

USE OF TIME DOMAIN REFLECTOMETRY FOR CONTINUOUS MONITORING OF NITRATE-NITROGEN IN SOIL AND WATER

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ABSTRACT. Nitrate-Nitrogen ($\text{NO}_3\text{-N}$) losses to ground and surface water are an environmental and agronomic concern in modern crop production systems in the Central Great Plains. Monitoring techniques for nitrogen use in agricultural production are needed to increase crop yield, optimize nitrogen use, and reduce $\text{NO}_3\text{-N}$ leaching. Time domain reflectometry (TDR) could potentially be calibrated to continuously measure $\text{NO}_3\text{-N}$ in soil and water. The objectives of this study were to: (1) evaluate the effect of different factors affecting the response of the bulk electrical conductivity (ECb) sensed by TDR, (2) compare the sensitivity and differences between vertically-installed and horizontally-installed probes for measuring $\text{NO}_3\text{-N}$ leaching in the soil profile, and (3) evaluate the feasibility of using TDR to measure changes in $\text{NO}_3\text{-N}$ concentration in an irrigated agricultural soil. Studies were conducted in the laboratory and in the field at the University of Nebraska West Central Research and Extension Center in North Platte, Nebraska. Temperature of the medium (T_s), solute concentration, TDR cable length, and volumetric soil water content (θ_v) all influenced and were linearly related to the bulk electrical conductivity (ECb) sensed by the TDR probes. In the field, measured soil $\text{NO}_3\text{-N}$ correlated well with values estimated using TDR measurements of ECb, corrected for changes in θ_v and T_s . These results indicated that TDR, if properly calibrated for a particular soil, could be used to continuously monitor $\text{NO}_3\text{-N}$ in soil, and should also be well-suited for monitoring $\text{NO}_3\text{-N}$ in groundwater and surface water. It is, however, important to perform the calibration over a long enough period of time to include the expected range of θ_v , T_s , and $\text{NO}_3\text{-N}$ values to obtain adequate accuracy.

Keywords. Time domain reflectometry, TDR, Nitrate, Nitrogen, Electrical conductivity, Salinity.

Nitrate-Nitrogen ($\text{NO}_3\text{-N}$) losses to ground and surface water are an environmental and agronomic concern in modern crop production systems in the Central Great Plains. For example, in Nebraska the application of commercial fertilizers and manures to continuous corn and other cropping systems has increased $\text{NO}_3\text{-N}$ concentrations in ground water (Owens et al., 1995). Gosselin et al. (1997) found that in Nebraska, 19% of over 1800 domestic wells tested exceeded the national primary drinking water standard of $10 \text{ mg L}^{-1} \text{ NO}_3\text{-N}$ imposed by the U.S. Environmental Protection Agency (EPA). Best management practices are currently being used and developed to increase the N use efficiency of crops and reduce $\text{NO}_3\text{-N}$ leaching to ground water. Improved monitoring of soil $\text{NO}_3\text{-N}$ is important in assessing current best management practices

and developing new ones. Time domain reflectometry (TDR) is a technique that could potentially be adapted for continuous monitoring of $\text{NO}_3\text{-N}$ in soil and water.

In the TDR method, a very fast rise time step voltage increase is applied to a coaxial cable that carries the pulse to a probe that is placed in the soil, water, or other medium. A combination of cable tester and oscilloscope is commonly used to provide the voltage step and capture the reflected waveform (Evet, 2000a). Typically, multiple TDR probes can be attached to a single cable tester via multiplexers. The system is usually controlled by a personal computer or datalogger, which may include software to interpret the reflected waveform. The characteristics of the medium surrounding the probe can considerably affect the shape of the reflected waveform. The velocity of the applied pulse, and therefore its travel time along the length of the probe, is affected by the dielectric constant of the medium, which in soil is mainly dependent on water content. The amplitude of the reflected waveform, on the other hand, is mainly affected by the electrical conductivity of the medium (Campbell Scientific, Inc., 2002). Therefore, by properly interpreting the horizontal distance and amplitude (vertical distance) of the reflected waveform, characteristics of the medium, such as water content and bulk electrical conductivity, can be obtained from TDR measurements (Giese and Tiemann, 1975; Topp et al., 1980; Evett, 2000b).

In a heterogeneous medium like soil, TDR measurements integrate the characteristics of the soil mineral particles, soil solution, soil air spaces, and organic components. Since the TDR probes can only sense a very limited soil volume, it is important that probes are installed with good contact with the soil, which can be quite challenging. Perfect contact, however, is easy to obtain when measurements are made in

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a liquid and homogeneous medium like water. Also, as with any other sampling technique, probes need to be installed in representative areas to minimize the effect of spatial variability.

TDR technology has the potential to continuously monitor $\text{NO}_3\text{-N}$ in soil and has several potential advantages over traditional soil core sampling. Measurements from TDR can be automatically taken at the same location on a continuous basis with the use of dataloggers. The cost of soil analysis and labor restrictions prevents continuous measurement of soil $\text{NO}_3\text{-N}$ by soil sampling. Also, disturbance of the soil horizon due to the core extraction inhibits sampling in the same location over time.

The use of TDR technology in agriculture has mainly focused on monitoring soil water content (Topp et al., 1980), but TDR can also measure bulk electrical conductivity (ECb). Once installed, TDR is a non-destructive monitoring technique that can provide high temporal resolution, since TDR probes can be connected to a datalogger and sampled as often as needed. In recent years, interest in using TDR to measure ECb and thus follow $\text{NO}_3\text{-N}$ dynamics in agricultural soils has increased in part due to its automatic datalogging capabilities (Noborio et al., 2003). The rationale is that ions, such as $\text{NO}_3\text{-N}$, increase the ECb of the soil, and TDR probes inserted in the soil can sense these changes in ECb. If no electrolytes are applied to the soil, other than the $\text{NO}_3\text{-N}$ from irrigation water and/or fertilizer, then any change in ECb at a given depth in the soil could be assumed to be the result of changes in the concentration of $\text{NO}_3\text{-N}$. The concentrations of $\text{NO}_3\text{-N}$ in soil can then be determined by developing calibration curves relating $\text{NO}_3\text{-N}$ concentration and ECb measured by TDR (Mallants et al., 1996; Hart and Lowery, 1998; Nissen et al., 1998). TDR technology has been used successfully, mainly in laboratory experiments, to measure solute transport in soil columns using different electrolyte tracers (Wraith et al., 1993; Ward et al., 1994; Vancloster et al., 1995; Risler et al., 1996; Hart and Lowery, 1998).

Kim et al. (1998) developed a calibration method that can be applied to horizontally positioned TDR probes *in situ* in solute transport studies. They proposed a non-linear model assuming a two-pathway conductance. Using the quadratic form, the non-linear model equated electrical conductivity in the immobile phase of soil solution in a series-coupled pathway with electrical conductivity in the mobile phase of soil solution in a continuous pathway. They related bulk soil electrical conductivity to electrical conductivity of soil water, assuming constant electrical conductivity during breakthrough. They showed that a simple linear model was better than the non-linear model in terms of mass recovery. In addition, parameters of the solute transport model were not affected within 20% of uncertainty in the slope coefficient of the simple linear model when compared with the reference method. They concluded that the simple linear model was practical, especially for soil columns showing preferential flow, and that it could be readily applied to field conditions. Das et al. (1999) evaluated the potential use of TDR to simultaneously estimate volumetric soil water content, soil solution electrical conductivity, and soil $\text{NO}_3\text{-N}$ concentrations in an irrigated peppermint (*Mintha piperita* L.) field using simple models and calibration methods for a fine-sandy soil. They compared TDR-estimated $\text{NO}_3\text{-N}$ concentrations

with those obtained from soil cores and soil solution samplers at three depths, and over a wide range in applied potassium nitrate (KNO_3). Estimates of $\text{NO}_3\text{-N}$ concentrations using TDR exhibited similar pattern, magnitude, and variance to those based on direct soil measurements.

Vogeler et al. (2000) successfully followed solute movement in unsaturated leaching experiments in the laboratory using two soil columns. Their results suggested that TDR could be a valuable *in situ* technique for monitoring solute transport through soil. Lee et al. (2002) determined dispersion coefficient, immobile water content, and mass exchange coefficients using TDR and used them in a mobile-immobile model. They compared the TDR-estimated parameters and the measured parameters from the effluent data. They studied whether the TDR-determined parameters from the surface 2-cm soil layer could be used to predict effluent breakthrough curves at the 20-cm depth. The TDR-determined parameters were used to calculate effluent breakthrough curves. They found that calculated breakthrough curves were very similar to measured values, which led them to conclude that TDR data obtained from shallow soil layers could be used to describe solute transport through undisturbed soil cores.

Most of the afore-mentioned studies have been conducted under laboratory conditions using re-constructed soil columns from coarse-textured soils. Few data relating field-measured and TDR-estimated $\text{NO}_3\text{-N}$ concentration under field conditions exist. In addition, there is a need to investigate parameters such as temperature of the medium, water content, and cable length that might influence the response of the bulk electrical conductivity, as measured with TDR, in medium-textured soils. The objectives of this study were to: (1) evaluate the effect of different factors affecting the response of the bulk electrical conductivity (ECb) sensed by TDR, (2) compare the sensitivity of vertically-installed and horizontally-installed probes for measuring $\text{NO}_3\text{-N}$ leaching in soil, and (3) evaluate the feasibility of using TDR to measure changes in $\text{NO}_3\text{-N}$ concentration in an irrigated agricultural soil.

MATERIALS AND METHODS

EXPERIMENTS AND SITE DESCRIPTION

This study included a series of laboratory and field experiments (in soil and water) to evaluate the effect of different factors on the measurement of ECb using TDR. The factors evaluated were: TDR cable length, temperature of the medium (soil or water), solute concentration, soil water content, and probe orientation. Since the ultimate goal was to monitor $\text{NO}_3\text{-N}$ dynamics in agricultural soil, the solute used in this study was ammonium nitrate (NH_4NO_3), which is a common source of nitrogen fertilizer in agricultural production. The study was conducted at the University of Nebraska West Central Research and Extension Center, in North Platte, Nebraska (41.1°N, 100.8°W, elevation = 861 m), from 2001 to 2004. The soil used in the study is mapped as a Cozad silt loam (*Fluventic Haplustolls*); however, soil analysis of samples taken from the research site showed that the top 1.2 m of the soil profile has a loam texture. This soil has water content at field capacity of $0.29 \text{ m}^3 \text{ m}^{-3}$ and permanent wilting point of $0.11 \text{ m}^3 \text{ m}^{-3}$ (Klocke et al., 1999). The soil profile properties at the

Table 1. Soil profile properties at North Platte.^[a]

Soil Depth (m)	O.M		BD (Mg m ⁻³)	NH ₄ OAc Exchangeable Bases (mg kg ⁻¹)				CEC (cmol _c kg ⁻¹)	EC (dS m ⁻¹)	Soil Texture ^[b]	Particle Size Distribution (%)		
	pH	(%)		K	Ca	Mg	Na				Sand	Silt	Clay
0–0.2	6.0	2.4	1.55	626	1950	387	57	15.8	1.80	L	41	38	21
0.2–0.6	7.3	1.4	1.45	289	2340	332	18	15.3	0.90	L	41	38	21
0.6–0.9	7.6	0.9	1.39	204	2320	340	13	15.0	0.84	L	36	43	21
0.9–1.2	7.8	1.1	1.39	256	2570	314	18	16.2	0.92	L	41	38	21
1.2–1.5	7.7	0.9	1.40	258	2240	247	30	14.1	0.84	SaL	61	23	16
1.5–1.8	7.8	1.1	–	323	2390	250	43	15.0	0.80	SaCL	61	18	21
1.8–2.1	7.7	1.5	–	404	2770	313	93	17.9	0.92	L	51	28	21

[a] pH was measured using a 1:1 (soil:water) ratio, O.M = organic matter, BD = bulk density (adapted from Klocke et al., 1993), CEC = cation exchange capacity, EC = soil electrical conductivity,

[b] L = loam, SaL = sandy loam, SaCL = sandy clay loam.

research site obtained from samples taken in 2004 are shown in table 1.

DESCRIPTION OF TDR SYSTEM

All measurements were made using equipment obtained from Campbell Scientific Inc., (Logan, Utah). Bulk electrical conductivity was measured using CS610 TDR probes. Each probe had three stainless steel rods (30 cm long × 0.476-cm diameter, and 4.5-cm spacing between the outer rods) and was connected to the data acquisition system through a RG8 low loss coaxial cable. TDR cable lengths of 12 and 24 m were used to determine the effect of cable length on the EC_b measurements. The cables were connected to a TDR100 cable tester through a SDMX50 multiplexer. Measurements were taken either manually or automatically for different stages of the study. For the manual measurements, the TDR100 system was connected to a laptop computer. The PCTDR software (version 2.07) supplied by the manufacturer of the TDR100 system was used to collect TDR waveforms and to calculate EC_b and soil water content. Continuous automatic measurements were taken by connecting the TDR100 system to a CR10X datalogger. During the laboratory experiment, the temperature of the medium was measured using TCAV averaging thermocouple probes, which were also connected to the CR10X datalogger. Power for the TDR100 and the CR10X was supplied by a 12-V battery. The PCTDR and datalogger softwares used in this study calculated EC_b by analyzing the TDR waveform based on the theory of Giese and Tiemann (1975) as:

$$EC_b = K_p (Z_c)^{-1} (1 - \rho)(1 + \rho)^{-1} \quad (1)$$

where

EC_b = bulk electrical conductivity (S m⁻¹)

K_p = probe constant

Z_c = cable impedance (50 ohm)

ρ = reflection coefficient (unitless), which is the ratio of the reflected voltage to the applied voltage (-1 ≤ ρ ≤ 1).

The probe constant (K_p) can be determined empirically; however, the manufacturer recommended a value of K_p = 174 for the CS610 probes used in this study (Campbell Scientific, Inc., 2002).

LABORATORY EXPERIMENTS IN WATER

Effect of Solute Concentration on EC_b

The relationship between EC_b readings and solute concentration in water was tested in a laboratory experiment

conducted on 12 April 2001. Five liters of distilled water were added to a plastic container (fig. 1). NH₄NO₃ was added to the water, first in 0.1 g L⁻¹ incremental rates from 0.1 to 2 g L⁻¹ and then in 1 g L⁻¹ incremental rates from 3 to 14 g L⁻¹. A TDR probe with a cable length of 12 m was inserted in the solution and EC_b readings were taken after each incremental addition of NH₄NO₃. The average of four readings from each concentration was recorded. The TDR waveforms produced by solutions with NH₄NO₃ concentrations of 0.008, 0.19, and 0.32 S m⁻¹ were also recorded using the PCTDR software. Each TDR waveform consisted of 250 data points.

Effect of Cable Length on EC_b

The effect of cable length on EC_b reading was tested during a laboratory experiment conducted on 17 July 2001. EC_b readings from solutions at three different NO₃-N concentrations were measured using TDR probes with two cable lengths. Six of the TDR probes had cable lengths of 24 m and five had lengths of 12 m. One of the concentrations tested was plain distilled water. The other two solutions were prepared by adding 5 and 10 g of NH₄NO₃ fertilizer to 5 L of distilled water in the plastic container shown in figure 1. The average of three EC_b readings from each of 11 TDR probes inserted in the solutions was recorded.

Effect of Water Temperature on EC_b

The effect of temperature on EC_b readings was tested during a laboratory experiment conducted during 15-



Figure 1. Performing water TDR calibrations in the laboratory.

24 October 2001. During this experiment, ECb readings were taken from solutions with five different NH_4NO_3 concentrations. Solutions with concentrations of 0, 0.2, 0.6, 0.8, and 1.2 g L^{-1} were prepared in separate plastic containers (fig. 1). ECb readings from each solution were taken using TDR probes with cable lengths of 12 and 24 m. The temperature of the solutions was adjusted from approximately 10°C to 38°C by immersing the containers in cold and hot water baths. A thermocouple was immersed in a separate container to monitor water temperature. ECb and temperature readings were taken automatically every 10 min using a CR10X datalogger.

LABORATORY EXPERIMENTS IN SOIL

Effect of Soil Water Content, Soil Temperature, and Solute Concentration

The effect of soil water content, soil temperature, and solute concentration on ECb reading in soil under unsaturated conditions was evaluated using a laboratory experiment conducted during 4 April to 21 June 2001. For this experiment, five plastic containers were filled with 7 kg of oven-dried surface soil collected at the research site, which was previously sieved and mixed (fig. 2). Soil was placed in the containers by adding small increments and packing thin layers (approximately 0.10 m) in order to create a soil mass of relatively uniform bulk density. The soil in each container was then wetted to near saturation with one of five solutions with different NH_4NO_3 concentrations, which had ECb readings of 0.007, 0.0166, 0.0299, 0.0540, and 0.0959 S m^{-1} . A TDR probe was inserted in the soil of each container to measure ECb and volumetric soil water content. A TCAV averaging soil thermocouple was inserted vertically at the surface of two of the containers to measure the average soil temperature. TDR and soil temperature measurements were taken three times a day during the daytime, at approximately 8:30, 12:00, and 16:30 h. During this period, water in the containers was allowed to evaporate, resulting in soil water contents ranging from near-saturation to near permanent wilting point.

Effect of TDR Probe Orientation and Soil Temperature on ECb

A laboratory experiment using two lysimeters was conducted during 12-29 November 2001 to compare the



Figure 2. Performing soil TDR experiments in the laboratory.

sensitivity of vertically- and horizontally-installed probes for measuring $\text{NO}_3\text{-N}$ movement in soil (fig. 3). The two lysimeters contained disturbed top soil (described in table 1) collected near North Platte, Nebraska. One of the lysimeters had three TDR probes installed horizontally at a distance of 10, 25, and 41 cm from the surface of the soil inside the lysimeter. Two TDR probes were installed vertically from the top of the soil surface in the other lysimeter. In order to measure the sensitivity of the vertically- and horizontally-installed TDR probes to changes in $\text{NO}_3\text{-N}$ concentration, the same amount of NH_4NO_3 fertilizer was applied to the top of each lysimeter, at a rate of 224 kg N ha^{-1} . This application rate was within a range that is commonly applied in irrigated corn production in Nebraska. Prior to fertilizer application, excess water was applied to the lysimeters for several days to leach out the initial residual $\text{NO}_3\text{-N}$ from mineralization and past fertilizer applications. The lysimeters were continuously irrigated with a drip system, so that near-saturation conditions were maintained. A TCAV averaging soil thermocouple was inserted vertically at the surface of each lysimeter to measure the average soil temperature. The 30-min averages of ECb, soil water content, and soil temperature were continuously recorded using a CR10X datalogger. This lysimeter setup was also used on 3 September to 14 October 2001 to evaluate the effect of soil temperature on ECb under near-saturated conditions.

FIELD EXPERIMENT

To evaluate the feasibility of using TDR to estimate $\text{NO}_3\text{-N}$ concentration and movement in an irrigated agricultural soil, TDR and soil thermocouple probes were installed in a corn field. The field is used to grow sprinkler-irrigated corn under a no-till system. The CS610 TDR probes and type T soil thermocouples (105T) (Campbell Scientific Inc., Logan, Utah) were installed in two adjacent corn research plots on 17 May 2002 (fig. 4). All of the TDR probes installed in the north plot had cable lengths of 12 m, and those installed in the south plot had cable lengths of 24 m. Six TDR probes were installed horizontally at 0.3-m depth increments to



Figure 3. Laboratory lysimeter setup.

a depth of 1.8 m in each plot. The sensors were installed in a pit, which was dug by hand to avoid disturbing the site more than absolutely necessary. The pit was just big enough to allow a person to install the sensors. The soil thermocouples were installed at the same depths as the TDR probes. The sensors were installed assuring good contact with the soil. Once the sensors were in place, the pit was back-filled and packed trying to re-construct original soil characteristics such as soil horizons, bulk density, etc. as much as possible around the sensors. The TDR probes were attached to the data acquisition system, which consisted of a combination of a TDR100 cable tester, two SDM50 multiplexers, and a CR10X Measurement and Control System datalogger (Campbell Scientific Inc., Logan, Utah). Power to the system was supplied with a 12-V battery, which was continuously recharged from an AC power outlet using a trickle charger. Hourly soil water content, soil temperature, and ECb data were collected during 2002-2004.

Several times each year, three 10-cm soil core samples were taken from 0.3-m depth increments to a depth of 1.8 m. The soil cores were taken from a distance of approximately



Figure 4. TDR probes and soil thermocouples installed in the field.

4.5 m east of the TDR probes. Sampling dates were 11 April, 31 May, 19 June, 1 August, 16 September, and 7 November in 2002, and 1 May, 4 June, 24 July, and 28 October in 2003. In 2004, soil samples were taken on 5 May, 23 June, 30 June, 30 July, and 5 August. Depending on crop height, soil samples were taken using either a manual soil probe or a hydraulic soil probe mounted on a tractor (Giddings Machine Company, Inc., Windsor, Colo.). For each sampling date, three cores for each depth were combined and a sub-sample was analyzed for $\text{NO}_3\text{-N}$ concentration using the procedures outlined by Keeney and Nelsen (1982). Each year, the corn plots received 75 L ha^{-1} (8 gal acre^{-1}) of 10-34-0 starter fertilizer at planting time and 202 kg N ha^{-1} ($180 \text{ lb N acre}^{-1}$) as NH_4NO_3 (34-0-0) when the crop reached a height of approximately 40 to 50 cm (16 to 20 in.). Irrigation to the plots was applied with a solid-set sprinkler system as part of a larger deficit irrigation experiment. Irrigation, soil water, and rainfall supplied approximately 89%, 79%, and 91% of seasonal crop water requirements during 2002, 2003, and 2004, respectively. More details about irrigation management have been given in Tarkalson et al. (2006) and Payero et al. (2006).

The effect of soil temperature on ECb in soil under unsaturated conditions was evaluated in the field using TDR data collected at 12:00 h during the non-growing season (15 October to 25 December 2003). By this time, the sensors had been installed in the field for two complete growing seasons. During this period, the soil water content at each depth was practically constant due to lack of rain or irrigation combined with low evapotranspiration rates. Even though soil water content was near-constant for a given depth, soil temperature changed significantly during this period at all soil depths. This situation enabled us to isolate and evaluate the effect of temperature on ECb readings under field conditions.

STATISTICAL ANALYSES

The statistical analyses were conducted using the SAS[®] System for Windows[®] statistical software (SAS Institute, Inc., Cary, N.C.). Analyses included simple and multiple linear regression and descriptive summary statistics (mean, standard deviation, number of values, maximum, minimum, and range). Regression analyses were used to develop relationships between $\text{NO}_3\text{-N}$ concentration, temperature and bulk electrical conductivity in water, and between $\text{NO}_3\text{-N}$ concentration, temperature, water content, and bulk electrical conductivity in soil.

RESULTS AND DISCUSSION

LABORATORY EXPERIMENTS IN WATER

Effect of Solute Concentration on ECb

The collected TDR waveforms were significantly affected by changes in solute concentration (fig. 5). The irregular shape of the waveforms is a result of changes in impedance as the step voltage travels through the coaxial cable, the probe handle, the probe rods, and the open circuit that occurs at the rod ends (Evet, 2000b). Changing the ECb of the solution from 0.008 to 0.32 S m^{-1} drastically changed the reflection coefficient measured at the maximum apparent distance from approximately 0.35 to -0.85 . These differences in amplitude of the waveform are the principle used to calculate ECb from

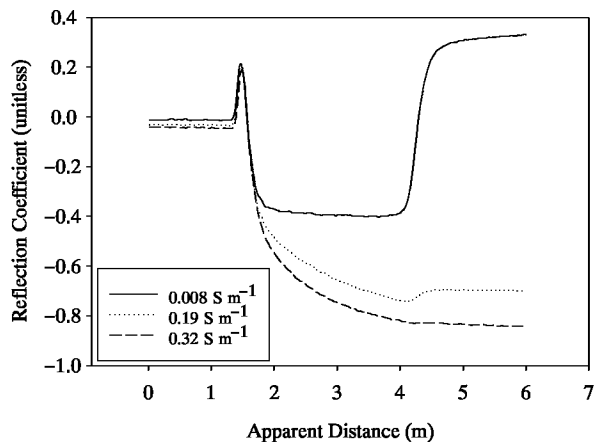


Figure 5. Waveforms obtained with a TDR probe immersed in solutions with three bulk electrical conductivities.

TDR measurements (Giese and Tiemann, 1975; Evett, 2000b; Castiglione and Shouse, 2003).

Figure 6 shows that a very good linear relationship existed between the concentration of NH_4NO_3 in the solution and the TDR ECb readings ($r^2 = 0.99$). These results suggest that TDR, if properly calibrated, could be used to accurately measure concentration of solutes that, like NH_4NO_3 , change the concentration of $\text{NO}_3\text{-N}$ in water. It should be noted, however, that other factors that could have changed the ECb reading (temperature and TDR cable length) were kept constant during this test. These factors are not necessarily constant in all situations; therefore, their effects should be evaluated and taken into account in other applications.

Effect of Cable Length on ECb

When the ECb readings from solutions with three different concentrations were measured using TDR probes with two different cable lengths, the average ECb reading increased linearly with concentration for each cable length (fig. 7). The linear relationship, however, was different for each of the two cable lengths, with the slope of the regression line increasing as cable length increased from 12 to 24 m. When the concentration was zero, both cable lengths resulted in

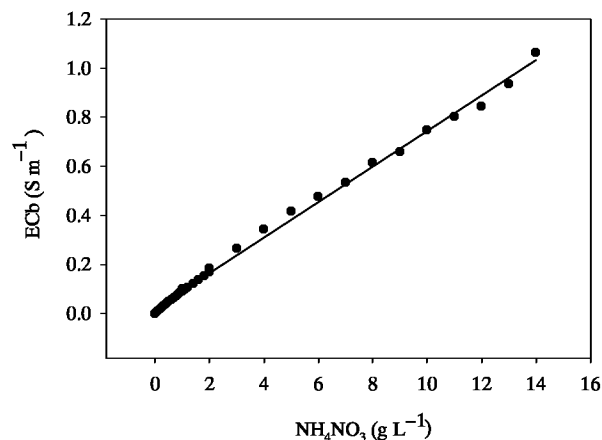


Figure 6. Relationship between solute concentration and bulk electrical conductivity (ECb) measured with TDR ($r^2 = 0.99$). Measurements obtained with TDR probes inserted into distilled water with additions of NH_4NO_3 at a constant temperature of 18°C and using a cable length of 12 m. Each point represents an instantaneous reading.

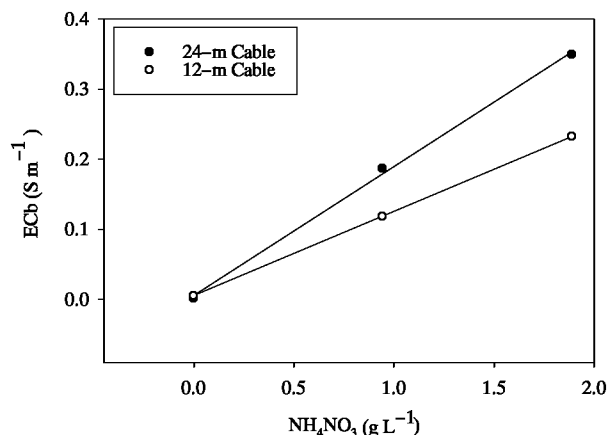


Figure 7. Effect of cable length on bulk electrical conductivity (ECb) as a function of NH_4NO_3 concentration. Measurements obtained TDR probes inserted into distilled water with additions of NH_4NO_3 at a constant temperature of 27°C . Each point represents the average of instantaneous readings obtained with six TDR probes (24-m cable) and five probes (12-m cable).

approximately the same ECb readings. However, as the concentration of the solution increased, the difference in ECb reading between the cable lengths also increased. Except when the concentration was zero, for a given concentration, the probes with the shorter cable length always resulted in lower ECb readings.

These results can be attributed to degradation of the signal emitted, which affected the TDR waveform as the cable length increased. Evett (2000b) indicated that cable length affects the waveform since the TDR cable acts as a low pass filter, which selectively attenuates the higher frequency components of the electrical pulse. More recently, Castiglione and Shouse (2003) found that for a given solution, the absolute value of the reflection coefficient decreased with the cable length and that the cable length effect was greater for highly conductive samples, which is consistent with the results shown in figure 7.

These results indicate that if several TDR probes are to be used to make comparisons between concentrations, it is important to keep the cable length constant between the probes or to develop procedures to account for the differences in cable length. Castiglione and Shouse (2003) found that the effect of cable length on ECb readings could be accounted for by scaling the reflection coefficient with respect to both the waveform in air and the waveform with the probe short-circuited. They proposed a procedure to correct for differences in cable length, which requires a relatively simple calibration. In this study, however, this procedure was not used since it required calibrating each of the TDR probes, which were already buried in the field.

Effect of Water Temperature on ECb

For a constant solute concentration, ECb readings in water increased linearly with temperature (table 2). However, results of regression analysis between temperature and ECb (table 2; fig. 8) indicated that the greater the concentration, the more pronounced effect of temperature on the ECb reading. The slopes of the lines for two different TDR cable lengths (table 2) also indicate that the shorter the TDR cable, the more significant the effect of temperature on the ECb readings. These results differ from those obtained by Persson

Table 2. Results of linear regression analysis between temperature (°C) and ECb (S m⁻¹ × 1000) for two TDR cable lengths and for five NH₄NO₃ concentrations in water.

NH ₄ NO ₃ (g L ⁻¹)	24-m Cable Length			12-m Cable Length		
	Slope	Intercept	r ²	Slope	Intercept	r ²
0	0.01	0.64	0.67	0.01	0.72	0.82
0.2	0.48	12.90	0.97	0.53	13.42	0.96
0.6	1.04	38.40	0.98	1.19	41.76	0.98
0.8	2.32	31.26	0.97	2.84	30.61	0.96
1.2	3.44	35.63	0.98	4.51	30.92	0.98

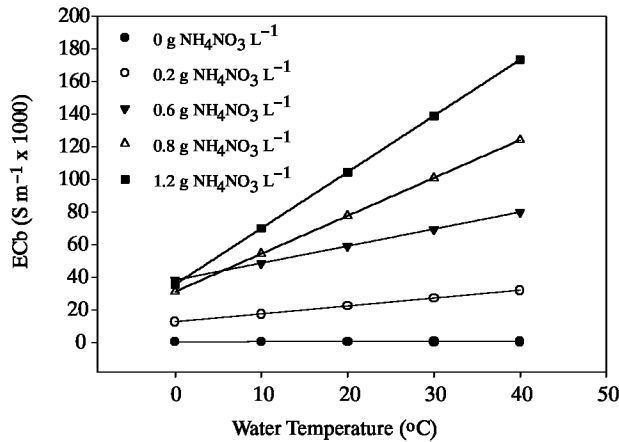


Figure 8. Relationship between temperature and ECb obtained with TDR for various solute concentrations. TDR probes (12-m cable) were inserted into distilled water with additions of NH₄NO₃ at rates of 0, 0.2, 0.6, 0.8, and 1.2 g L⁻¹. Each point was calculated from regression equations found in table 2.

and Berndtsson (1998) who found that the temperature dependency of the ECb readings was independent of soil type and that a temperature dependency factor could be defined as a linear function of the temperature at which the ECb measurement was taken, without taking into account solute concentration. The present results, however, suggest that the effects of temperature on ECb readings using TDR are more complex and depend on both solute concentration and cable length.

LABORATORY EXPERIMENTS IN SOIL

Effect of Soil Water Content, Soil Temperature, and Solute Concentration

The effect of soil water content (θ_v) and the combined effect of θ_v and soil temperature (Ts) on ECb for different NH₄NO₃ concentrations under unsaturated soil conditions was tested in the laboratory using the five soil containers experiment previously described. Results of regression analyses are shown in table 3. Strong linear relationships between ECb and θ_v were observed for all NH₄NO₃ concentrations ($r^2 \geq 0.95$). The effect of θ_v on ECb, however, varied with solute concentration. Although the inclusion of Ts in a multiple regression model did not increase the r^2 values in table 3 considerably, the P values indicate that θ_v and Ts both had a statistically significant effect on ECb for all three NH₄NO₃ concentrations. These results indicate that, in this soil, for a given NO₃-N concentration, more than 96% of the variation in the ECb readings was due to variations in soil water content and temperature, with variations in soil water content being the dominant factor.

Table 3. Results of simple and multiple linear regression analyses for TDR data collected using a 12-m TDR cable length.^[a]

Regression Parameters	ECb of Solution Added to Soil		
	0.0299 S m ⁻¹	0.0540 S m ⁻¹	0.0959 S m ⁻¹
Results of simple linear regression analysis of ECb vs. θ_v			
Slope (θ_v)	110.91	122.11	143.69
Intercept (θ_v)	3.43	1.65	-2.10
r ²	0.95	0.96	0.97
Results of multiple linear regression analysis of ECb vs. θ_v and Ts			
Intercept (θ_v , Ts)	-9.76	-7.97	-7.98
Slope (Ts)	0.54	0.39	0.24
Slope (θ_v)	117.34	127.10	146.44
r ²	0.96	0.97	0.97
P values			
Ts	< 0.001	< 0.001	0.031
θ_v	< 0.001	< 0.001	< 0.001

^[a] The dependent variable was bulk electrical conductivity (ECb) reading (S m⁻¹ × 1000), and the independent variables were volumetric soil water content (θ_v) (m³ m⁻³) and soil temperature (Ts) (°C).

Data were obtained in soil receiving solutions with three different NH₄NO₃ concentrations (concentration is indicated by the ECb of the solution). Regression analyses included 88 data pairs. The analyses included soil water content data in the range of 0.17-0.49 m³ m⁻³ and soil temperature in the range of 15.9-28.8°C.

The effect of soil temperature on ECb in soil under unsaturated conditions and nearly constant soil water contents was also evaluated using TDR data obtained using the field setup as described above. The P values in table 4 indicate that soil temperature had a statistically significant effect on the ECb readings for all depths. Results indicate that with constant soil water content, changes in ECb were linearly and positively correlated to changes in soil temperature, similar to effects of temperature in water (fig. 8). For four out of six depths, almost a perfect correlation was obtained, with r^2 values greater than 0.99. Table 4 also shows a different slope for each depth, which could be due to differences in both, solute concentration and soil water content among depths. The difference in slope can also be due to differences in contact between the soil and each of the probes, which would make it difficult to generalize relationships obtained in water and apply them to soil.

The effect of temperature on ECb under near-saturated soil conditions was also evaluated using data collected with the laboratory lysimeter setup described above during the period of 3 September to 14 October 2001. The high r^2 values in table 5 show that a good linear relationship between ECb and soil temperature existed for all probes. Under near-saturated soil conditions, for a given cable length, the slope of the line increased with increasing concentration. For the 12-m cable length, the slope of the line increased from 0.580 when the average ECb was 23.3 to 0.906 when the average ECb was 28.9. A similar trend was observed for the TDR probes with the 24-m cable lengths. This is consistent with the results obtained when the effect was evaluated in water with different NH₄NO₃ concentrations (fig. 8).

Effect of TDR Probe Orientation on ECb

Data collected using the laboratory lysimeter setup previously described show that the horizontally-installed probes were much more sensitive to changes in NO₃-N

Table 4. Results of simple regression analysis between bulk electrical conductivity (ECb) ($S\ m^{-1} \times 1000$) and soil temperature (Ts) ($^{\circ}C$) for data obtained in the field at six soil depths with nearly constant soil water content (θ_v) ($m^3\ m^{-3}$). [a]

Regression Parameter	Soil Depths					
	0.3 m	0.6 m	0.9 m	1.2 m	1.5 m	1.8 m
Intercept	17.44	8.21	14.81	12.98	11.98	16.24
Slope	0.586	0.308	0.572	0.510	0.450	0.369
r^2	0.90	0.76	0.998	0.998	0.996	0.992
P values						
Intercept	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Slope	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Data Ranges and Average ECb						
θ_v range	0.21–0.22	0.10–0.11	0.13–0.14	0.11	0.13–0.14	0.16–0.17
Ts range	0.96–13.3	2.6–13.9	4.3–14.7	6.1–15.5	7.8–15.8	9.2–16.0
ECb range	16.4–26.2	7.7–14.1	17.2–23.1	16.1–20.8	15.5–19.2	19.6–22.2
Average ECb	20.6	10.5	20.0	18.4	17.4	21.0

[a] Data include values obtained at 12:00 h in North Platte, Nebr., from 15 October to 25 December 2003.

Table 5. Effect of temperature on ECb under near-saturated soil conditions for TDR probes with two cable lengths. [a]

Probe Number	Cable Length (m)	ECb ($S\ m^{-1} \times 1000$)		Linear Regression Results		
		Range	Average	Intercept	Slope	r^2
1	12	19.9–27.5	23.5	11.15	0.58	0.94
2	12	23.9–32.5	27.9	14.62	0.62	0.89
3	12	24.6–35.4	28.9	9.61	0.91	0.93
4	24	23.4–33.7	27.3	11.03	0.76	0.94
5	24	23.3–34.2	27.5	8.66	0.88	0.92

[a] The soil temperature during this period ranged from 14.8 $^{\circ}C$ to 28.7 $^{\circ}C$.

concentration in the soil than the vertically-installed probes (fig. 9). The horizontally-installed probes responded to the addition of NH_4NO_3 fertilizer by abruptly increasing their ECb readings. For instance, for the horizontal probe installed close to the surface of the lysimeter (10 cm horizontal probe), the ECb increased from approximately 22 to around 49 $S\ m^{-1} \times 1000$. With the horizontally-installed probes it was possible to follow the movement of the fertilizer as it leached down the lysimeter.

The ECb readings for the vertically-installed probes, on the other hand, increased very little, from around 25 to 30 $S\ m^{-1} \times 1000$. This limited response made it difficult to distinguish when the nitrogen was applied and to follow solute movement. The lower sensitivity of the vertically-installed probes can be explained by a dilution effect. For instance, while the horizontally-installed probes sense the concentration increase of the downward moving fertilizer in the whole length of the probe at once, the vertically-installed probes are initially exposed to the increased concentration in only a portion of the length of the probe. Therefore, since the upper part of the probe is initially sensing a high concentration and the lower part is sensing a low concentration, the average concentration reading results. As the fertilizer pulse moves down, its concentration becomes more diluted as it is distributed in a larger soil volume. Consequently, the vertically-installed probes never sense the instantaneous high concentrations as the vertically-installed probes do.

Figure 9 also shows that the ECb of the vertically-installed probes roughly followed a similar trend as the soil temperature. Probe orientation (vertical vs. horizontal installation), however, should be chosen depending on the pursued

purpose, including desired sensitivity and ease of installation. It is commonly accepted that the horizontal option should be preferred where the user is interested in a detailed profile of the soil water content and solute concentration. This might be advantageous for soil hydraulic conductivity or infiltration rate measurement studies. On the other hand, although less sensitive to changes in solute concentration, vertical installation has the advantage that the probe integrates the usually non-uniform soil water content and solute distribution in the soil profile (Nadler et al., 2002). Probes are also much easier to install vertically in the field than horizontally, especially as soil depth increases.

FIELD EXPERIMENT

To evaluate the feasibility of using TDR to estimate NO_3-N concentration and movement in an irrigated agricultural soil, we tested the hypothesis that empirical equations could be derived to estimate NO_3-N concentrations based on measured ECb, soil water content (θ_v), and soil temperature (Ts). Multiple linear regression analysis was used to derive equations to estimate soil NO_3-N content, using TDR and Ts data obtained at six depths from two plots in a corn field using the field TDR setup described previously. Measured soil NO_3-N contents used in the regression analyses were obtained from soil samples taken from each of the two plots at the same depth as the TDR probes on several dates throughout the growing season.

Descriptive summary statistics for the data collected during 2002-2004 from each plot and soil depth that were included in the multiple regression analyses are shown in table 6. Separate regression analyses were conducted for each year, and for the combined (pooled) data from all years (2002-2004). For each period (individual year and pooled data), separate analyses were also conducted for each depth and for all depths combined. Results of the multiple regression analyses, including the intercept, regression coefficient for each variable, root mean squared error (RMSE), and r^2 values are shown in table 7. With a few exceptions, high r^2 and low RMSE values were obtained when the analyses were conducted for each year, depth, and cable length. The only poor results were obtained for the 0.3-m depth with the 12-m cable during 2004, which

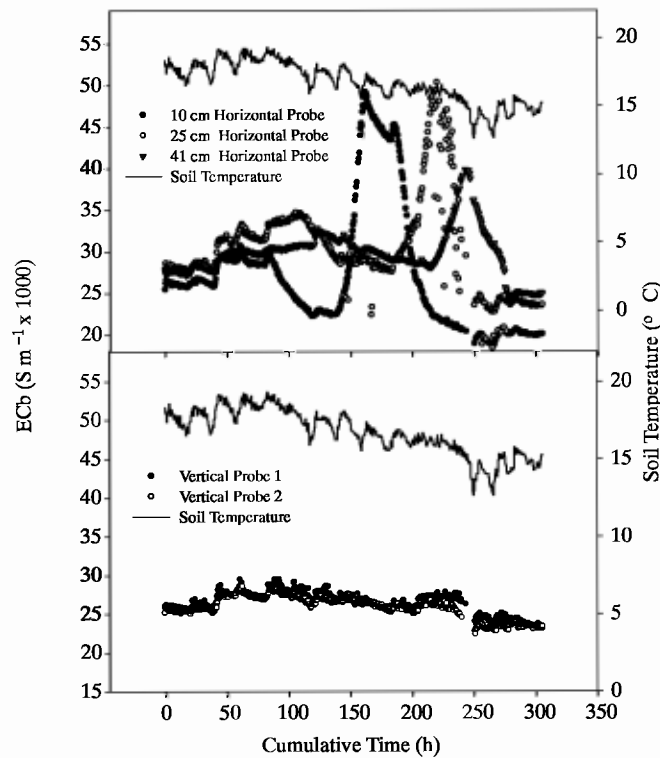


Figure 9. Electrical conductivity measurements from probes inserted horizontal to the soil surface to depths of 10, 25, and 41 cm, and probes inserted vertically at the soil surface. Measurements were collected over time after the application of NH_4NO_3 fertilizer at a rate of 224 kg ha^{-1} and the start of continuous water application. The soil was uniformly saturated over the measurement period.

Table 6. Descriptive summary statistics for the data used in the multiple regression analyses for 2002-2004 at North Platte.

Soil Depth	Variable ^[a]	North Plot (12-m cable) ^[b]						South Plot (24-m cable)					
		Mean	SD	n	Min	Max	Range	Mean	SD	n	Min	Max	Range
0.3 m	$\text{NO}_3\text{-N}$	41.9	15.4	139	8.0	55.9	47.9	29.7	16.0	151	8.0	53.0	45.0
	Ts	14.6	6.3	139	4.8	24.5	19.7	14.7	6.1	151	4.8	24.5	19.7
	θ_v	0.3	0.1	139	0.2	0.6	0.4	0.2	0.0	151	0.2	0.3	0.1
	ECb	40.2	14.3	139	0.8	62.1	61.3	28.9	5.4	151	14.6	35.3	20.7
0.6 m	$\text{NO}_3\text{-N}$	22.0	11.1	141	4.0	39.7	35.7	12.4	6.9	133	4.0	34.0	30.0
	Ts	14.5	5.1	141	7.3	23.0	15.7	15.0	5.2	133	7.3	23.0	15.7
	θ_v	0.2	0.1	141	0.1	0.3	0.2	0.1	0.0	133	0.1	0.2	0.1
	ECb	30.4	11.1	141	16.0	48.0	32.0	17.7	6.6	133	11.0	30.0	19.0
0.9 m	$\text{NO}_3\text{-N}$	20.2	20.0	136	0.0	52.3	52.3	8.4	8.0	131	0.0	26.0	26.0
	Ts	15.1	4.1	136	9.4	21.7	12.3	14.7	4.3	131	9.4	21.7	12.3
	θ_v	0.2	0.1	136	0.1	0.4	0.2	0.2	0.1	131	0.1	0.4	0.2
	ECb	31.6	16.9	136	16.0	60.3	44.3	31.4	16.6	131	16.0	60.5	44.5
1.2 m	$\text{NO}_3\text{-N}$	20.4	26.0	119	2.0	77.7	75.7	11.6	11.5	131	2.0	34.9	32.9
	Ts	15.1	3.5	119	9.0	20.4	11.4	15.5	3.2	131	9.0	20.4	11.4
	θ_v	0.1	0.1	119	0.1	0.3	0.2	0.2	0.1	131	0.1	0.3	0.2
	ECb	25.6	17.6	119	12.8	61.4	48.6	25.6	14.6	131	11.5	48.0	36.5
1.5 m	$\text{NO}_3\text{-N}$	15.5	15.9	133	3.0	48.3	45.3	21.8	23.8	136	3.0	69.2	66.2
	Ts	15.3	2.7	133	8.7	19.3	10.6	15.2	2.7	136	8.7	19.3	10.6
	θ_v	0.1	0.0	133	0.1	0.2	0.1	0.2	0.1	136	0.1	0.3	0.2
	ECb	15.5	6.3	133	9.3	28.2	18.8	23.7	9.4	136	13.4	39.0	25.7
1.8 m	$\text{NO}_3\text{-N}$	9.6	4.6	134	5.0	17.1	12.1	22.1	29.2	131	5.0	85.9	80.9
	Ts	14.9	2.4	134	8.5	18.3	9.7	15.1	2.2	131	8.5	18.3	9.7
	θ_v	0.2	0.0	134	0.2	0.3	0.1	0.2	0.0	131	0.2	0.3	0.1
	ECb	25.4	3.2	134	19.6	32.0	12.4	28.2	7.6	131	18.5	39.2	20.7

[a] $\text{NO}_3\text{-N}$ = soil nitrate (ppm), Ts = soil temperature ($^{\circ}\text{C}$), θ_v = soil water content ($\text{m}^3 \text{ m}^{-3}$), ECb = bulk electrical conductivity ($\text{S m}^{-1} \times 1000$).

[b] SD = standard deviation, n = number of data points, Min = minimum, Max = maximum.

suggests the possibility of unreliable data for that depth. Unreliable data could be due to problems during soil sampling, chemical sample analysis, or during TDR and Ts data collection, or possibly due to the malfunction of the probe installed at that depth.

For the pooled data (2002-2004), good predicting models resulted for the probes with the 12-m cable for all depths, except for the 0.3-m depth. The poor results for the 0.3-m depth for the pooled data appeared to be due to the poor results obtained during the 2004 season for that depth. The pooled data, however, resulted in lower r^2 values for the probes with the 24-m cable compared with those with a 12-m cable. The regression for the 24-m cable, however, resulted in P values that were still statistically significant at the

0.01 probability level for all depths. Differences for the two cable lengths could be due to variations in the range of values for each variable (Ts, θ_v , ECb, and $\text{NO}_3\text{-N}$) included in the analyses (table 6). These variations result from soil spatial variability, since the probes with the 12-m and 24-m cable were installed in separate plots.

Table 7 also shows that low r^2 and high RMSE values resulted when the analyses were conducted combining all depths, indicating that a separate calibration should be performed for each depth. The calibration may change with depth due to changes in soil texture, bulk density, root density, organic matter content, and differences in contact between the soil and each probe. The intercept and the regression coefficients for each of the variables (Ts, θ_v , and

Table 7. Results of multiple regression analyses of measured soil nitrate concentration ($\text{NO}_3\text{-N}$, ppm), as the dependent variable, and soil temperature (Ts, °C), soil water content (θ_v , $\text{m}^3 \text{m}^{-3}$) and bulk electrical conductivity (ECb, $\text{S m}^{-1} \times 1000$) as the independent variables. ^[a]

Regression Parameter	Results of Analysis for each Soil Depth											
	North Plot (12-m cable)						South Plot (24-m cable)					
	0.3 m	0.6 m	0.9 m	1.2 m	1.5 m	1.8 m	0.3 m	0.6 m	0.9 m	1.2 m	1.5 m	1.8 m
Year 2002												
Intercept	-4.4	58.6	35.9	9.6	0.7	0.4	10.9	14.3	35.8	23.1	8.7	7.5
Ts [b]	-1.7	1.2	2.4	1.0	0.9	0.6	0.2	-3.3	2.2	0.8	1.4	0.8
θ_v	65.3	-6.9	1.9	-23.0	-2.1	-1.4	-49.9	-733.8	-35.2	-192.5	-9.5	-2.7
ECb	1.9	-3.1	-3.7	-1.2	-0.9	-0.2	1.4	9.34	-3.3	-0.8	-1.5	-0.6
r^2	0.98	0.42	0.97	0.92	0.99	0.99	0.98	0.66	0.97	0.82	0.99	0.99
RMSE[c]	0.84	4.02	0.22	0.36	0.04	0.03	0.77	3.08	0.22	0.54	0.06	0.04
Year 2003												
Intercept	-12.2	5.5	17.6	-16.2	-14.0	-11.2	-105.2	-0.3	0.8	-19.4	-13.4	-6.6
Ts	-0.2	-1.9	-2.3	1.6	1.4	-0.1	-1.2	-0.4	0.9	1.3	1.2	0.4
θ_v	9.2	2.4	6.6	3.9	-1.2	2.4	345.4	113.3	8.3	81.1	0.5	0.6
ECb	0.7	1.2	1.3	0.4	0.5	0.8	2.1	0.6	0.1	0.3	0.4	0.4
r^2	1.00	1.00	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
RMSE	0.09	0.10	0.13	0.08	0.04	0.05	0.89	0.21	0.09	0.18	0.05	0.03
Year 2004												
Intercept	72.4	-27.4	78.1	258.1	2.4	96.1	-100.3	-1.2	19.4	279.4	26.8	1781
Ts	-1.4	0.04	-9.8	-34.1	-2.8	4.2	2.0	0.6	3.4	1.8	-8.5	-56.4
θ_v	-7.6	154.0	5.1	83.4	47.8	-119.9	323.6	-8.2	-24.6	-181.5	-224.3	-4655
ECb	0.1	0.4	2.4	6.1	2.9	-4.3	0.1	-0.003	-1.0	-5.2	6.3	8.9
r^2	0.19	0.98	0.96	0.86	0.98	0.71	0.95	0.88	1.00	0.97	0.98	0.71
RMSE	5.12	1.02	1.53	7.04	2.26	1.02	1.66	0.14	0.47	2.09	2.75	17.96
Years 2002-2004												
Intercept	19.6	-6.0	15.1	-8.9	19.5	33.0	16.5	27.8	34.3	9.3	-0.4	111.5
Ts	-0.1	-0.6	-1.5	-1.0	-1.5	-2.1	-0.3	-1.0	-1.2	-0.5	-2.5	-5.3
θ_v	110.0	228.7	-372.9	114.0	-446.9	-444.7	-181.9	-98.6	-690.4	-217.7	-272.3	-1762
ECb	-0.2	-0.3	3.2	1.1	4.9	4.2	2.1	0.8	4.1	1.8	4.7	12.6
r^2	0.14	0.91	0.93	0.94	0.93	0.78	0.42	0.45	0.76	0.56	0.95	0.67
RMSE	14.25	3.28	5.23	6.36	4.08	2.15	12.24	5.11	3.94	7.68	5.29	16.76
Results of Analysis Combining All Soil Depths												
Year	r^2			RMSE			r^2			RMSE		
2002	0.66			9.56			0.56			10.85		
2003	0.46			5.56			0.21			6.70		
2004	0.53			11.62			0.10			22.34		
2002-2004	0.63			11.81			0.26			16.66		

[a] Analyses were conducted for TDR probes with two cable lengths (12 and 24 m) installed in a corn field at six different soil depths (0.3 to 1.8 m).

[b] Numbers are the regression coefficient (slope) for each variable (Ts, θ_v , and ECb). For instance, the equation to estimate $\text{NO}_3\text{-N}$ for the 0.3-m depth and 12-m cable length in 2002 would be $\text{NO}_3\text{-N} = -4.4 - 1.7\text{Ts} + 65.3\theta_v + 1.9\text{ECb}$.

[c] RMSE = Root Mean Squared Error (ppm $\text{NO}_3\text{-N}$).

ECb) varied considerably with depth, year, and cable length. These results suggest that the calibration had a strong dependency on the range of T_s , θ_v , and ECb values included in the analyses, which can vary considerably with time, depth, and location within the field. The calibration, therefore, should be performed over a long enough period of time to include the expected range of values of all variables used in the regression analyses. Soil sampling timing for $\text{NO}_3\text{-N}$ analysis to be used in the calibration should be adjusted to include a variety of ranges of $\text{NO}_3\text{-N}$ contents, and should be frequent enough to provide enough data points to be able to perform meaningful statistical analyses. The good results obtained in this study, however, show that using the procedure proposed in this study it is possible to develop good empirical functions to continuously estimate soil $\text{NO}_3\text{-N}$ from TDR and T_s measurements for specific soils. It should, however, be kept in mind that this study was conducted in a non-saline soil and results would not apply for saline soil conditions or when irrigating with saline water.

CONCLUSION

The ECb measurements from TDR in water were well correlated with measured $\text{NO}_3\text{-N}$ concentrations. The relationship between ECb and $\text{NO}_3\text{-N}$ concentration, however, was strongly affected by changes in temperature. The effect of temperature on ECb was more pronounced as the solute concentration increased. In soil, the ECb readings were strongly affected by both temperature and soil water content. In both, soil and water, the ECb readings were also affected by the length of the TDR coaxial cable. The results of this study show that, if properly calibrated, taking into account changes in temperature, soil water content, and cable length, TDR can be used to estimate $\text{NO}_3\text{-N}$ concentrations in non-saline soils. It is important, however, to perform the calibration over a long enough period of time to include the expected range of temperatures, soil water contents, and $\text{NO}_3\text{-N}$ concentration. The results of this study also suggest that it is much easier to calibrate TDR to estimate $\text{NO}_3\text{-N}$ in water than in soil because of potential problems with contact between the probe and soil. Because of perfect contact between the probe and water, ECb readings in water were mainly affected by changes in temperature, $\text{NO}_3\text{-N}$ concentration, and cable length. Therefore, TDR should potentially be well-suited for continuous monitoring of $\text{NO}_3\text{-N}$ in soil and water.

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