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Estimating Soil Solution Nitrate Concentration from Dielectric Spectra Using Partial Least Squares Analysis

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Abstract
Fast and reliable methods for in situ monitoring of soil NO$_3$–N concentration could help guide efforts to reduce NO$_3$–N losses to ground and surface waters from agricultural systems. While several studies have been done to indirectly estimate NO$_3$–N concentrations from time domain spectra, no research has been conducted using a frequency domain technique. Hence, the goal of this laboratory study was to estimate NO$_3$–N concentrations 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 contents (VWC) with 24 solutions containing different concentrations of KNO$_3$ and KCl were analyzed using a partial least squares (PLS) regression method. Global models could not estimate NO$_3$–N concentrations with sufficient accuracy. Models based on the imaginary part of the permittivity were better than those based on the real part. The PLS model estimates were improved when low VWC data and high Cl$^-$ concentration were eliminated, reducing the RMSE for NO$_3$–N from 57 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 performance of these models improved with increasing VWC level, reaching the lowest RMSE of 18 mg L$^{-1}$ at VWC of 0.30 m$^3$ m$^{-3}$.

Disciplines
Agriculture | Bioresource and Agricultural Engineering | Life Sciences | Soil Science

Comments

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Estimating Soil Solution Nitrate Concentration from Dielectric Spectra Using Partial Least Squares Analysis

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Fast and reliable methods for in situ monitoring of soil NO$_3$–N concentration could help guide efforts to reduce NO$_3$–N losses to ground and surface waters from agricultural systems. While several studies have been done to indirectly estimate NO$_3$–N concentrations from time domain spectra, no research has been conducted using a frequency domain technique. Hence, the goal of this laboratory study was to estimate NO$_3$–N concentrations 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 contents (VWC) with 24 solutions containing different concentrations of KNO$_3$ and KCl were analyzed using a partial least squares (PLS) regression method. Global models could not estimate NO$_3$–N concentrations with sufficient accuracy. Models based on the imaginary part of the permittivity were better than those based on the real part. The PLS model estimates were improved when low VWC data and high Cl$^-$ concentration were eliminated, reducing the RMSE for NO$_3$–N from 57 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 performance of these models improved with increasing VWC level, reaching the lowest RMSE of 18 mg L$^{-1}$ at VWC of 0.30 m$^3$ m$^{-3}$.

**Abbreviations:** EC, electrical conductivity; EM, electromagnetic; LV, latent variable; OM, organic matter; PLS, partial least squares; VWC, volumetric water content.

Typically, N-rich fertilizers are applied uniformly to agricultural fields, often resulting in over- and underapplication of N in various parts of the field due to the spatiotemporal variation of the crop N demand. Unused N can leach from the fields to ground and surface waters, mostly in the form of 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 the lack of a robust and fast measurement system for real-time monitoring of NO$_3$–N dynamics in soil water (Zhang et al., 2002). In situ monitoring of NO$_3$–N concentrations can help to optimize the application of N-rich fertilizers, reduce the risk of NO$_3$–N leaching to water bodies, and evaluate the efficiency of best management practices targeted on the improvement of N uptake by plants during the growing season (Roberts et al., 2002, 2010; Koch et al., 2004). Traditional methods for measuring soil NO$_3$ concentration 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 concentrations. Ultraviolet spectroscopy has been used to estimate aqueous NO$_3$–N concentrations (Karlsson et al., 1995; Dahlén et al., 2000; Tuli et al., 2009); however, the high cost of the measurement system limits...
its field-scale application. Eigenberg et 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 also been used by other methods, particularly the time domain reflectometry (TDR) technique, to predict pore water NO$_3$–N concentrations (Das et al., 1999; Krishnapillai and Sri Ranjan, 2009). Originally TDR probes were used to estimate the VWC of the soil by measuring the relative permittivity of the medium (Topp et al., 1980). Dalton et al. (1984) first demonstrated the use of the TDR method for simultaneous measurement of soil moisture content and bulk electrical conductivity (EC). Later, the probes were adapted for continuous monitoring of NO$_3$–N or other ionic solutes in soil and water in both laboratory and field experiments (Nissen et al., 1998; Das et al., 1999; De Neve et al., 2003; Payero et al., 2006; Krishnapillai and Sri Ranjan, 2009). 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 EC, and soil NO$_3$–N concentrations in an irrigated peppermint ($\textit{Mentha \times \textit{piperita}}$ L.) field using simple models and calibration methods. They compared TDR-estimated NO$_3$–N concentrations 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 the NO$_3$–N concentration in an irrigated agricultural soil and concluded that TDR probes could be used to measure NO$_3$–N in nonsaline soil and water after the proper calibration for a long enough period of time to include the expected variations in VWC, temperature, and NO$_3$–N. There are several drawbacks associated with the TDR technique, however: 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 lengths (Robinson et al., 2003; Mojid 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 megahertz) and measure the apparent relative permittivity of the medium, which can be correlated with the VWC using factory-provided calibration models. Different studies have demonstrated that soil bulk EC has a negligible effect on the permittivity measurement at frequencies > 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 bulk EC becomes stronger.

Zhang et al. (2004) developed a capacitance-type sensor with a Wenner array configuration capable of making multifrequency 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 the VWC and soil salinity with frequency-response data using PLS regression. The results of these laboratory studies demonstrated the potential of measuring multiple soil properties by analyzing the patterns of the spectral data using the PLS regression method; however, no experimental work has been conducted to determine the feasibility of this method for estimating the ionic concentration of pore water. Thus, the goal of this laboratory study was to estimate the soil VWC and NO$_3$–N concentration from dielectric spectral data obtained from 5 Hz to 13 MHz using PLS analysis.

### Theory

Application of an electrical 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 et al., 2001). Dielectric permittivity ($\varepsilon_r$) is a frequency-dependent parameter that describes the ability of the medium to polarize in response to an external electrical field. For practical reasons, in this study and many others, the term permittivity stands for relative permittivity ($\varepsilon_r$), which is a value normalized with respect to the permittivity of a vacuum ($\varepsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$):

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0}$$  \[1\]

The permittivity is a complex quantity and can be expressed as

$$\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$$  \[2\]

where $\varepsilon_r'$ is the real part, describing the ability of a material to store energy from an applied electrical field, $\varepsilon_r''$ is the imaginary part, representing dielectric losses due to dissipation of energy by the material, and $j^2 = -1$ is an imaginary number. Losses due to relaxation and conduction contribute to the imaginary part of permittivity in the following manner:

$$\varepsilon_r'' = \frac{\varepsilon_d''}{\omega \varepsilon_0} + \frac{\sigma}{\omega \varepsilon_0}$$  \[3\]

where $\varepsilon_d''$ is the relaxation component, $\sigma$ (S m$^{-1}$) is the ohmic conduction, and $\omega = 2\pi$ is the angular frequency, where $\pi$ is the frequency (Hz). At sufficiently high frequencies (typically >100 kHz), $\sigma$ is approximated by a direct-current EC (Robinson et al., 2008).

The EC of bulk soil ($\sigma_b$) is a function of the soil structure and geometry, the tortuosity of the current pathways, soil moisture content ($\theta$), and soil solution EC ($\sigma_s$). Different models have been proposed in geophysics and soil science to describe this rela-
tionship (Rhoades et al., 1997; Heimovaara et al., 1995). A simple
empirical function was developed by Rhoades et al. (1976):

$$\sigma_b = \theta \sigma_w + \sigma_s$$

[4]

where $\sigma_s$ is the soil surface conductivity and $\tau$ is a tortuosity fac-
tor, which is defined as a linear function of $\theta$. For soils with small
specific surface, $\sigma_s$ is directly proportional to $\sigma_w$ (Santamarina
et al., 2001), which for its part is influenced by the concentra-
tion and composition of ions in the soil solution. Generally, the
conductivity of a pure electrolytic solution can be expressed as
(Oldham and Myland, 1994)

$$\sigma_w = F \sum_i \eta_i c_i |\zeta_i|$$

[5]

where $F = N_A Q_e$ is Faraday's constant describing the charge car-
ried by one mole of univalent ions (96485 C mol$^{-1}$), where $N_A$
and $Q_e$ are Avogadro's constant ($6.022 \times 10^{23}$ mol$^{-1}$) and the
elementary charge ($1.6022 \times 10^{-19}$ C), respectively, and for
each ionic species $i$, $\eta_i$ is the ionic mobility, $c_i$ is the ion con-
centration, and $|\zeta_i|$ is the ion charge number. For a given solute, $\eta_i$
is constant, hence the variation in $\sigma_w$ according to Eq. [5] is due to
a change in $c_i$, $\eta_i$, or both together. Linear relationships between
$\sigma_w$ and the concentration of different solutes in soil solutions
have been shown in numerous studies (Marion and Babcock,
1976; Heimovaara et al., 1995; Wraith and Das, 1998; Das et
al., 1999), thus confirming the feasibility of estimating the ionic
concentration via $\sigma_w$. Das et al. (1999) observed a linear corre-
lation between NO$_3$ concentration and $\sigma_w$ of soil solutions ex-
tracted from field sample cores ($R^2 = 0.98$), but they noted that
any calibrated relationship could provide only an approximate
estimate of the NO$_3$ level due to the spatiotemporal variation of
NO$_3$ contributions to the total soil solution ionic concentration.
Consequently, they concluded that this approach was applicable
to situations where changes in concentration of the ionic species
of interest were dominating changes in $\sigma_w$.

Ionic mobility, which describes an ionic’s ability to move un-
der the influence of an applied electrical field, is defined as the
terminal velocity of an ion under the influence of a unit electrical
field (Williams and Falkenhagen, 1929). It can also be related
to the ionic radius by the application of Stokes’ law to the ion of
interest (Santamarina et al., 2001):

$$u_i = \frac{v_i}{E} = \frac{|\zeta_i| Q_e}{6\pi \eta r_i}$$

[6]

where $v_i$ is the velocity of the $i$th ion, $E$ is the strength of the
electric field, $\eta$ is the viscosity of the solution, and $r_i$ is the hy-
drodynamic or Stokes’ radius for the hydrated ion (rather than
the radius of the crystal ion). It should be noted that Stokes’ law
assumes that ions are rigid spherical particles with homogeneous
charge distribution, which is not the case for most ions (Poirier,
1966). Despite this simplification, Eq. [6] provides insight into
the nature of ion dynamics in solutions. Particularly, it suggests
that $u_i$ is inversely proportional to the hydrodynamic size of the
ion; in other words, the smaller the $r_i$, the faster the ion moves
through a solution and the larger is its $u_i$. As a result, each ion
species will move at a different velocity under the influence of
an applied electrical field, hence the contribution of individual
ion species to $\sigma_w$ will be different even if their concentration and
charge number are equal. The number of hydrated water mol-
ecules, and consequently $r_i$, however, is not well defined (Poirier,
1966). In general, the hydration effect increases with increasing
ionic potential (the ratio of the electrical charge to the nonhy-
drated radius of an ion) making dissolved ions larger than the
corresponding crystal ions.

Equation [6], like most of the classical models, was devel-
oped for highly diluted solutions (Frank, 1966). In solutions
with finite dilution, interionic forces play an important role, in-
fluencing the mobility, $u_i$, of individual ions. The first adequate
theoretical explanation of this phenomenon was proposed by
Debye and Hückel (1923a, 1923b) by introducing the concept of
an ionic atmosphere of opposite sign surrounding every ion
in a solution (Glasstone, 1942). According to the theory, when
no external electrical field is applied to the solution, each ion is
located in the center of the spherically symmetrical ionic atmos-
phere formed as a result of the presence of Coulomb forces act-
ing between the ions (Williams and Falkenhagen, 1929). If an
external field is applied, however, this equilibrium is disturbed.
When the time for one oscillation of an alternating electric field
(1/2f) is large compared with the relaxation time of the ionic
atmosphere, the latter will be in its asymmetrical state, causing
a retarding effect on the ion motion (in addition to the electro-
phoretic force, which resists the movement of an ion in one di-
rection due to counterions heading in the opposite direction). At
these frequencies, the EC of the solution will be decreased due to
an asymmetrical distribution of charges around the ions.

If the frequency of an applied external field is high, so that
the time of one oscillation is smaller than the relaxation time, the
ionic atmosphere will not be able to reach the asymmetrical state.
Consequently, the retarding force due to the relaxation effect will
partially or entirely disappear, causing an increase in the velocity of
ions (Falkenhagen and Williams, 1929). At these frequencies, the
conductivity of a solution will be higher than at lower frequencies.
The model explaining the phenomena of frequency-dependent re-
laxation of the ionic atmosphere involves mathematical complexi-
ties that are beyond the scope of this study and can be found in
the literature on physical electrochemistry (Williams and Falken-
hagen, 1929; Falkenhagen and Williams, 1929).

According to the theory, the time of relaxation of the
ionic atmosphere depends on the mobility of the ions and the
forces between them. Hence, different ion species will show an
increase in conductivity at different frequencies. It should be
noted, however, that the ionic relaxation, like other relaxation
processes, is spread across a wide frequency range and its width,
shape, and true scale change with temperature, concentration,
permittivity of the solvent, and other physical factors (Arnold
Despite these complexities, this dispersion of conductivity, predicted by Debye and Falkenhagen (1928) at megahertz frequency for diluted solutions, was observed experimentally for different binary electrolytes, and the results were found to be in satisfactory quantitative agreement with the theory, thus confirming its validity (Arnold and Williams, 1936). Although these concepts provide great insight into the nature of ionic conductivity in solutions and allow important qualitative predictions to be made, it is difficult to use them as a basis for quantitative calculations for complex solutions with finite dilution, not to mention solutions contained in a soil–air–water matrix. One of the main reasons is the lack of a complete theory that will include all static and dynamic effects in a self-consistent manner rather than dealing with them independently (Cole, 1989). Before such a theory becomes available, empirical study of the macroscale response of the medium using high-frequency dielectric measurements may help to reveal microscale information about the composition of a material. Thus, for this study, we applied an empirical PLS approach to interpret dielectric spectra rather than attempting to develop a full theoretical model for the spectra.

MATERIALS AND METHODS

Soil
The soil used in this laboratory study was collected from the 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 a Clarion loam (a fine-loamy, mixed, superactive, mesic Typic Hapludoll). The particle size distribution was determined using the hydrometer method (Gee and Or, 2002). 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 air-dry bulk density of the sieved 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. The organic matter (OM) content was found to be about 4.9% by the loss-on-ignition method.

The Coaxial Transmission Line Test Fixture
Three identical coaxial transmission line test fixtures were constructed by the Department of Energy’s 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, forming together an enclosed transmission line within which material can be placed for measurement. To ensure a uniform electrical field throughout the soil sample and to reduce the effect of fringe capacitance on the measured permittivity, only the middle part was filled with soil. Rexolite, which has a constant relative permittivity of 2.53 within the measurement spectra used in this experiment, was placed in both rear caps. As a result, the soil sample could remain fixed in the middle part. Unwanted impedances (parasitics) induced by the test fixture were later removed from the measurements using the open-short compensation technique to obtain the true permittivity of the tested soil samples (Santamarina et al., 2001).

The rear caps were built using a stainless steel pipe with an inner diameter of 10.31 cm. Cylindrical pieces of Rexolite with an outer diameter of ∼10.31 cm were inserted into both rear caps and attached using four metal screws. Both BNC and banana connectors protruding from opposite faces of the rear caps were connected to each other through a hole in the Rexolite. The 7.62-cm high middle part of the fixture was made from the same stainless steel pipe as the rear caps and had grooves for O-rings on both sides to ensure a hermetical seal. This part was filled with soil. The central rod was made of stainless steel with an outside diameter of 1.91 cm and had special holes on both ends to be connected with banana plugs of the rear caps during assembly. 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 cm³. To facilitate homogeneous soil density during packing, the inner side of the middle part was marked at uniform distances, dividing its volume into four equal sections of 153.7 cm³.
Solutions

Twenty-four solutions with six different concentrations of KNO₃ and four different concentrations of KCl were prepared at the Iowa State University Water Quality Laboratory. The concentration of NO₃⁻-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 NO₃⁻-N concentration in Iowa fields normally ranges from 0 to >100 mg L⁻¹ during dry years and rarely exceeds 60 mg L⁻¹ during wet years (Balkcom et al., 2003; Killorn, 1990). The concentration of Cl⁻ in the prepared solutions varied from 0 to 500 mg L⁻¹, with the intention of representing 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 m³ 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 VWC. A total of five VWC levels were used during the experiment, from 0.10 to 0.30 m³ m⁻³ in increments of 0.05 m³ 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 two subsamples drawn from each individual soil sample. The first subsample was taken before packing the prepared soil mixture into the test fixture, while the second one was obtained after the spectral measurement, which took place about 10 h later. The average difference in VWC between these two subsamples was 0.001 m³ m⁻³ with a standard deviation of <0.003 m³ m⁻³. The actual soil moisture content of the samples was estimated by averaging the VWC of the subsamples measured before and after the test.

The test fixture was mounted vertically on a special stand and the top rear section was removed to get access to the middle void section while the central rod stayed fixed into the bottom rear section. The mixed soil was then transferred to the middle part of the test fixture and packed to a uniform bulk density in sections corresponding to the marked intervals. After the middle part was filled with soil, the rear section was replaced, and all sections of the test fixture were tightened down using the threaded rods and wing nuts and placed vertically into a temperature chamber for about 9 h to allow the soil sample to reach equilibrium at 25°C. Because there were three identical test fixtures, three different samples were prepared and measured each time.

After reaching equilibrium, the test fixture was removed from the chamber and connected to a Hewlett-Packard 4192A LF impedance analyzer using a 16095A probe test fixture (Agilent Technologies Japan). Data collection was accomplished via a USB-1208LS USB-based data acquisition module (Measurement Computing Corp. interfaced with a personal computer. A program written in Visual Basic for Applications for Microsoft Excel was used to automate the data acquisition process.

Data Processing and Statistical Analysis

The complex admittance (the inverse of the complex impedance) of the coaxial test fixture filled with the soil was measured at 63 frequencies ranging from 5 Hz to 13 MHz. Each sample was scanned three times across all spectra, and average values of the complex admittance were calculated at each frequency to minimize random noise variations caused by the limited precision of the measurement equipment. The open-short compensation technique was applied to the collected data to remove measurement errors induced by the test fixture (Santamarina et al., 2001). The computed error-free admittance of the sample was later used to calculate the complex relative permittivity of the soil (Agilent Technologies, 2009). Therefore, the size of the resulting data set of spectral measurement was 120 (the number of the samples) × 126 (the real and imaginary parts of the permittivity measured at 63 frequencies).

To build quantitative calibration models, PLS analysis was applied to the frequency-response data using JMP software (SAS Institute). Partial least squares is a powerful multivariate method that is widely used in analytical and measurement science to extract information about the chemical composition of a substance from spectral data (Lavine and Workman, 2005). It was originally developed for modeling high-dimensional, strongly collinear data, which is not feasible by classical least squares. Unlike other multivariate methods (such as principal components regression) that choose components based on only independent (X) variables, PLS utilizes both the independent and dependent (Y) variables to iteratively find the PLS components, called latent variables (LVs). Specifically, PLS regression searches for a set of LVs that performs a simultaneous decomposition of X and Y matrices with the objective that these LVs maximize the covariance between X and Y (Otto, 2007). This feature makes PLS models more robust for discovering hidden relationships in spectral data that are based on physical or chemical properties of materials. On the other hand, however, PLS models are only valid within the experimental domain for which they were constructed and cannot be extrapolated beyond it.

Determination of the optimal number of LVs to be included in a PLS regression model is very important for preventing an overfitting of the model. Using fewer LVs in the model can result in omitting relevant information, while using too many will incorporate noise inherent to all spectral measurements (Geladi and Kowalski, 1986). Leave-one-out cross-validation was used in our analysis to select the optimal number of LVs in the final PLS model. This method fits calibration models with different numbers of LVs to all data points except one and then uses the developed models to predict the response for the omitted point. The procedure is repeated for each data point, and the prediction residual sum of squares (PRESS) is calculated for each number of LVs using the cumulative prediction errors obtained from all models with the same number of LVs (Zhang et al., 2004; Otto, 2007; SAS Institute, 2010). The optimum number of LVs is the one that yields a minimal PRESS, although its location is not always simple to define (Geladi and Kowalski, 1986). Further
details about the PLS regression method and its statistical basis can be found in the literature (Geladi and Kowalski, 1986; Otto, 2007; Varmuza and Filzmoser, 2008).

To enhance the efficiency of the PLS method through the prevention of computational errors, the data were standardized by mean centering and scaling of all variables, so that both independent and dependent variables had a mean of 0 and standard deviation of 1 (Geladi and Kowalski, 1986; Chin et al., 2003). The real or imaginary parts of the permittivity or both together were used to estimate the soil VWC and NO$_3$–N concentration of the applied solutions. Information about the Cl$^–$ concentration in the wetting solutions was not included in any model construction. All developed models had access to the complete 63-point spectrum.

RESULTS AND DISCUSSION

Spectral Response

The measured dielectric spectra showed little variation of shape across all samples tested during the experiment, but the magnitude of the measurements changed substantially with changing VWC. The frequency dependence of the real part of the relative permittivity, the imaginary part of the relative permittivity, and the bulk EC at five different moisture levels for soil samples wetted with the solution containing 25 mg L$^{-1}$ NO$_3$–N and 50 mg L$^{-1}$ Cl are shown in Fig. 2. As expected, the real 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 at <2 MHz (Fig. 2a). Particularly, the deviation between spectral responses at 0.10 and 0.15 m$^3$ m$^{-3}$ was greater than those between the measurements at any other adjacent VWC levels. This difference diminished with increasing ionic concentration of the applied solutions (not shown).

This kind of behavior at low water content we believe to be related to a bound water effect. In general, when an aqueous solution is added to soil, a portion of the water is tightly bonded to the charged surfaces of clay particles or OM, hence making it “partially invisible” for dielectric sensing. The rest of the water is “free” and can follow the oscillating EM field before it reaches the relaxation frequency of the free water (~17 GHz). When the total soil moisture content is below or at the bound water capacity, most of the water is associated with the clay particles or OM; consequently, the free water is a small portion of the total water. By increasing the soil moisture content, more water is added to the free water pool than to the bound water, resulting in a change in the proportions between these two in favor of the free water. At some soil moisture level (in our case, near 0.15 m$^3$ m$^{-3}$), the addition of more water is mostly contributing to the free water pool. At this point, the change in dielectric response becomes proportional to the amount of added water. This VWC-proportional separation can be seen in Fig. 2a between 0.15 and 0.30 m$^3$ m$^{-3}$ soil moisture levels across all spectra.

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

Fig. 2. Change in the (a) real and (b) imaginary parts of relative permittivity and (c) the bulk electrical conductivity (EC) with volumetric water content (VWC) for soil wetted with a solution containing 25 mg L$^{-1}$ NO$_3$–N and 50 mg L$^{-1}$ Cl.
The measured imaginary permittivity was inversely proportional to the frequency, having a slope of $-1$ on the log–log plot, which indicated a constant bulk EC (Fig. 2b). Correspondingly, Fig. 2c reveals frequency-independent plateaus <1 MHz, which represent the bulk direct-current (DC) conductivity of the soil sample at each moisture level (Gulich et al., 2009). An increase in the VWC from 0.10 to 0.30 m$^3$ m$^{-3}$ on average resulted in an increase in the bulk DC conductivity values by a factor of 25. At the 1 MHz frequency, the slope of the imaginary permittivity deviated slightly from the inverse frequency relationship, and the bulk EC was no longer constant. This deviation was more pronounced at low water contents (Fig. 2b and 2c), which is believed to be related to the continuity of different pathways explained by Rhoades et al. (1989). The pathways need to be continuous for current to flow. At low soil water content, when there is little or no “free” water, the current is slowed through thin sorbed water paths close to colloid surfaces.

The effect of the NO$_3$–N concentration of the applied solutions on the soil dielectric response is shown in Fig. 3, where the real part of the relative permittivity, the imaginary part of the relative permittivity, and the bulk EC are plotted as a function of frequency for samples wetted to 0.20 m$^3$ m$^{-3}$ VWC. The concentration of Cl$^-$ in these solutions was fixed at 50 mg L$^{-1}$. Both the real and imaginary parts of the permittivity showed the same trend of increasing magnitude with increasing NO$_3$–N concentration, but the overall change was one to two orders of magnitude smaller than that induced by the change in VWC, demonstrating the dominant influence of moisture content on the soil dielectric response. Again, the imaginary permittivity 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 bulk DC conductivity in the kilohertz range, with clear NO$_3$–concentration-induced separations between spectra. The change in NO$_3$–N concentration from 0 to 200 mg L$^{-1}$ yielded an increase in the bulk DC conductivity value by a factor of only 1.4, approximately 18 times smaller than the one induced by the change in VWC. The result illustrates that the imaginary permittivity and, consequently, the bulk EC of the soil samples were more influenced by changes in VWC than by changes in the solution NO$_3$–N concentration within the ranges of moisture and NO$_3$ content tested. The effect of a change in the Cl$^-$ concentration of the wetting solutions was comparable to that observed with NO$_3$–N (data not shown). The magnitude, shape, and pattern of the spectral response were similar to those presented in Fig. 3.

Spikes in the measured bulk EC values were observed for all soil samples at >0.8 MHz. We believe that this was an artifact of the test fixture parasitics that the open-short compensation technique could not thoroughly eliminate. Because 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 the 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 real part of the relative permittivity and the VWC was slightly curvilinear (Fig. 4a). Near the 1 MHz frequency, the dependence was mostly linear (Fig. 4c). Furthermore, with an increase of the measurement frequency, the real permittivity data became less scattered, which contributed to improved model performance. The highest $R^2$ values of 0.99 were obtained for the linear models.
fitted to the real permittivity data taken at the highest frequencies (6–13 MHz), while similar models fitted to the data measured at 30 to 50 Hz had the lowest $R^2$ value of 0.83. Generally, models developed using the low-frequency (<1 MHz) data resulted in high real permittivity values at the lowest VWC level (0.10 m$^3$ m$^{-3}$). This agreed with our discussion above about the unequal separation in the real permittivity spectra observed in Fig. 2a. Similar analyses of the imaginary permittivity revealed a slightly curvilinear relationship between the imaginary part of the relative permittivity and the VWC at all frequencies. Hence, the linear models fitted to the imaginary permittivity data could not perform better than those fitted to the real permittivity at higher frequencies but did a noticeably better job at frequencies <5 kHz (with $R^2 = 0.94–0.96$). Table 1 shows the results of the models relating the real and imaginary parts of the relative permittivity to the VWC at four representative frequencies. It is worth mentioning that second-order models fitted to the data yielded better results, although the overall tendency remained the same.

### Partial Least Squares Analysis

Partial least squares models are very sensitive to changes in environmental, sampling, and instrument conditions (Brown et al., 2005). The degree to which each factor affects the applicability of specific PLS models to a wider range of conditions or experimental setups can vary significantly. For this reason, we do not report the mathematical formulations of the PLS models here.

The summary of the PLS regression analysis for different models using the dielectric response data from all soil moisture and ionic concentration levels across all spectra is shown in Table 2. All three global models performed well in estimating the VWC (each model capturing about 99% of variation in soil moisture) having an RMSE of 0.02 m$^3$ m$^{-3}$, the same as that achieved by Zhang et al. (2004), yet none of them managed to estimate the NO$_3^-$-N concentration of the applied solution with good accuracy. The model based on the imaginary part of the permittivity performed the best, explaining about 33% of NO$_3^-$-N variation with a RMSE of 57 mg L$^{-1}$, but this was about four times greater than the RMSE of the global model reported by Payero et al. (2006), although the

### Table 1. Output of linear regression models relating the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the permittivity to the volumetric water contents (VWC) at individual frequencies.

<table>
<thead>
<tr>
<th>Linear model</th>
<th>Model parameters</th>
<th>$R^2$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon' = f(VWC)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 Hz</td>
<td>$-548,779$</td>
<td>50,868</td>
<td>0.831</td>
</tr>
<tr>
<td>100 Hz</td>
<td>$-72,466$</td>
<td>7,521</td>
<td>0.837</td>
</tr>
<tr>
<td>1 kHz</td>
<td>$-1,400$</td>
<td>196</td>
<td>0.875</td>
</tr>
<tr>
<td>13 MHz</td>
<td>$1.183$</td>
<td>0.171</td>
<td>0.986</td>
</tr>
<tr>
<td>$\varepsilon'' = f(VWC)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 Hz</td>
<td>$-2,597,580$</td>
<td>246,091</td>
<td>0.922</td>
</tr>
<tr>
<td>100 Hz</td>
<td>$-840,903$</td>
<td>80,156</td>
<td>0.917</td>
</tr>
<tr>
<td>1 kHz</td>
<td>$-85,998$</td>
<td>8,324</td>
<td>0.917</td>
</tr>
<tr>
<td>13 MHz</td>
<td>$-6.761$</td>
<td>0.734</td>
<td>0.923</td>
</tr>
</tbody>
</table>

### Table 2. Output of partial least squares models for estimating the volumetric water content (VWC) and NO$_3^-$-N concentration simultaneously using the spectral response obtained at all moisture and ionic concentration levels.

<table>
<thead>
<tr>
<th>Data used in model</th>
<th>LV†</th>
<th>PRESS‡</th>
<th>Variation Explained for</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>VWC  NO$_3^-$-N</td>
</tr>
<tr>
<td></td>
<td>no.</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Real permittivity ($\varepsilon'$)</td>
<td>2</td>
<td>0.683</td>
<td>98.78</td>
</tr>
<tr>
<td>Imaginary permittivity ($\varepsilon''$)</td>
<td>6</td>
<td>0.619</td>
<td>98.88</td>
</tr>
<tr>
<td>Both ($\varepsilon'$ and $\varepsilon''$)</td>
<td>4</td>
<td>0.671</td>
<td>99.19</td>
</tr>
</tbody>
</table>

† Latent variables
‡ Prediction residual sum of squares.

---

Fig. 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.
range in soil water NO$_3$–N concentrations in their study (maximum concentration <90 mg L$^{-1}$) was less than half the range in NO$_3$–N in the wetting solutions used in our study. The RMSE values of the other two models were 65 and 63 mg L$^{-1}$.

The slight advantage of the model based on the imaginary permittivity in estimating the NO$_3$–N concentration stems from the fact that EC primarily manifests through the imaginary part of the permittivity. On the other hand, it should be noted that the number of LVs used by this model was the highest compared with 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 using only the imaginary permittivity data. The dashed lines are 1:1 fits corresponding to the ideal estimation. It can be easily seen that the PLS model underestimated the NO$_3$–N concentration at the high end and overestimated it at the low end.

Because the contribution of $\sigma$$_w$ (according to Eq. [4]), hence the effect of pore water ionic concentration on permittivity measurements, 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 3. In general, all models estimated the VWC better than the change in NO$_3$–N concentration of the wetting solution. This could be explained by the fact that the soil water content has a stronger effect on both the real and imaginary parts of the 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 the spectral response. The RMSE of the models for moisture content varied only from 0.015 to 0.018 m$^3$ m$^{-3}$. Furthermore, accuracy of the VWC estimations by the models using the real permittivity, the imaginary permittivity, or both together were not statistically different ($P = 0.05$).

As was expected, estimation of NO$_3$–N concentration improved noticeably by elimination of the low-VWC data (Table 3). Again, the models constructed using only the imaginary permittivity performed better than those based on only the real permittivity or both together (Table 3). This advantage of the models based on only the imaginary permittivity over those that used both the real and imaginary permittivity data, which might seem strange, stems from the nature of the PLS regression technique. Particularly, PLS uses all available data to build a calibration model by discerning signal (i.e., useful information) from noise. Because the real permittivity data carried less information about the NO$_3$–N concentration, adding them to the imaginary permittivity only amplified the noise in the combined data, thus diminishing the PLS’s ability to see the variation pattern related to the NO$_3$–N concentration.

Subsequent removal of the low-VWC data further enhanced the NO$_3$–N estimation accuracy of the developed models. This Table 3. Results of partial least squares models for estimating the volumetric water content (VWC) and NO$_3$–N concentration obtained through elimination of the low moisture concentration data.

<table>
<thead>
<tr>
<th>Data used in model</th>
<th>LV†</th>
<th>PRESS‡</th>
<th>Variation Explained for VWC</th>
<th>NO$_3$–N</th>
</tr>
</thead>
<tbody>
<tr>
<td>VWC &gt; 0.10 m$^3$ m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Real permittivity ($\varepsilon'$)</td>
<td>2</td>
<td>0.670</td>
<td>98.43</td>
<td>16.52</td>
</tr>
<tr>
<td>Imaginary permittivity ($\varepsilon''$)</td>
<td>6</td>
<td>0.595</td>
<td>98.24</td>
<td>41.26</td>
</tr>
<tr>
<td>Both ($\varepsilon'$ and $\varepsilon''$)</td>
<td>4</td>
<td>0.650</td>
<td>98.84</td>
<td>25.56</td>
</tr>
<tr>
<td>VWC &gt; 0.15 m$^3$ m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Real permittivity ($\varepsilon'$)</td>
<td>2</td>
<td>0.650</td>
<td>98.14</td>
<td>23.49</td>
</tr>
<tr>
<td>Imaginary permittivity ($\varepsilon''$)</td>
<td>6</td>
<td>0.553</td>
<td>97.73</td>
<td>56.19</td>
</tr>
<tr>
<td>Both ($\varepsilon'$ and $\varepsilon''$)</td>
<td>5</td>
<td>0.587</td>
<td>98.54</td>
<td>46.11</td>
</tr>
<tr>
<td>VWC &gt; 0.20 m$^3$ m$^{-3}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Real permittivity ($\varepsilon'$)</td>
<td>2</td>
<td>0.640</td>
<td>94.36</td>
<td>33.20</td>
</tr>
<tr>
<td>Imaginary permittivity ($\varepsilon''$)</td>
<td>5</td>
<td>0.539</td>
<td>94.23</td>
<td>64.60</td>
</tr>
<tr>
<td>Both ($\varepsilon'$ and $\varepsilon''$)</td>
<td>2</td>
<td>0.623</td>
<td>96.22</td>
<td>36.28</td>
</tr>
</tbody>
</table>

† Latent variables
‡ Prediction residual sum of squares.
confirmed that the contribution of the solution ionic conductivity to the bulk soil EC (hence to the imaginary part of the permittivity) had a larger effect at high VWC levels, making it easier to estimate the change in the NO₃–N concentration. Despite this improvement, the RMSE of the PLS models constructed using the imaginary part of the permittivity measured at 0.25 and 0.30 m³ m⁻³ of VWC was only 27% better than the RMSE of the similar model using all VWC spectra (41 compared with 57 mg L⁻¹).

It should also be emphasized that the models constructed using the imaginary permittivity had the highest number of LVs determined through the cross-validation process. Normally, it is regarded as a good sign if the number of LVs selected is close or equal to the number of major factors influencing the variation pattern in the spectral data. The high number of LVs indicated that there was a high variation in the imaginary permittivity spectra that could not be sufficiently explained by changes in VWC and NO₃–N concentration only. One of the main sources of this variation was the changing Cl⁻ concentration in the soil, mostly stemming from the samples that were wetted with the solutions containing 500 mg L⁻¹ Cl⁻. Therefore, alternative PLS models were developed to test the effect of the wetting solution Cl⁻ concentrations on NO₃–N estimation using solely the imaginary part of the permittivity.

The measurements from the samples wetted with the solutions containing 500 mg L⁻¹ Cl⁻ were removed from the data. The PLS models were constructed to estimate the NO₃–N concentration and soil moisture content at fixed VWC levels. It should be noted that the actual moisture content of the soil samples deviated slightly from each other at each designed VWC level. Because the influence of VWC on the permittivity measurement was much greater than that of NO₃–N, these little deviations in VWC could propagate through PLS regression as an error. To eliminate this unwanted error, we decided to include the actual soil moisture content in the PLS regression. Figure 6 summarizes the outcomes of the fitted models. In general, the calibration capability of the PLS regression method significantly improved when the VWC level was higher. The best models were found at the 0.25 and 0.30 m³ m⁻³ moisture levels, having $R^2$ values of 0.87 and 0.93 and RMSE values of 25 and 19 mg L⁻¹, respectively. The results of the actual vs. estimated NO₃–N for these best models are shown in Fig. 7.

**CONCLUSIONS**

In this laboratory study, the influence of soil moisture content and NO₃–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. Partial least squares regression analysis was used for simultaneous estimation of VWC and NO₃–N concentration using the permittivity measurements.

The PLS models based on the real and imaginary parts of the permittivity (both separately and together) gave equally good estimates of the soil moisture content, with RMSE < 0.02 m³ m⁻³. Linear models using the real permittivity measured at a single frequency >1 MHz performed better (RMSE < 0.01 m³ m⁻³) than the models based on lower frequency measurements. This
agrees with our visual observation made on the dielectric spectra that the VWC-induced changes in the real part of the permittivity at <2 MHz were disproportional to the VWC levels. As a result, the PLS models that used the data from all spectra incorporated the noise associated with the low-frequency measurements, which diminished the models’ ability to recognize major variation patterns in the VWC. Hence, to improve the accuracy of the PLS regression models, soil moisture content should be estimated using measurements obtained at >1 MHz or using linear models developed for the same frequencies.

The NO$_3$–N concentration was estimated with low accuracy by all three global models compared with the results of Payero et al. (2006). The RMSE values of the models developed by the latter were four times smaller than those obtained with our global models. This difference may be attributed to the fact that the fertilizer (NH$_4$NO$_3$) applied to the soil in their study contained only NO$_3$ anions, while the solutions added to the soil samples in our experiment also included Cl anions with a maximum concentration exceeding that of NO$_3$. When we removed the measurements of the samples having Cl contents greater than that of NO$_3$, however, the RMSE values of the obtained PLS models decreased by a factor of three, thus becoming comparable to those reported by Payero et al. (2006). Another reason for the relatively poor performance of our models could be that the NO$_3$–N concentration of the added solutions rather than of the pore water was used in the PLS analysis. The actual soil water NO$_3$–N concentration might have changed from that of the applied solution after the 9-h thermal equilibration process due to biotic or abiotic N cycling. Therefore, using NO$_3$–N concentrations of the actual soil solutions rather than of the applied solutions could further improve the accuracy of the PLS models and should be taken into account in future studies.

The results of PLS analysis showed that the imaginary part of the permittivity carried more information about NO$_3$ and less noise than the real part. As a result, the models constructed using the imaginary permittivity performed significantly better in estimating the NO$_3$–N concentration than those based on the real part or the real and imaginary parts of the permittivity. In addition, the study revealed that the accuracy of NO$_3$–N concentration estimates improved with increasing soil moisture content, particularly by the elimination of low-VWC measurements. For example, the RMSE of the PLS model constructed using the imaginary part of the permittivity measured at 0.25 and 0.30 m$^3$ m$^{-3}$ of VWC was 41 mg L$^{-1}$ compared with 57 mg L$^{-1}$ for the global model developed using the similar data from all VWC levels.

As a whole, the study had limited success in estimating the soil solution NO$_3$–N concentration with desirable accuracy (RMSE < 5 mg L$^{-1}$). The introduction of a high Cl$^-$ concentration into the soil solution hindered the PLS analysis’s capability to detect variation patterns in the spectral data associated with NO$_3$. When NO$_3$ was the dominant anionic species in the solution and VWC was high (>0.20 m$^3$ m$^{-3}$), however, the accuracy achieved by the PLS models was very close to those reported in the literature, hence demonstrating the feasibility of the proposed approach to monitor NO$_3$–N dynamics in soil. It should be noted that these experiments were conducted at constant temperature with the intention of eliminating temperature-induced variation in the soil dielectric response; therefore, the obtained results are likely to be better than what would be observed in the field. To explore the true potential of the proposed approach, we believe that more extensive laboratory studies are needed that will incorporate several soil types, various solutions with different ionic concentrations and temperatures, and a broader frequency range. Particularly, extension of the permittivity measurements to higher frequencies (up to 1 GHz), where ion-specific dispersion of conductivity should manifest due to the Debye–Falkenhagen effect, would be of great interest.

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