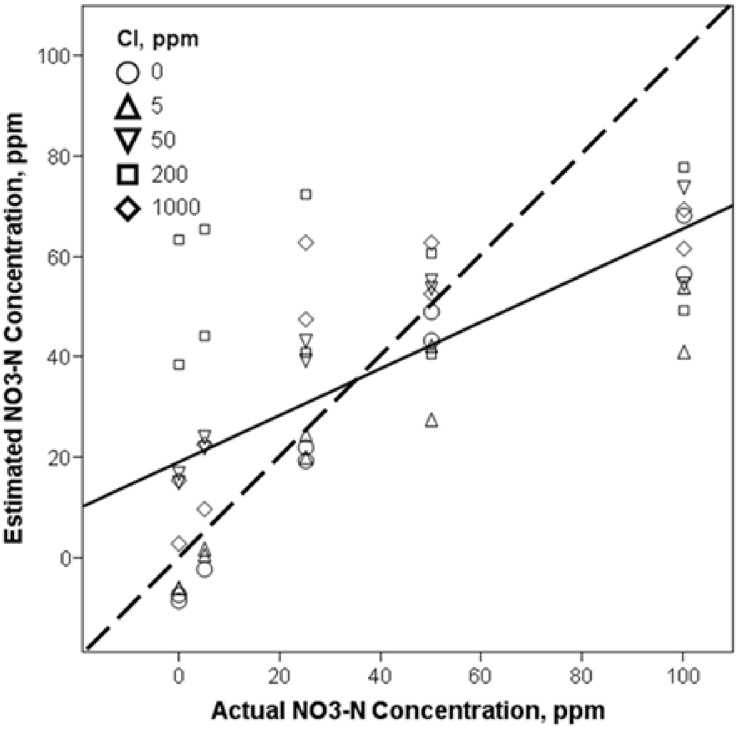

Figure 7. Actual vs. estimated NO_3-N concentration based on the imaginary part of permittivity using data with NO_3-N concentration below 200 ppm (R^2 = 0.47).

located at the lower end, and the highest NO_3-N concentration (100 ppm) used in this model was twice that of the next lowest concentration (50 ppm). As a result, the model again underestimated NO_3-N concentration at the high end (100 ppm), thus supporting our assumption. When a similar model was built using data with approximately uniformly distributed NO_3-N concentrations (0, 50, 100 and 200 ppm of NO_3-N), performance of the PLS regression was slightly improved, particularly the estimations at high NO_3-N levels. Thus, in the future, for accurate calibration of PLS models it is important to uniformly cover the range of interest of a studied variable.

It was also noted that when Cl concentration was 200 ppm the PLS models were giving the poorest estimation of NO_3-N concentration (Fig. 6). This deterioration of the performance was not solely related to the high Cl concentration, since we did not observe poorer or the same behavior with the solutions containing 1000 ppm of Cl. One of the possible sources of this noise could be related to the variation in solution temperature during the spectroscopic measurement. Examining the actual temperatures by Cl concentration revealed some fluctuations (Fig. 8). The average temperature was found to be the lowest when the measurements were made on the solutions with Cl concentration of 200 ppm, which we believe resulted in an increased error in NO_3-N estimation for these solutions. Low average temperature was also recorded during the dielectric measurement on the solutions with Cl concentration of 5 ppm, but due to the relatively low ionic concentration its effect was supposedly smaller and, hence, did not manifest in the actual vs. estimated concentration plots.

Comparison of the developed PLS models relating dielectric spectra to NO_3-N concentration showed substantial improvements in cross validation for models developed

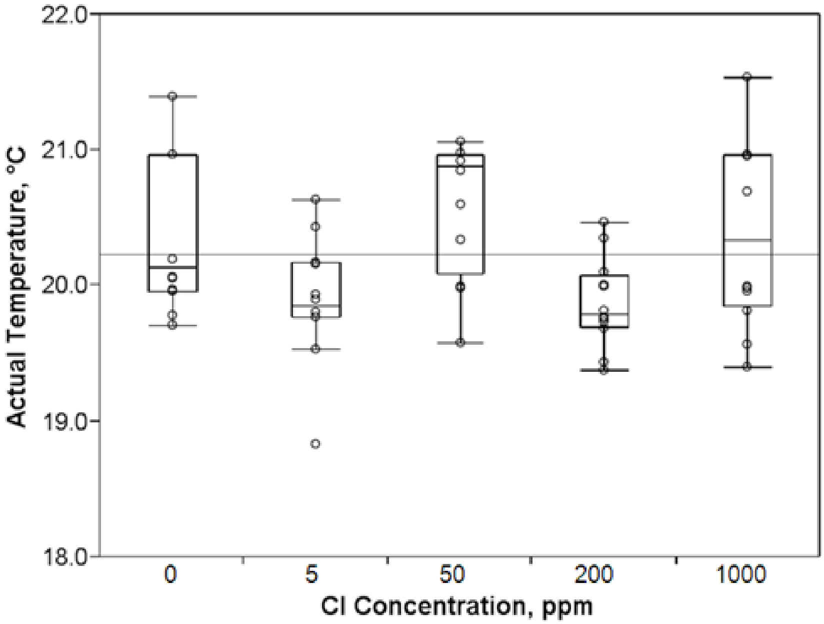

Figure 8. Actual temperature variation during the spectroscopic measurement for the solutions with different concentration of Cl.

for the solutions with fixed Cl concentrations compared to those developed across multiple Cl concentrations (Table 1). R^2 of the former models ranged from 0.93 to 0.99. It is to be emphasized that the models developed for the solutions with lower Cl concentration performed slightly better than the ones with higher Cl concentration. This improvement was not surprising, since at fixed Cl levels change in EC was linearly related to KNO_3 (hence to NO_3-N) concentration, which enhanced the PLS analysis's ability to recognize major variation patterns in the measured spectra. The slight decrease in the models' performance with increasing Cl content could be related to noises created by changes in the dynamical processes in the solutions (e.g., change in ion mobility, or forming ion-pairs with increasing ionic concentration). This could introduce some bias in the linearity of the frequency-response data resulting in observed weakening of the model's calibration capability.

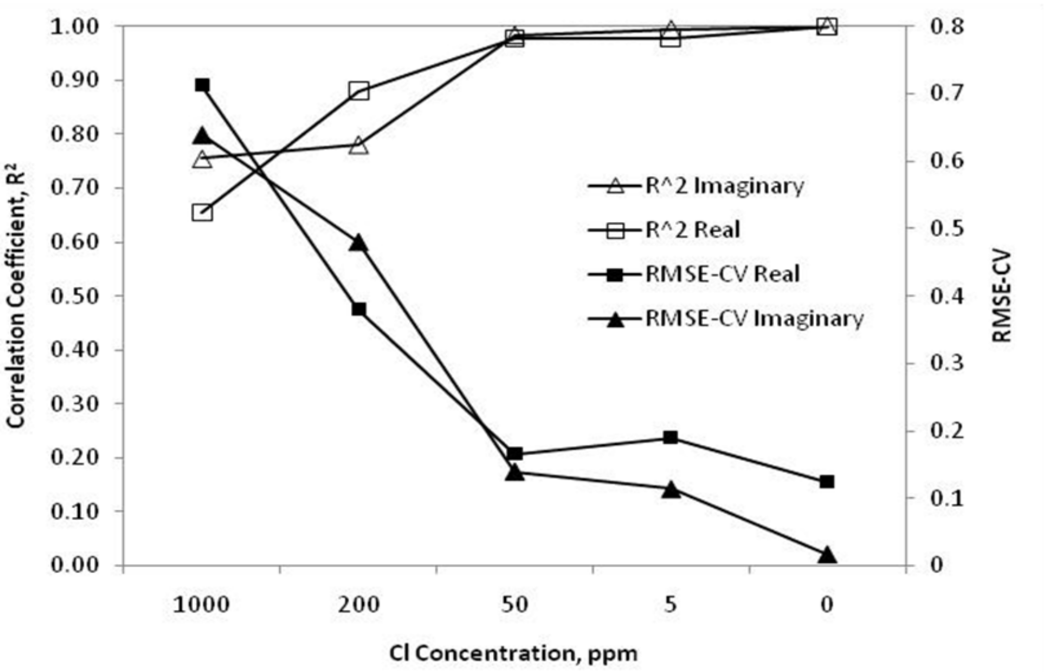

Figure 9. Dependence of RMSE-CV and R^2 of PLS models developed based on the real and imaginary parts of permittivity on Cl concentration in the solutions.

Dependence of the model performance on Cl concentration is presented in Fig. 9. The model corresponding to Cl concentration of 1000 ppm used the whole data set, while each subsequent model was developed by removing the data corresponding to the samples containing higher Cl concentration, for example the third model corresponding to Cl concentration of 50 ppm was constructed using data without solutions containing 1000 and 200 ppm Cl. Again, models constructed using the real and imaginary part of permittivity performed similarly, with the models employing the loss factor showing a little advantage. This minor superiority of the models using the loss factor is related to the fact that ionic concentration of the solutions primarily manifests through the imaginary part of permittivity due to increased EC effect at the tested frequency range. In both cases with decrease of the Cl concentration accuracy of the estimation was significantly

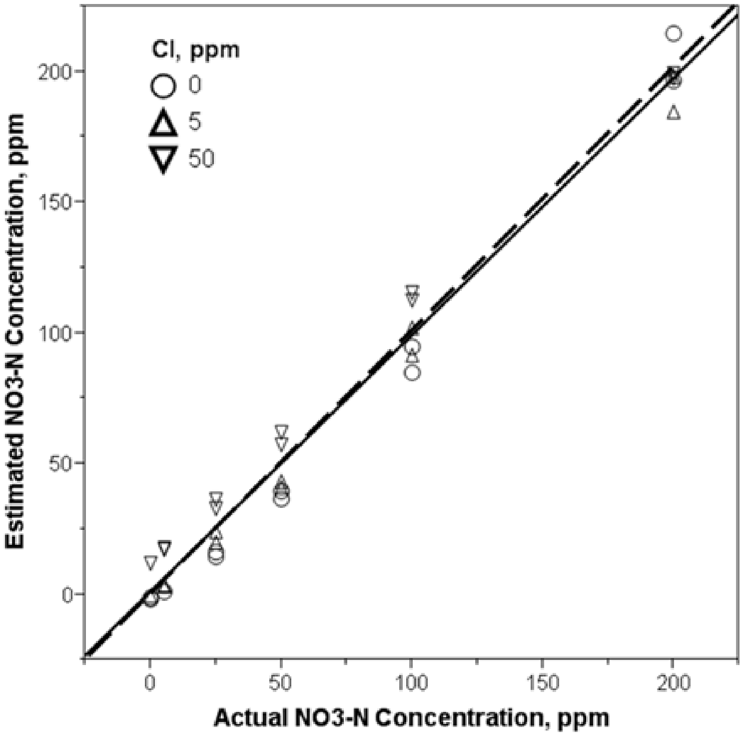

Figure 10. Actual vs. estimated NO_3-N concentration based on the imaginary part of permittivity after removing solutions with the highest Cl concentration from the data (R^2 = 0.98, RMSE = 9 ppm).

improved. The results of the actual vs. estimated NO_3-N concentration when the imaginary permittivity spectra of the solutions with Cl concentration of 50 ppm and less were used is shown in Fig. 10. Eliminating of the samples with high Cl concentration helped to reduce the noise introduced by Cl variation. Consequently, trends in the frequency-response data was mainly associated with changes in NO_3-N concentration, which help the PLS model to detect spectral pattern more clearly.

As noted earlier, the PLS model is constructed using a linear combination of the PLS components, which limits its calibration capabilities for non-linearly related data. Therefore it is always recommended to try to avoid a possible non-linearity by modifying both the response and the independent variable with different functions. The following functions were used for transformation of the dielectric spectra and the NO_3-N concentration: f_i^2, $1/f_i$, $1/\sqrt{f_i}$, $1/f^2$, $ln(f_i)$. None of these functions improved the performance of the PLS models; although the treatment of the dielectric spectra with a square function gave similar results but did not enhance them. These results indicated that the relationship between spectral bands and ionic concentration is mainly linear within the concentration range and frequencies tested, hence applying the PLS analysis to unmodified data was reasonable.

In addition to the magnitude of the dielectric spectra, derivatives of the measurements were used to build the PLS regression models for estimation of NO_3-N concentration. The derivatives at each frequency (except of the first and the last ones) were obtained as a slope of the tangent line of the log-normal and the log-log graphs. The main reason for analyzing the derivatives was to obtain information such as an interrelation between the change of the magnitude of the dielectric response and the value of the corresponding frequency into the PLS model construction. Again, none of the global models improved NO_3-N estimation, but when the solutions containing 1000 ppm of Cl were removed from the data the PLS models constructed based on the log-normal derivatives performed slightly better than the models based on the magnitude of the dielectric spectra. The percentages of variation of NO_3-N captured by the models were 88.5% and 79.7% for the real and imaginary permittivity data, respectively. This indicated that there was additional information in the dispersion shape of the spectral response that the PLS regression due to its nature (PLS is indifferent to actual values of the measurement frequency) could not incorporate into analysis. Hence other multivariate chemometric techniques (such as, the neural networks) could be of more use for estimation of aqueous NO_3-N concentration.

Conclusions

In the present paper we demonstrated a use of a multivariate chemometric technique to estimate NO_3-N concentration in the electrolytic solutions from the dielectric spectra measurement in laboratory conditions. A cross-validation procedure was used to improve the performance of the PLS regression models relating the real and imaginary parts of permittivity to NO_3-N concentration. The results of the analysis showed that it was possible without a priori knowledge of the system to estimate NO_3-N content with good accuracy ($R^2 = 0.98$, RMSE = 9 ppm) when NO_3 was a dominant anion in the electrolytic solutions. The PLS models developed for the solutions with fixed Cl concentration were capable of capturing from 94 to 99 percent of the NO_3-N variation with decreasing calibration capabilities as the level of the "background" anion (Cl) increased. The global model that incorporated all solutions was able to estimate NO_3-N concentration with less accuracy having the lowest RMSE of 34 ppm when the imaginary permittivity was used. This can be sufficient for certain applications where some error is tolerable.

Based on the results, it can be concluded that the PLS regression method coupled with the dielectric spectral measurement at frequencies below several MHz can be used for estimation of NO_3-N concentration in electrolytic solutions. The advantages of the present statistical tool are that (i) any number or type of additional variables, such as temperature or concentration of other ions, can be introduced into the model without problem, and (ii) new experimental data can be easily incorporated into the existing data enabling to update the system. But one should be aware that PLS analysis does not provide any specific chemical information about the system and prediction is mostly limited to the experimental domain. Therefore before practical use of this statistical tool further work is needed that should include actual solutions from agricultural environment (samples obtained from drainage water or solutions extracted from soil cores) with larger range and number of NO_3-N concentration.

Acknowledgements

The research was supported in part by the National Science Foundation under the grants NSF-ECCS-0601570, and NSF-ECCS-0926029. We are grateful to Loren Shiers for his assistance with the solution preparation. We also want to acknowledge Alexandra Olivares and Jonuthan Dimitriou for their help in conducting laboratory experiments.

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CHAPTER 4. ESTIMATION OF NITRATE-NITROGEN CONCENTRATION IN SOIL SOLUTION FROM DIELECTRIC SPECTRA USING PLS ANALYSIS

A paper to be submitted to *the Soil Science Society of America Journal*

G. Chighladze, A. Kaleita, S. Birrell, S. Logsdon

Abstract

Fast and reliable methods for *in situ* monitoring of soil nitrate-nitrogen (NO_3-N) concentration are vital for reducing NO_3-N losses to ground and surface waters from agricultural systems. While several studies have been done to indirectly estimate NO_3-N concentration from time domain spectra, no research has been conducted using a frequency domain technique. Hence, the goal of this laboratory study was to estimate the change in NO_3-N concentration from frequency-response data obtained in a frequency range of 5 Hz to 13 MHz. Dielectric spectra of soil samples wetted to five different volumetric water content (VWC) with 24 solutions containing different concentration of potassium nitrate ($K\ NO_3$) and potassium chloride (KCl) were analyzed using partial least squares (PLS) regression method. The global models that incorporated the whole data estimated the VWC with R^2 value of 0.99, but could not estimate the change in applied NO_3-N concentration with sufficient accuracy. In general, the models based on the imaginary part of the permittivity performed better than those based on the real part or both the real and imaginary parts of permittivity, particularly in estimating the NO_3-N

concentration. Capabilities of the PLS models to estimate NO_3-N concentration were improved with elimination of the data obtained at low VWC level and high Cl content. As a result, the root means square error (RMSE) for NO_3-N was reduced from 57 mg L^{-1} to 28 mg L^{-1}. The best results were obtained when the PLS models were constructed at fixed VWC levels using the data without high Cl concentration. The performances of these models were improving with increasing VWC level, reaching the lowest RMSE of 18 mg L^{-1} at VWC of 30 m^3 m^{-3}.

Introduction

Currently, nitrogen-rich fertilizers are uniformly applied to agricultural fields in most of the Mid West often resulting in over- and underapplication of nitrogen (N) in various parts of the field due to the spatio-temporal variation of the crop N-demand. Unused N can leach from the fields to ground and surface water mostly in the form of nitrate (NO_3) causing environmental and health problems stretching beyond the original agricultural fields (NRCS, 1997; Gupta et al., 2000; Ward et al., 2005). Although precise application of N is attainable through variable-rate technology, a great challenge facing its widespread utilization is a lack of a robust and fast measurement system for real time monitoring of NO_3 dynamics. *In situ* monitoring of NO_3-N concentration can help to optimize application of nitrogen-rich fertilizers, reduce risk of NO_3-N leaching to water bodies and evaluate efficiency of best management practices targeted on improvement N uptake by plants during the growing season. Traditional methods for measuring soil properties are accurate, but at the same time they are labor intensive, time consuming, expensive and destructive, which limits their application in real-time *in situ* monitoring for large areas.

In recent years several methods have been developed and tested for indirect measurement of NO_3-N concentration. All these methods were using electrical properties of a medium measured by different equipment. Ultraviolet spectroscopy has been used to estimate aqueous NO_3-N concentration (Karlsson et al., 1995; Dahlen et al., 2000, Tuli et al., 2009), however high cost of the measurement system limits its field-scale application. Eigenberg at al. (2002) used the electromagnetic (EM) induction method to detect changes in available soil N near the soil surface resulting from field application of cattle feedlot manure. They found that soil conductivity was a reliable indicator of the soil N dynamics.

The conductive behavior of soils has been also used by other methods, particularly by time domain reflectometry (TDR) technique, to predict pore water NO_3-N concentration (Das et al., 1999; Krishnapillai and Sri Ranjan, 2009). Originally TDR probes were used to estimate the volumetric water content (VWC) of soil by measuring the dielectric constant of the medium (Topp et al., 1980). Dalton et al. (1984) first demonstrated using of the TDR method for simultaneous measurement of soil moisture content and electrical conductivity (EC). Later the probes have been often adapted for continuous monitoring of NO_3-N or other ionic solutes in soil and water both in laboratory and field experiments. The operational principals and recent advancements in dielectric and EC measurements using TDR were reported by Robinson et al. (2003).

Das et al. (1999) evaluated the potential to use TDR to simultaneously estimate volumetric soil water content, soil solution electrical conductivity, and soil NO_3-N concentrations in an irrigated peppermint field using simple models and calibration methods. They compared TDR-estimated NO_3-N concentration with those obtained from direct soil measurements (soil cores and soil solution samples) and found that estimates from all methods were comparable, having similar pattern, magnitude and variance. Payero et al. (2006) also evaluated feasibility of using TDR to monitor changes in NO_3-N concentration in an irrigated agricultural soil and concluded that TDR probes could be used to measure NO_3-N in non-saline soil and water after the proper calibration over a long enough period of time to include the expected variations in VWC, temperature and NO_3-N. But there are several drawbacks associated with the TDR technique: a need for relatively expensive equipment (a voltage pulse generator and a signal analyzer), limited measurement volume, problems with extracting accurate parameters from the received waveforms, difficulties in detecting the reflected signal in saline soils, and measurement dependence on cable and probe length (Robinson et al., 2003).

Capacitance-type probes are an alternative to TDR probes offering inexpensive measurement of soil moisture content. Most of the commercially available probes operate at a single frequency (generally above a few MHz) and measure the apparent dielectric constant of the medium, which can be correlated with VWC using factory-provided calibration models. Different studies have demonstrated that the EC of soil has a negligible effect on the permittivity measurement at frequencies above 50 MHz making capacitance-type sensors insensitive to soil salinity (Campbell, 1990; Kizito et al., 2008), but with decreasing measurement frequency, the effect of soil EC becomes stronger.

Zhang et al. (2004) developed a capacitance-type sensor with a Wenner array configuration capable of making multi-frequency measurements ranging from 1 Hz to 15

MHz, hence covering the conductive part of the permittivity spectra. Later the sensor was modified to extend the frequency range to 100 MHz (Lee et al., 2007; Lee and Zhang, 2007). They successfully established calibration models relating VWC and soil salinity with frequency-response data using a multivariate chemometric analysis, particularly partial least squares (PLS) regression. The results of these laboratory studies demonstrated the potential to measure multiple soil properties by analyzing the patterns of the spectral data using PLS regression method; however no experimental work has been conducted to determine the feasibility of this method for estimating ionic concentration of pore water. Thus, the goal of this study was to establish PLS models for estimating VWC and NO_3-N concentration simultaneous using dielectric spectral data obtained from 5 Hz to 13 MHz range.

Materials and Methods

Soil

The soil used in the laboratory study was collected from a top 0.20 m layer at the Iowa State University Agronomy Research Farm situated in Boone County, Iowa. According to the NRCS soil survey it was mapped as Clarion loam (a fine-loamy, mixed, superactive, mesic Typic Hapludolls). The particle size distribution of a sample was determined using the hydrometer method. The analysis confirmed its textural classification as a loam (29% sand, 47% silt) based on the USDA textural triangle.

The soil was air dried, ground, and sieved to ≤2 mm. The bulk density of the soil was found to be 1.04 g cm^{-3}. All soil samples prepared for the test were packed to this bulk density. An air-dry soil sample was analyzed for soluble salt by Ward Laboratories

(Kearney, NE) using 1:1 soil/water suspension and the soil salinity was determined to be 0.31 dS m^{-1}. Organic matter content was found to be about 4.9%.

Test Fixture

Three identical cylindrical test fixtures were constructed by the D.O.E. Ames Laboratory (Ames, IA). Figure 1 shows a cross-sectional view of the test fixture. Each test fixture consisted of two rear caps, a middle cylindrical part and a central rod. A stainless steel pipe with an inner diameter of 10.31 cm was used to build the rear caps. Cylindrical pieces of Rexolite (dielectric constant of 2.53) with outer diameter of ~10.31 cm were inserted into the both rear cups and attached using four metal screws. BNC and banana connectors protruding from opposite faces of the rear cups were connected to each other through a hole in the Rexolite. The middle part of the fixture was made from the same stainless steel pipe of 7.62 cm height as the rear caps and had grooves for o-rings on both sides to insure a hermetical seal. This part was filled with soil. The central rod was made of the stainless steel rod with outside diameter of 1.91 cm and had special holes on both ends to be connected with banana plugs of the rear caps during assembling. Four threaded rods and wing-nuts were used to hold the final assembly together. The volume of the middle void space when all parts were set up was about 615 cm^3. In order to facilitate homogeneous soil density during the packing the inner side of the middle part was marked at uniform distances dividing its volume into four equal sections of 153.7 cm^3.

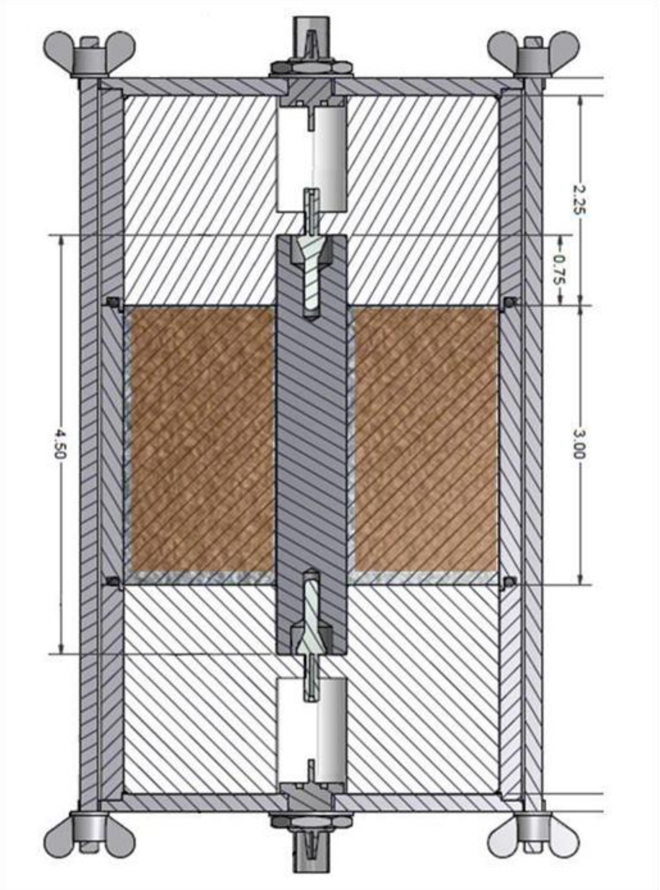

Figure 1. Design of the test fixture (dimensions are in inches).

Solutions

24 solutions with six different concentrations of potassium nitrate (KNO_3) and four different concentrations of potassium chloride (KCl) were prepared at the Iowa State University Water Quality Lab. Concentration of nitrate-nitrogen (NO_3-N) was limited to the maximum levels found in groundwater in agricultural ecosystems in the Corn Belt region and ranged in our experiment from 0 to 200 mg L^{-1}. For comparison, the NO_3-N concentration in Iowa fields normally changes from less than 10 to more than 100 mg L^{-1} during dry years and hardly exceeds 60 mg L^{-1} during wet years (Balkcom et al., 2003; Killorn, 1990). Concentration of chloride in the prepared solutions varied from 0 to 500

mg L^{-1}, with an intention to represent the total concentration of other anions that can be found in soil pore water.

Preparation of the Soil Samples

The air-dried soil, with an initial volumetric water content of 0.034 m^3 m^{-3}, was uniformly wetted with each solution to prepare individual soil samples. Each sample was thoroughly mixed on a tray gradually adding the required amount of specific solution to arrive at the designed volumetric water contents (VWC). A total of five VWC levels were used during the experiment, from 0.10 to 0.30 m^3 m^{-3} in increments of 0.05 m^3 m^{-3}. As a result, 120 samples were prepared, one for each solution and moisture level combination. The actual VWC of each mixture was determined by oven drying subsamples collected from each individual soil sample. One subsample was taken before packing the prepared soil sample and another after taking the spectral measurement.

The test fixture was mounted vertically on a special stand and one of the rear sections was removed to get access to the middle void section while the central rod stayed installed into the second rear section. Then the mixed soil was transferred to the middle part of the text fixture and packed to the uniform bulk density in sections corresponding to the marked intervals. After filling the middle part with soil the rear section was placed back, all sections of the test fixture were tightened down using the threaded rods and wing-nuts, and placed into a temperature chamber for about 9 hours to allow the soil sample to reach equilibrium at 25°C.

Dielectric Measurement System

After reaching equilibrium the test fixture was removed from the chamber and connected to an HP 4192A LF Impedance Analyzer (Hewlett-Packard, Palo Alto, CA, USA) using a 16095A Probe Test Fixture (Agilent Technologies Japan, Ltd., Hyogo, Japan). Dielectric response (conductance and susceptance) of the samples was measured at 63 frequencies ranging from 5 Hz to 13 MHz. Each soil sample was scanned 3 times across the whole spectra and the average value was calculated at each frequency in order to minimize random noise variations from the impedance measurement. Data collection was accomplished via a USB-based data acquisition module, USB-1208LS (Measurement Computing Corp., Norton, MA) interfaced with a personal computer. A program written in Visual Basic for Application (VBA) language with Microsoft Excel (Microsoft Corp., Redmond, WA) was used to automate the data acquisition processes. Open-Short compensation technique was applied to the collected data to remove the measurement error induced by the test fixture (Santamarina et al., 2001).

Data Analysis

All statistical analyses were performed using data obtained by averaging the 3 spectral scans of each soil sample. This helped to reduce the matrix of the complex impedance measurement into a vector. The size of the resulting data set of spectral measurement was 120 (the number of the samples) by 126 (the real and imaginary part of the permittivity measured at 63 frequencies). Average values of the VWC measured before and after the test from the subsamples were used as an actual soil moisture content of the samples to be estimated by constructed models.

In order to build quantitative calibration models partial least squares (PLS) analysis was applied to the averaged spectral response using the JMP software (SAS Institute Inc., Cary, NC, USA). All developed models had access to the complete spectra. The real or the imaginary parts of permittivity, or both together were used to estimate the VWC and NO_3-N concentration of the applied solutions. Information about Cl concentration in the wetting solutions was not included in any model construction. To enhance performance of the PLS method the data were centered and scaled so that both independent and dependent variables have mean of 0 and standard deviation of 1.

One-at-a-time cross validation was used to choose the number of latent variables in the final model. Determination of the optimal number of latent variables is crucial, since using few components in the model can result in omitting relevant information, while using too many will incorporate noise in the model through overfitting the data. The root mean square error of cross validation (RMSE-CV) was used as a measure of model performance (Zhang et al., 2004).

In addition to the PLS method, a linear regression analysis relating the real and imaginary part of permittivity to soil moisture content was performed to evaluate the model's capability for estimating VWC using the soil response at individual frequencies.

Results

Spectral Response

Measured dielectric response showed little variation of shape across all samples tested during the experiment, but large in magnitude with change of VWC. The frequency-dependence of the dielectric constant (a), the loss factor (b) and the real part of conductivity (c) at five different moisture levels for soil samples wetted with the solution containing 25 mg L^{-1} of NO_3 and 50 mg L^{-1} of Cl is shown in Fig. 2. As was expected the real part of permittivity increased with increasing soil water content throughout the whole frequency range, however separation of spectra between VWC levels was not proportional to their moisture values below MHz frequency range (Fig. 2a). Particularly, the real permittivity measurements at 0.10 m^3 m^{-3} were always separated from the spectral responses at other VWC levels. This difference was noticeably decreasing with increasing ionic concentration of the applied solutions.

This kind of behavior at lower frequencies can be explained by two molecular mechanisms: the bound water effect and the cation fixation by clay minerals. In general,

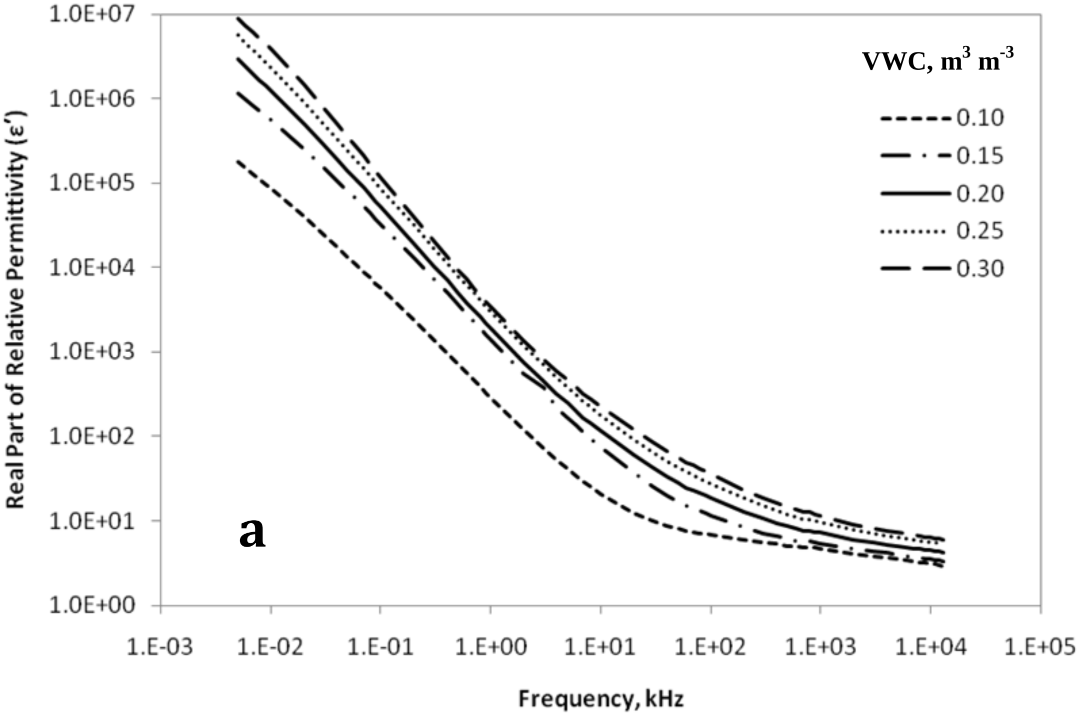

Figure 2. Change of the real (a) and the imaginary (b) parts of permittivity and the real part of conductivity (c) with VWC for soil wetted with the solution containing 25 mg L^{-1} of NO_3 and 50 mg L^{-1} of Cl.

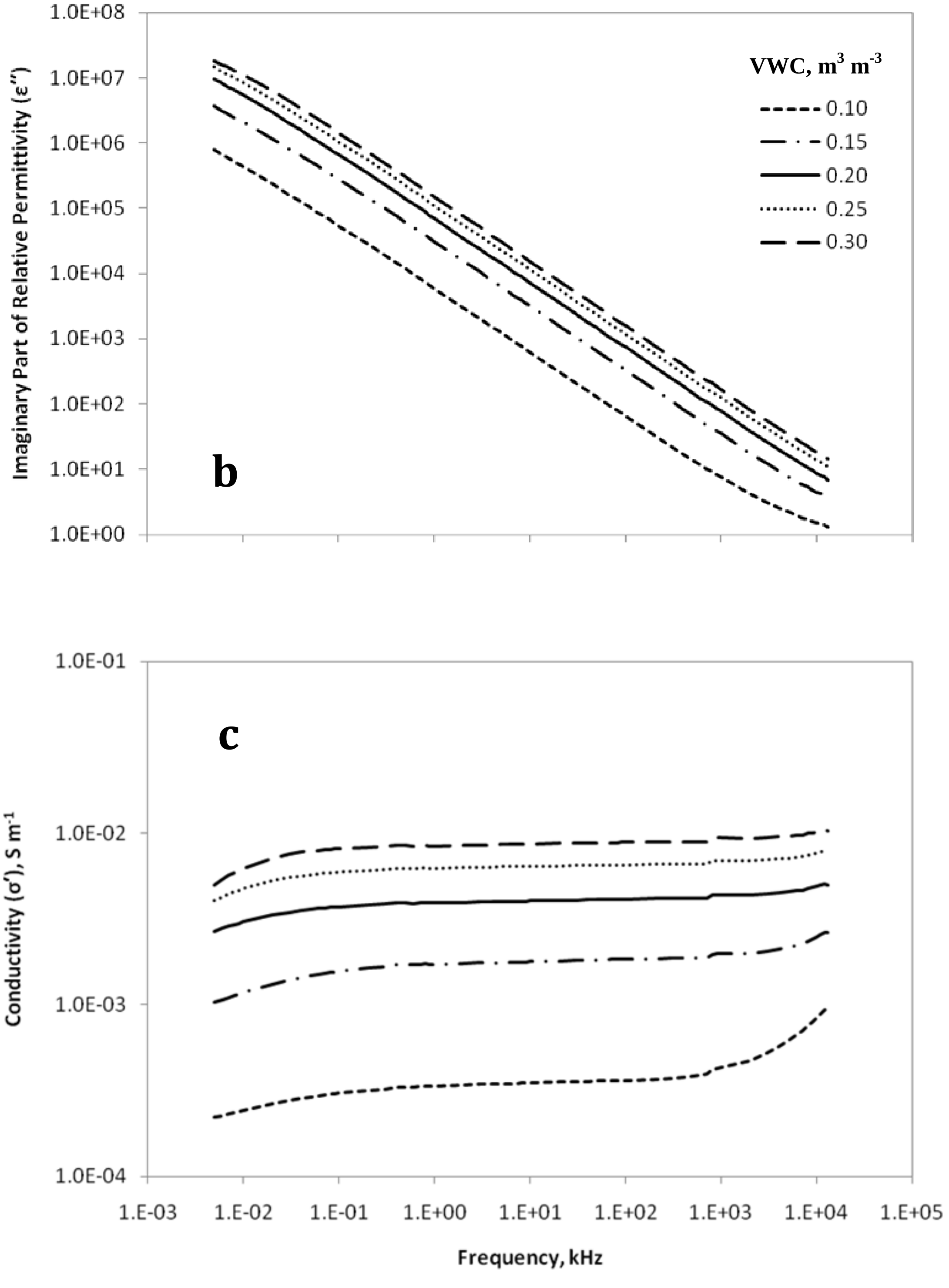

Figure 2. (continued) Change of the real (a) and the imaginary (b) parts of permittivity and the real part of conductivity (c) with VWC for soil wetted with the solution containing 25 mg L^{-1} of NO_3 and 50 mg L^{-1} of Cl.

when the solution was initially added to the soil sample a portion of the free water was tightly bonded to the surface of clay particles or organic matter, hence making it invisible for dielectric sensing. Khaled and Stucki (1991) have shown that reduction in soil moisture content results in less fixation of interlayer potassium (K), in particular for smectites, due to change in electrical and structural charges. The release of K in Clarion loam was observed during air-drying by Luebs et al. (1956). However, distribution of K ions between clay mineral and solution depends on the activity of K in these places (Bray and DeTurk, 1939). Particularly, low concentration of K in pore water can trigger the release of fixed K by clay minerals, while high concentration can stimulate its fixation. Hence, when the ionic concentration of the applied solutions was increased the activity of K in aqueous phase was also increased. This resulted in fixation of K ions by clay minerals thus reducing their electric charge. Consequently, number of water molecules tightly hold by K ions in the solution and by clay minerals on their surfaces or edges was reduced, while the number of free water molecules increased. As a result the measured dielectric constant of the soil was raised with increase of ionic concentration of the applied solution. (It is worth mentioning that in general the real part of permittivity of the soil was increasing with increasing ionic concentration of applied solution within the whole frequency range tested (Fig. 3)).

The imaginary part of the permittivity of the soil sample also showed increase in magnitude with increasing VWC attributed mostly to increased ionic conductivity of the soil solution (Fig. 2b). This type of response corresponds to the simple model developed by Rhoades et al. (1976), where the bulk soil electrical conductivity was partitioned into the surface and the liquid phase conductivities. Contribution of the later was increasing with increasing water content, while the former were regarded as a constant for a specific soil. The rationale behind this and other similar models is the idea of continuity of liquid phase in the soil matrix. Since electrical conduction in soils occurs primarily through pore water, better connection between the pores, which is related to moisture content, enhances its bulk conductivity.

In Figure 2b the measured dielectric loss is inversely proportional to the frequency, having a slope of -1 on the log-log plot, which indicates constant real conductivity. Correspondingly Fig. 2c reveals the frequency-independent plateaus below MHz range which represent the DC conductivity of the soil sample at each moisture level. Increase of VWC from 0.10 to 0.30 $m^3 m^{-3}$ on average resulted in increase of the DC conductivity values by a factor of 25. At the MHz frequency the slope of the dielectric loss slightly deviates from inverse frequency relationship and the real part of conductivity is no longer constant.

The effect of NO_3-N concentration of the applied solutions on the soil dielectric response is shown in Fig. 3, where the dielectric constant (a), the loss factor (b) and the real part of conductivity (c) are plotted as a function of frequency for samples wetted to 0.20 $m^3 m^{-3}$ VWC. Concentration of Cl in these solutions was fixed at 50 mg L^{-1}. Both the real and imaginary parts of permittivity showed the same trend of increase in magnitude with increasing NO_3-N concentration, but the overall change was not as large as that induced by change in VWC demonstrating the dominant influence of moisture content on soil dielectric response. Again, the dielectric loss of the soil samples showed the familiar inverse relationship with frequency on the double-logarithmic scale (Fig. 3b). Figure 3c shows corresponding frequency-independent plateaus of the DC conductivity at

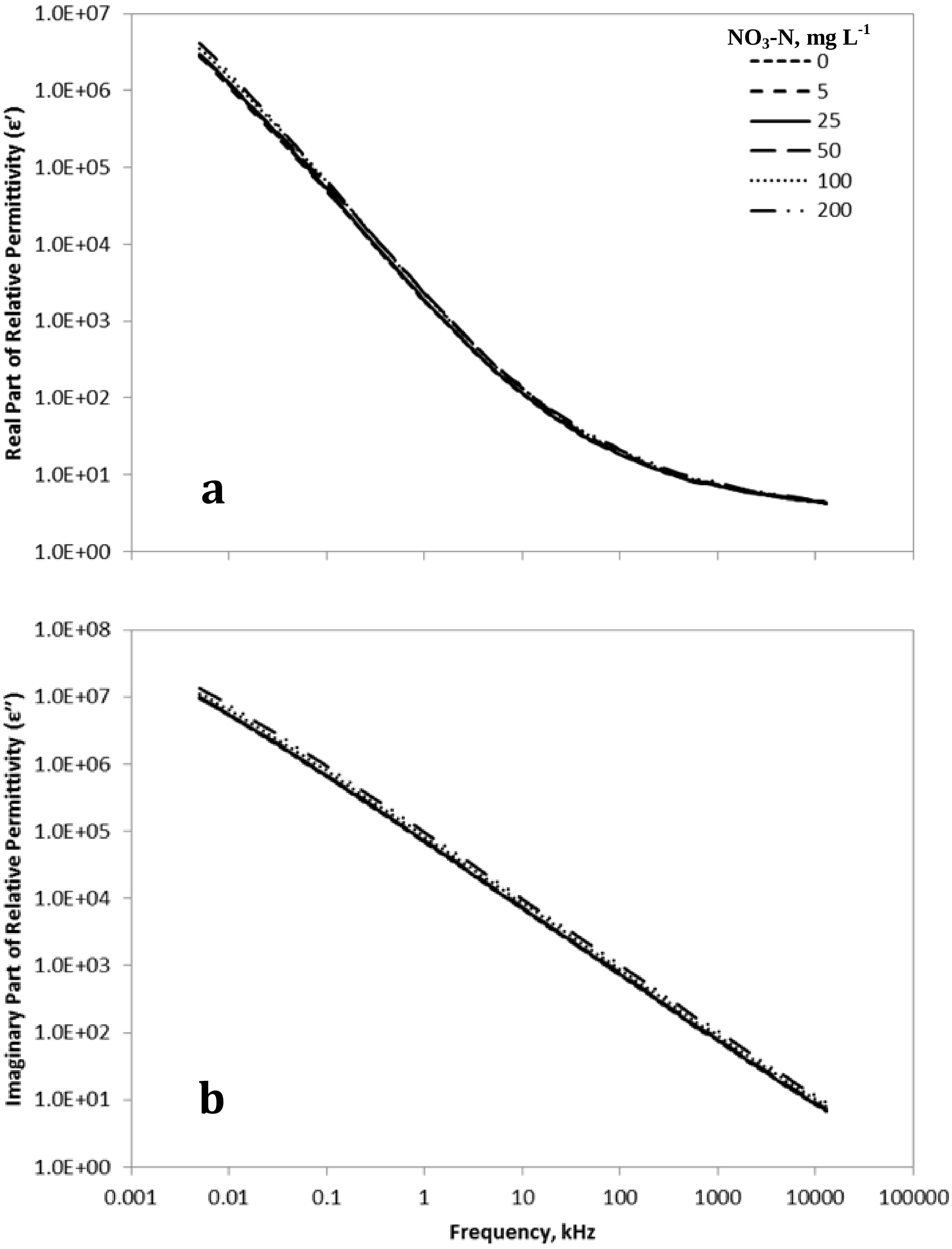

Figure 3. Change of the real (a) and the imaginary (b) parts of permittivity and the real part of conductivity (c) with increase of NO_3-N concentration of the applied solution with fixed Cl concentration of 50 mg L^{-1} at 0.20 m^3 m^{-3} VWC. Spikes in the conductivity measurements observed at frequencies above 0.8 MHz is believed to be an artifact of the text fixture parasitics that was not removed by the compensation.

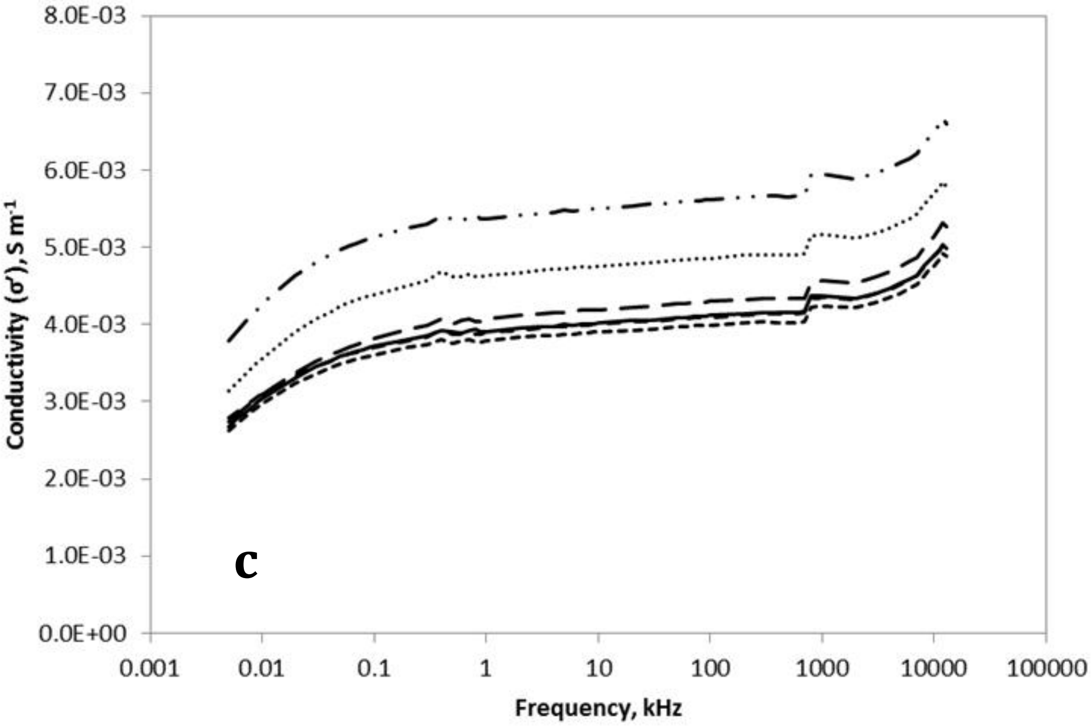

Figure 3. (continued) Change of the real (a) and the imaginary (b) parts of permittivity and the real part of conductivity (c) with increase of NO_3-N concentration of the applied solution with fixed Cl concentration of 50 mg L^{-1} at 0.20 m^3 m^{-3} VWC. Spikes in the conductivity measurements observed at frequencies above 0.8 MHz is believed to be an artifact of the text fixture parasitics that was not removed by the compensation.

kHz range with clear NO_3-concentration-induced separations between spectra. The change of NO_3-N concentration from 0 to 200 mg L^{-1} yielded an increase of the DC conductivity value by a factor of only 1.4, approximately 18 times smaller than one induced by the VWC change. The result revealed that the dielectric loss and, consequently, the bulk conductivity of the soil samples were more influenced by change in VWC than by change in the solution NO_3-N concentration within the moisture level and NO_3 content tested. The effect of change of Cl concentration of the wetting solutions was comparable to that observed with NO_3-N (data are not shown). The magnitude, shape and pattern of spectral response were similar to those presented in Fig. 3.

Spikes in the measured bulk conductivity values were observed for all soil samples at a frequency range above 0.8 MHz. We believe that this is an artifact of the text fixture parasitics that the open-short compensation technique could not thoroughly eliminate. Since the error introduced by this drawback was relatively small and equal across all samples, we decided not to correct or remove the spiked data during statistical analysis.

Soil Moisture

Linear regression analyses were conducted using the measurements from all soil samples to correlate the actual soil moisture content and the real part of the permittivity at each frequency. Figure 4 demonstrates the relationship between these two variables for readings made at 100 Hz, 1 kHz and 13 MHz frequencies. In general, at low frequencies correlation between the bulk dielectric constant and VWC was slightly curvilinear (Fig. 4a). Near the MHz frequency the dependence was mostly linear (Fig. 4c). Furthermore, with increase of the measurement frequency the real permittivity data were becoming less scattered, which contributed to improved model performance. The highest R^2 values of 0.987 were obtained for the models fitted to the real permittivity data taken at the highest frequencies (9-13 MHz), while the models fitted to the data measured at 30-50 Hz had the lowest R^2 value of 0.831. Generally, models developed using the low frequency (< MHz) data resulted in high real permittivity values at the lowest VWC level (0.10 m^3 m^{-3}). This agrees with our previous discussion about unequal separation in the real permittivity spectra observed in Fig. 2a. Similar analyses of the dielectric loss revealed a slightly curvilinear correlation between the imaginary part of the permittivity and VWC across the whole frequency range. Hence the models fitted to the data could not perform better

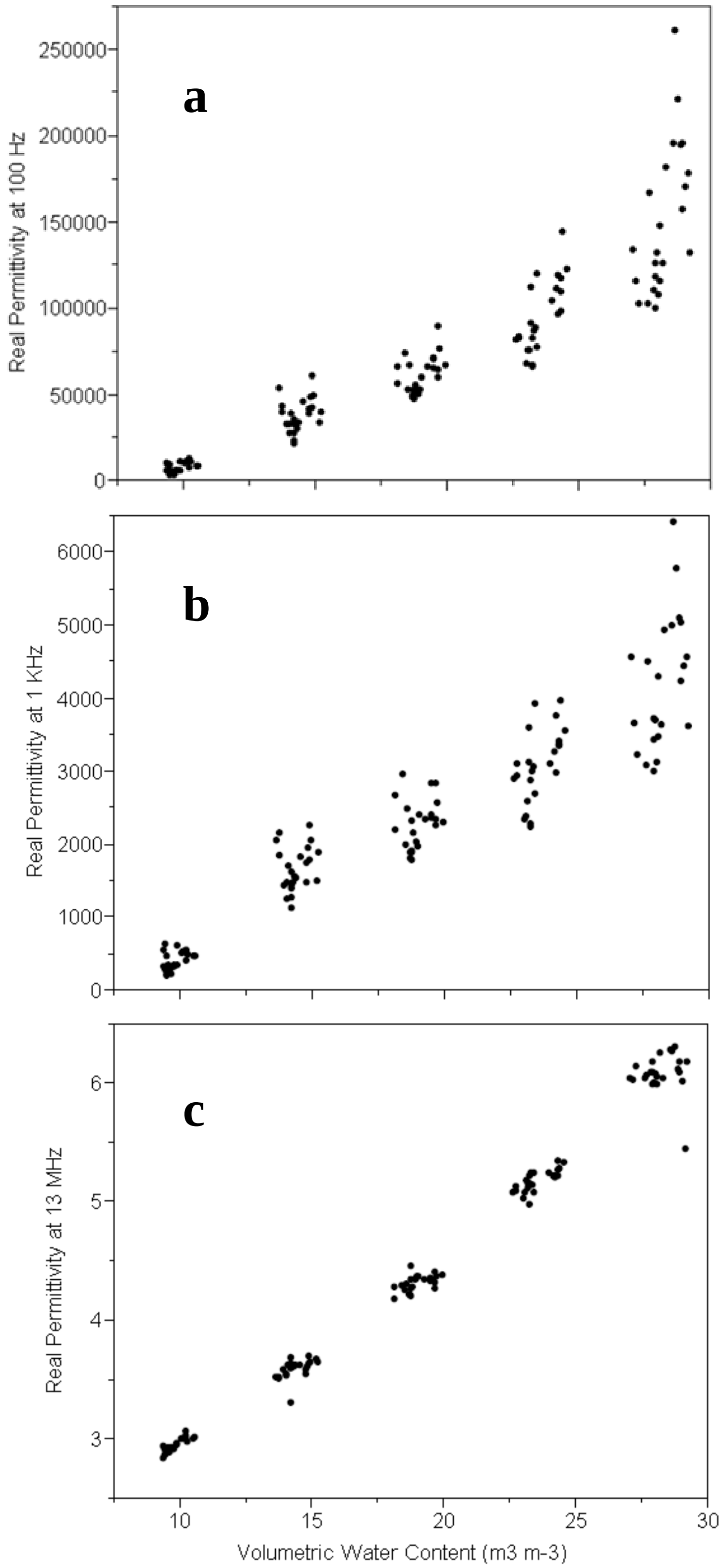

Figure 4. Dependence of the real part of permittivity measured at 100 Hz, 1 kHz and 13 MHz frequencies on soil moisture content across all soil samples.

than those discussed above at higher frequencies, but did a noticeably better job at frequencies below kHz (with R^2 value ranging from 0.94 to 0.96).

PLS Analysis

Table 1 summarizes the results of the PLS regression analysis for different models using the dielectric response data from all soil moisture and ionic concentration levels across the whole spectra. All three global models performed well in estimating the VWC (each model being able to capture about 99% of variation in soil moisture content), but none of them managed to estimate change in NO_3-N concentration of the applied solution with good accuracy. The model based on the imaginary part of permittivity performed the best explaining about 33% of NO_3-N variation having the root mean square error (RMSE) of 57 mg L^{-1}. RMSE of the other two models were 65 and 63 mg L^{-1}. This little superiority of the loss factor to estimate the NO_3-N concentration stems from the fact that electrical conduction primarily manifests through the imaginary part of the permittivity.

Table 1. Output of PLS models for estimating VWC and NO_3-N concentration simultaneously using the spectral response obtained at all moisture and ionic concentration levels.

Data Used in Model	**# LV***	**RMSE-CV†**	**% Variation Explained for**	
			VWC‡	**NO_3-N**
Real permittivity (ε′)	2	0.683	98.78	12.15
Imaginary permittivity (ε″)	6	0.619	98.88	32.93
Both (ε′ and ε″)	4	0.671	99.19	17.70

* # LV, number of latent variables
† RMSE-CV, root mean square of error for cross-validation
‡ VWC, volumetric water content

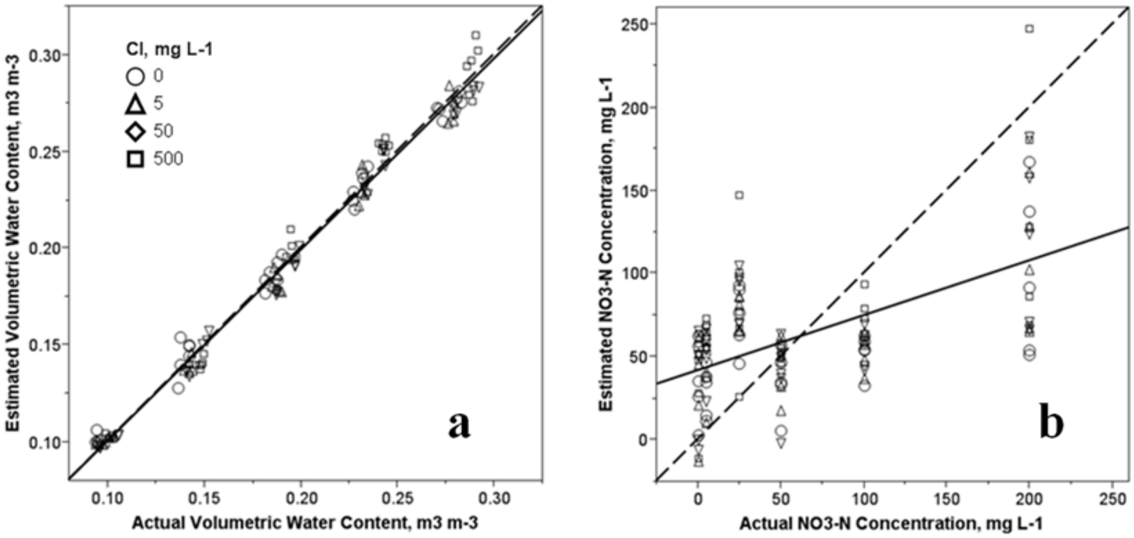

Figure 5. Actual vs. estimated (a) volumetric water content and (b) NO_3-N concentration for the global model based on the imaginary part of permittivity. Solid lines are linear regressions fitted to the data, and dashed lines are 1:1 fits (perfect fit).

On the other hand it should be noticed that the number of latent variables used by this model was the highest compared to the other two, which could also contribute to its enhanced calibration capability. Figure 5 shows the results of the actual vs. estimated VWC and NO_3-N concentration for the model employing only the loss factor data. The dashed lines are 1:1 fits corresponding to the ideal estimation. It can be easily seen that the PLS model underestimates NO_3-N concentration at the high end and overestimates at the low end.

Since contribution of the soil aqueous phase electrical conduction (hence the effect of pore water ionic concentration on permittivity measurement) increases with increasing soil moisture content, we developed several PLS models that did not incorporate spectral response data from low VWC samples. As a result, three types of models were constructed by excluding the data obtained at VWC $\leq$ 0.10, 0.15 and 0.20 $m^3\ m^{-3}$, respectively. The results of these analyses are given in Table 2. In general, all models estimated the VWC better than the change in NO_3-N concentration of the wetting solution. This can be explained by the fact that soil water content has a stronger effect on both the real and imaginary parts of permittivity than the change in soil solution ionic concentration, which was observed earlier during visual analysis of the VWC- and NO_3-N-induced changes in spectral response. RMESP of the models for moisture content was varying only from 0.015 to 0.018 $m^3\ m^{-3}$. Furthermore, accuracy of the VWC estimation by the models employing the dielectric constant, the loss factor, or both together was not statistically different ($p = 0.05$).

Table 2. Results of PLS models for estimating VWC and NO_3-N concentration obtained through elimination of the low moisture concentration data.

Data Used in Model	**# LV**	**RMSE-CV**	**% Variation Explained for**	
			VWC	**NO_3-N**
VWC > 0.10 $m^3\ m^{-3}$				
Real permittivity (ε')	2	0.670	98.43	16.52
Imaginary permittivity (ε")	6	0.595	98.24	41.26
Both (ε' and ε")	4	0.650	98.84	25.56
VWC > 0.15 $m^3\ m^{-3}$				
Real permittivity (ε')	2	0.650	98.14	23.49
Imaginary permittivity (ε")	6	0.553	97.73	56.19
Both (ε' and ε")	5	0.587	98.54	46.11
VWC > 0.20 $m^3\ m^{-3}$				
Real permittivity (ε')	2	0.640	94.36	33.20
Imaginary permittivity (ε")	5	0.539	94.23	64.60
Both (ε' and ε")	2	0.623	96.22	36.28

As was expected, estimation of NO_3-N concentration improved noticeably by elimination of the low VWC data. Again, the models constructed using only the loss factor performed better than those based on only the dielectric constant or both loss factor and dielectric constant. Moreover, subsequent removal of the low VWC data further enhanced the calibration capability of the developed models. This confirms that contribution of the ionic conduction to the bulk soil conductivity (hence to the dielectric loss) has a larger effect at high VWC levels making it easier to estimate the change in NO_3-N concentration. Despite of this improvement RMSE of the PLS model constructed using the imaginary part of permittivity measured at 0.25 and 0.30 $m^3\ m^{-3}$ of VWC was only 27% better than the RMSE of the similar model using the whole VWC spectra (41 compared to 57 mg L^{-1}).

It should also be emphasized that the models constructed using the imaginary part of the permittivity had the highest number of latent variables determined through the cross validation process. Normally it is regarded as a good sign if the number of latent variables selected is close or equal to the number of major factors influencing the variation pattern in the spectrum data.

The high number of latent factors indicated that there was a high variation in the dielectric loss spectra that could not be sufficiently explained by change in moisture content and NO_3-N concentration. One of the main sources of this variation could be the changing Cl concentration in the soil, particularly stemming from the samples that were wetted with the solutions containing 500 mg L^{-1} of Cl.

Therefore alternative PLS models were developed to test the effect of Cl concentration in the wetting solutions on NO_3-N estimation using solely the imaginary

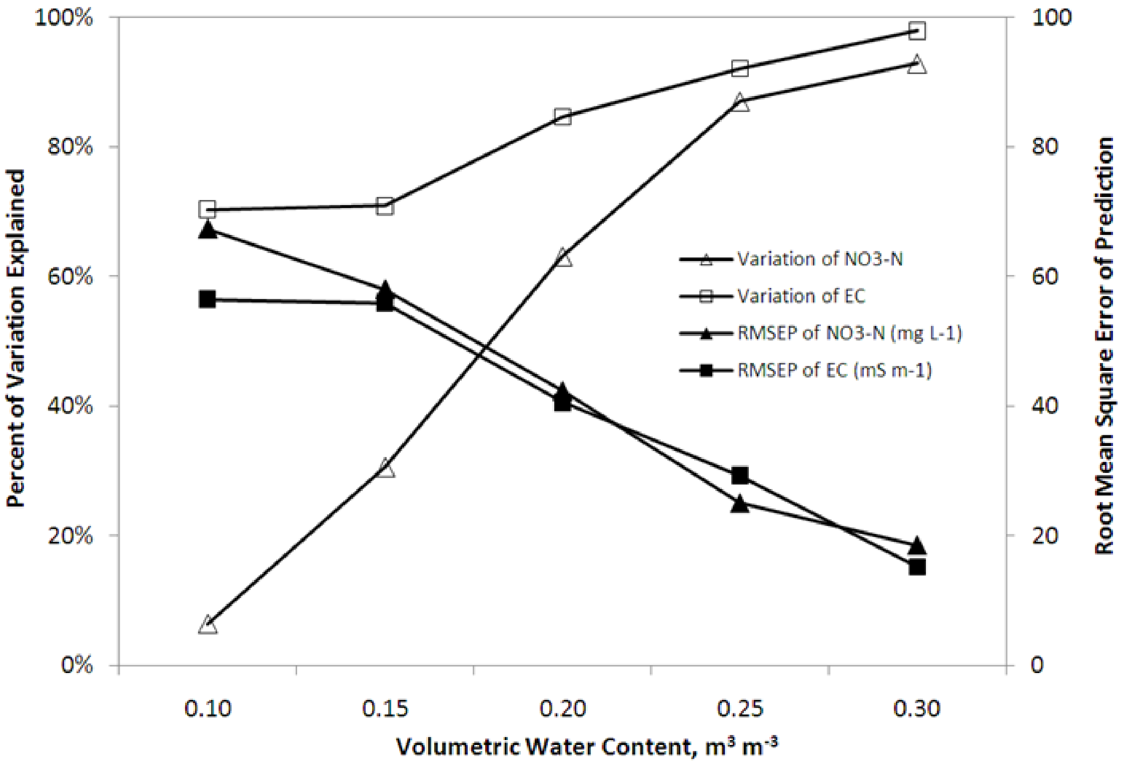

Figure 6. Dependence of RMSE-CV and percent of variation explained of NO_3-N and EC for PLS models developed based on the imaginary part of permittivity on VWC.

part of permittivity. The measurements from the samples wetted with the solutions containing 500 mg L^{-1} of Cl were removed from the data. PLS models were constructed to estimate NO_3-N concentration and soil moisture content at fixed VWC levels. The soil moisture content was included in the models because there was slight variation in actual VWC from sample to sample that could mask the NO_3-N-induced change in the spectral response. Figure 6 summarizes the outcomes of the fitted models. In general, the calibration capability of the PLS regression method significantly improved when VWC level was higher. The best models were found at the 0.25 and 0.30 m^3 m^{-3} moisture levels having R^2 values of 0.87 and 0.93 and RMSE of 25 and 19 mg L^{-1}, respectively. The results of the actual vs. estimated NO_3-N for these best models are shown in Fig. 7.

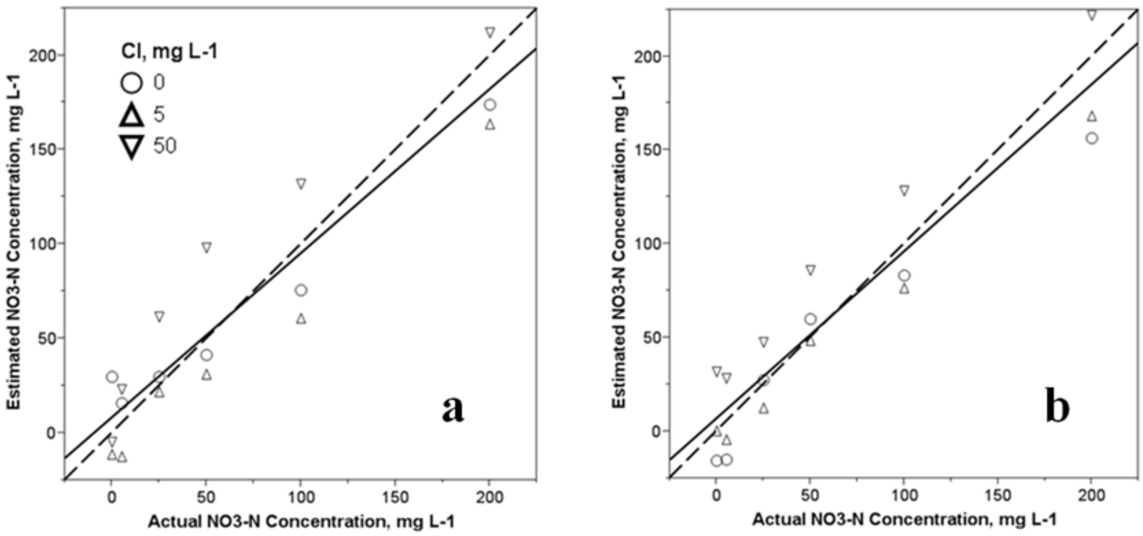

Figure 7. Actual vs. estimated NO_3-N concentration of the models developed using the imaginary part of permittivity measured at (a) 0.25 and (b) 0.30 m^3 m^{-3} volumetric water content after removing the samples wetted with solution containing 500 mg L-1 of Cl.

In addition to NO_3-N concentration, similar PLS models were developed to estimate the electrical conductivity of the wetting solutions using the imaginary part of permittivity data. Performance of different models is summarized in Table 3 and Fig. 6. In general, these models outperform the models developed for simultaneous estimation of VWC and NO_3-N concentration. Again, the calibration capabilities of the models were

Table 3. Estimation of the VWC and electrical conductivity of the wetting solutions by the PLS models based on the loss factor data. The results were obtained through elimination of the low moisture concentration data.

Data Used in Model	# LV	RMSE-CV	% Variation Explained for	
			VWC	Solution EC
Global (all data)	5	0.584	98.88	41.33
VWC > 0.10 m3 m-3	5	0.549	98.33	51.24
VWC > 0.15 m3 m-3	4	0.486	96.62	65.03

VWC > 0.20 m3 m-3	4	0.362	94.36	85.78

improving with increasing soil moisture content, but unlike the PLS models developed to estimate NO_3-N concentration these models demonstrated a relatively good performance at low VWC levels too being able to capture 70% of the variation (Fig. 7).

Conclusions

In this laboratory study, an influence of soil moisture content and NO_3-N concentration of the wetting solutions on the bulk soil spectral response was tested. Dielectric measurements were made at 63 frequencies ranging from 5 Hz to 13 MHz. PLS regression analysis was employed for simultaneous estimation of the VWC and change in applied NO_3-N concentration using the real and imaginary parts of permittivity (separately and together). In addition similar models were constructed to estimate VWC and EC of the wetting solutions.

The PLS models based on the real and imaginary parts of permittivity (both separately and together) gave equally good estimation of soil moisture content having RMSE <0.02 m^3 m^{-3}. The linear models using the dielectric constant measured at a single frequency in MHz range demonstrated better performance having RMSE <0.01 m^3 m^{-3}. The outcome of the models agrees with our visual observation of the dielectric spectra when the VWC-induced changes in the real part of the permittivity at below-MHz frequency range were found to be disproportional to the VWC levels. As a result, the PLS models that used the data from the whole spectra incorporated the noise associated with the low frequency measurements, which diminished the models’ ability to recognize major variation patterns. Hence, to improve accuracy of the PLS regression models soil moisture content should be estimated using data obtained at MHz frequency, or using linear models developed for the same frequency range.

The change in the wetting solution NO_3-N concentration was estimated with different accuracy depending on the PLS models. In general, the models constructed using the imaginary part of permittivity performed significantly better than those based on the real part or the real and imaginary parts of permittivity. Moreover, calibration capabilities of the models improved with increase of the soil moisture content. For example, RMSE of the PLS model constructed using the imaginary part of permittivity measured at 0.25 and 0.30 m^3 m^{-3} of VWC was 41 mg L^{-1} compared to 57 mg L^{-1} of the global model developed using the similar data from all VWC levels. The best estimation of NO_3-N was attained when nitrate was the dominant anion in the wetting solutions having RMSE of less than 19 mg L^{-1} at VWC of 0.30 m^3 m^{-3}. As a whole, the results of the PLS analyses showed that it was possible to estimate the NO_3-N concentration with sufficient accuracy if a nitrate-containing salt was dominant in the soil solutions and VWC was high (above 0.20 m^3 m^{-3}).

The models developed to estimate electrical conductivity of the wetting solution simultaneously with soil moisture content performed better than the identical models developed for NO_3-N estimation. Again, calibration capability of the models improved with increase of soil moisture content, and the models built using the imaginary part of permittivity overperformed the others. RMSE of the PLS model constructed using the imaginary part of permittivity measured at 0.25 and 0.30 m^3 m^{-3} of VWC was 50% better than the RMSE of the similar model using the whole VWC spectra (0.391 compared to 0.795 dS m^{-1}). What is remarkable, PLS models developed at fixed VWC levels were able to estimate the change in the added solution electrical conductivity even at very low VWC levels with R^2 >0.70. In general, the laboratory test results demonstrated that the PLS regression analysis had a good potential to estimate changes in soil solution electrical conductivity simultaneously with soil moisture content at a wide VWC range.

These new features of the spectral analysis can be utilized only by dielectric-based sensors capable of measuring the real and imaginary parts of permittivity at multiple frequencies within the range tested here. To our knowledge only Zhang et al. (2004) has developed such a sensing system using a Wenner array configuration. RMSE of their PLS model for estimating moisture content was similar to that of our model (0.02 m^3 m^{-3}), but RMSE for estimating soil solution EC was twice that in this study. Their experimental study, however, did not include NO_3-N estimation. Results of such a study with the measurement extended to higher frequencies would be of great interest.

Acknowledgements

The research was supported in part by the National Science Foundation under the grants NSF-ECCS-0601570, and NSF-ECCS-0926029. We acknowledge Loren Shiers for assistance with the solution preparation and Mark Lott for technical support provided in his workshop during construction of the temperature chamber. We are also grateful to Dr. Robert Webber for sharing his equipment and providing valuable technical advice on spectral measurement.

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CHAPTER 5. GENERAL CONCLUSIONS

Conclusions

Continuous in site monitoring of NO_3 is attracting a lot of attention in the Midwest in view of increasing importance of the environmental problems stemming from N losses from agricultural systems. Indirect estimation of NO_3-N concentration using soil permittivity measurement can become an elegant tool for studying N dynamics with sufficient special and temporal resolution in agricultural production. Frequency domain technique can be used to develop a new generation of dielectric probes capable of estimating several physical and chemical soil properties by exploiting multi-frequency measurements.

Dielectric measurements made at two fixed frequencies using the off-the-shelf capacitance type probes (ECH$_2$O EC-5 and EC-10) confirmed the feasibility of obtaining information about several soil parameters by employing abovementioned approach. The apparent permittivity sensed by EC-5 at a relatively high (70 MHz) frequency was mostly influenced by soil moisture content. On the other hand measurements made by EC-10 at a lower frequency (5 MHz) showed a statistically significant ($p=0.05$) contribution from the conductive part of the permittivity, in spite of the dominant effect of soil moisture content. Furthermore, the probe’s dielectric response was more sensitive to change in soil solution NO_3-N concentration than to equivalent (in mg L^{-1}) change of Cl concentration.

Hence the results demonstrate the feasibility to extract additional information about soil by combining dielectric measurements obtained at multiple frequencies. A need for further studies was emphasized in order to quantify the nature of the capacitance probe response to changes in pore water ionic concentration and its interaction with other field variables (e.g. soil moisture, temperature, soil texture, and pH) across a wide range of frequencies.

Since soil conductive behavior, which is related to pore water ionic concentration, increases with decreasing frequency, spectral measurements below several MHz were obtained to estimate NO_3-N concentrations in electrolytic solutions and in soils. An accurate estimation of aqueous NO_3-N concentration was attained through partial least squares (PLS) analysis when changes in “background” anion (chloride) concentration was less than or equal to changes in NO_3-N concentration (in mg L^{-1}). Very high concentration of the chloride anion in the electrolytic solutions had a negative effect on calibration capabilities of the PLS model, supposedly, through changing dynamic processes in the solution (e.g., change in ion mobility, or forming ion-pairs with increasing ionic concentration). In general, the results of the electrolytic solution experiment showed that it is possible without a priori knowledge of the system to estimate the NO_3-N concentration in solutions using PLS regression method when NO_3 is a major anion.

Simultaneous estimation of VWC and NO_3-N concentration in soil revealed that accuracy of the estimations, particularly for NO_3-N, was dependent on data used to contract the PLS mode. Good agreements were found between actual and estimated NO_3-N concentration when PLS models were built using permittivity data obtained at VWC $\geq$

0.20 m^3 m^{-3}. Improvement in estimation of NO_3-N was also achieved by removing from the analysis soil samples containing very high chloride concentration, but this improvement was less prominent that the one attained by the previous step. In general, the soil experiment demonstrated that the PLS regression method coupled with the dielectric measurements obtained at multiple frequencies below several MHz could be used to gain reliable estimations of NO_3-N concentration, but only in wet soils (VWC $\geq$ 0.20 m^3 m^{-3}). Hence, calibration of multi-frequency probes in the future should be performed at relatively high VWC to insure accurate estimations of NO_3-N concentrations. Furthermore, since loss of NO_3 in agricultural systems mostly take place through leaching usually after irrigation or precipitation event; it makes little sense to calibrate such probes at low VWC levels.

Suggestions for Future Research

During this study PLS regression models were developed using the whole spectra measured. In the future it will be interesting to see if an integration of a genetic algorithm wavelength selector in the PLS analysis can additionally improve the model's performance. This would help to optimize the number of measurement frequencies by selecting the ones carrying relevant information.

Another area to search for improvements can be utilization of a non-linear model, such as the neural network. Unlike PLS, which implies a linear relationship between the spectra and dependent variables, the neural network can provide more flexibility by allowing this relationship to be non-linear, which may be the case for the data obtained in this study.

APPENDIX 1. SHORT-OPEN COMPENSATION

Permittivity measurements of the solutions were conducted using an Agilent 16452A Liquid Test Fixture (Agilent Technologies, Hyogo, Japan) subjected to a constant electric field (Fig. 1). This fixture represents a typical four-terminal cell with two circular nickel-plated cobal (an alloy of 17% Cobalt, 29% Nickel, and 54% Iron) electrodes forming a parallel-plate capacitor containing the sample. Ceramic made of aluminum oxide (Al_2O_3) is used as an insulator around the electrodes. Sampling volume can be adjusted from 3.4 to 6.8 cm^3 using one of the four spacers of different thickness ranging from 1.3 to 3.0 mm. Additional details of the test fixture can be found in the operation and service manual (Agilent Technologies, 2000).

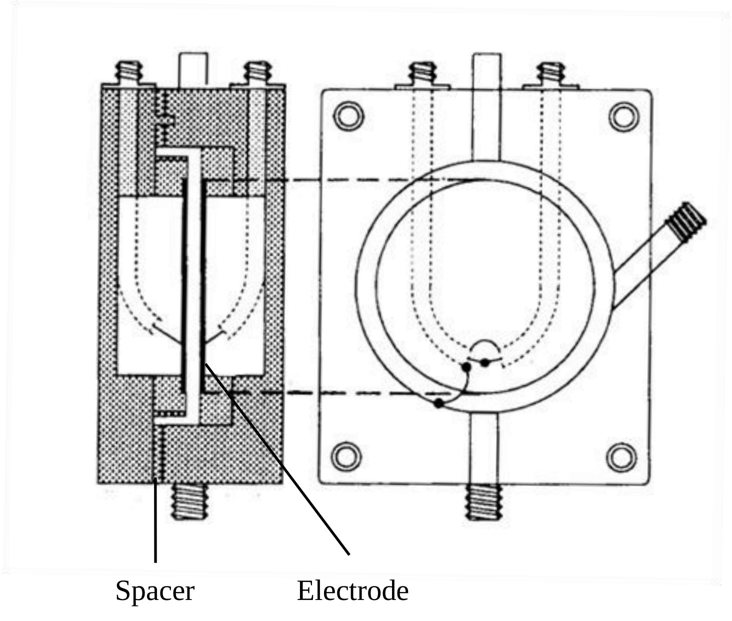

Figure 1. Cross-sectional views of the Agilent 16452A Liquid Test Fixture

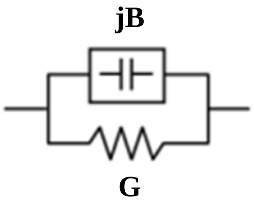

Figure 2. Parallel equivalent circuit mode

An HP 4192A LF Impedance Analyzer (Hewlett-Packard, Palo Alto, CA, USA) was used to measure admittance of the solutions in the frequency range 20 Hz to 13 MHz. The fixture was connected to the measurement instrument using a 4-terminal-pair BNC cable the 16048A Test Leads with a cable length of 1m. The electrical response of the samples was obtained using a parallel measurement circuit mode, which involves a resistor and a capacitor in parallel (Fig. 2). The measured complex admittance (Y^*) of the circuit can be expressed as (Agilent Technologies, 2009):

$$Y^* = \frac{1}{Z^*} = G + jB \quad [1]$$

where $Z^*$is the complex impedance; G and B are the real (conductance) and the imaginary (susceptance) parts of the admittance; $j^2 = -1$ is the complex number.

However, there are unwanted impedances (parasitics) in parallel and series associated with the measurement that can be represented by the equivalent circuit shown in Fig. 3 (Santamarina et al., 2001). The open/short compensation is the most popular compensation technique used to reduce the measurement errors induced by the text fixture. It involves determination of these unwanted parameters and their removal from the measurements in order to obtain the true impedance of the material under the test (MUT). According to this technique measurements are performed in two conditions: open circuit (i.e., air is the dielectric between the electrodes) and short circuit (i.e., the

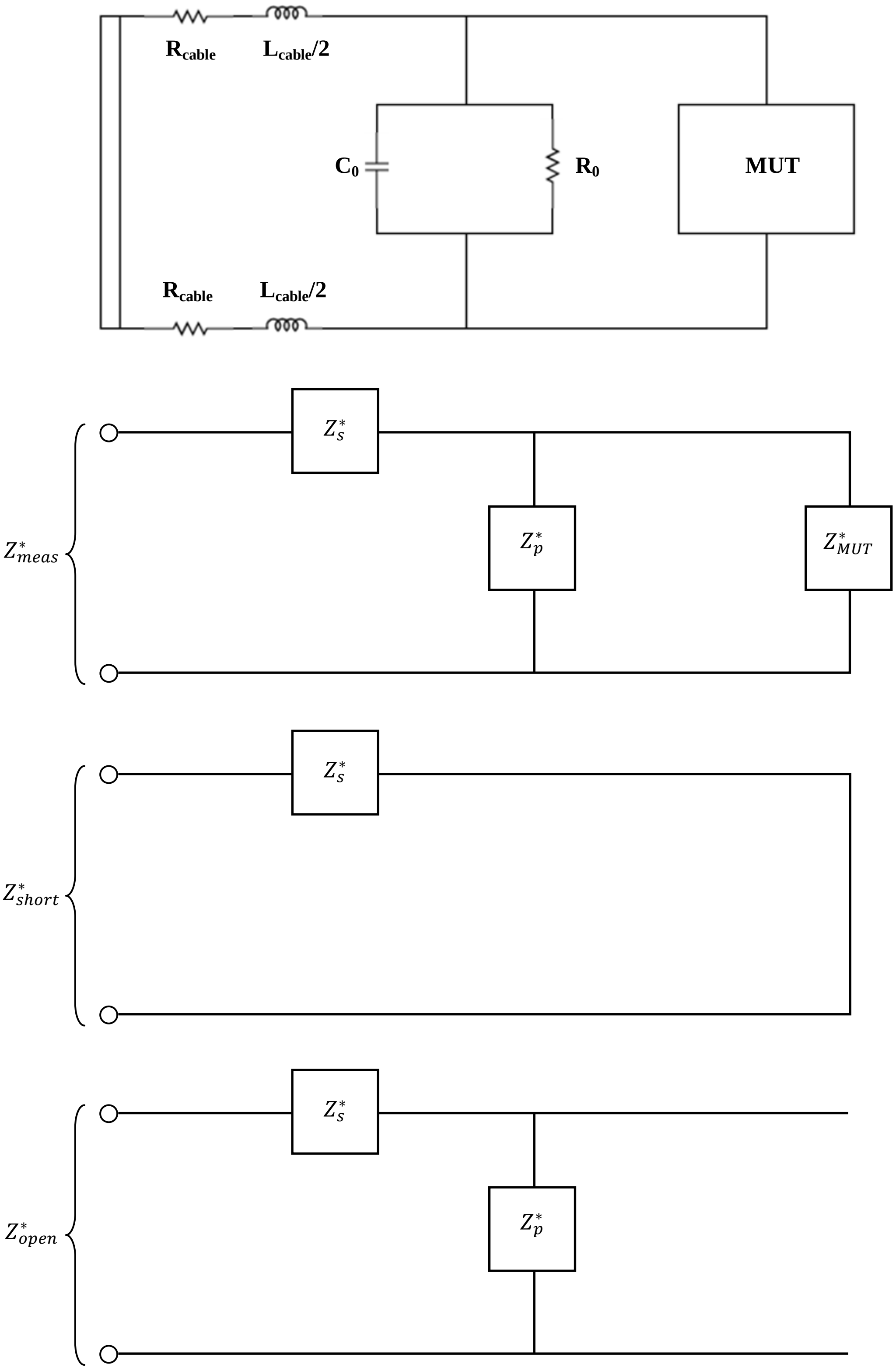

Figure 3. Removing unwanted impedances using the open/short compensation technique

electrode plates are in contact with each other). The short circuit condition effectively eliminates the unwanted impedance in parallel; therefore, the measurement Z_{short}^{*} determines the unwanted impedance Z_{s}^{*} in series with the MUT, such as in the test leads. The open circuit impedance Z_{open}^{*} combines the unwanted impedance in series Z_{s}^{*} and parallel Z_{p}^{*}. The true impedance of the MUT Z_{MUT} is computed from the measured impedance Z_{meas}^{*}, the short circuit impedance Z_{short}^{*} and the open circuit impedance Z_{open}^{*} as follow:

$$Y_{MUT}^{*} = \frac{1}{Z_{MUT}^{*}} = \frac{1}{Z_{meas}^{*} - Z_{short}^{*}} - \frac{1}{Z_{meas}^{*} - Z_{open}^{*}} \quad [2]$$

The complex relative dielectric permittivity (ε_{r}^{*}) of the solution can be calculated from the relationship (Agilent Technologies, 2000):

$$\varepsilon_{r}^{*} = \alpha\left(\frac{C_p}{C_0} - j\frac{1}{\omega C_0 R_p}\right) \quad [3]$$

where α is the correction coefficient for stray capacitance; C_p and C_0 are the parallel capacitance of the solution and air, respectively; R_p is the parallel resistance; $\omega = 2\pi f$ is the angular frequency and f is the frequency. The parallel capacitance and the resistance can be determined from the following relationships (Agilent Technologies, 2009):

$$C_p = \frac{\mathrm{Im}(Y_{MUT}^{*})}{\omega} = \frac{B_{MUT}}{\omega} \quad [4]$$

$$R_p = \frac{1}{\mathrm{Re}(Y_{MUT}^{*})} = \frac{1}{G_{MUT}} \quad [5]$$

The effect of stray capacitance can be cancelled by multiplying the data with α coefficient, which is calculated by following equation:

$$\alpha = \frac{100|\dot{\varepsilon}_{rm}|}{97.0442|\dot{\varepsilon}_{rm}| + 2.9558} \quad [6]$$

$$|\dot{\varepsilon}_{rm}| = \sqrt{\frac{C_p^2}{C_0^2} + \frac{1}{\left(\omega C_p R_p\right)^2}} \quad [7]$$

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