

IN SITU MEASUREMENT OF NITRATE CONCENTRATION USING TIME DOMAIN REFLECTOMETRY

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**Written for presentation at the
CSBE/SCGAB 2006 Annual Conference
Edmonton Alberta
July 16 - 19, 2006**

Abstract

Nitrates when found in excess in the groundwater, is a health hazard. Nitrates can easily be transported by groundwater movement and may eventually reach aquifers located far away from the contamination location. It is important to monitor the nitrate movement in the groundwater to predict the extent of nitrate contamination. Traditionally, nitrate movement is monitored by sampling groundwater and analyzing it in the laboratory. This paper presents an in situ method to measure nitrate concentration in a laboratory flow experiment using time domain reflectometry data.

Three flow cells (replicates) packed with a silty loam soil were subjected to a constant hydraulic gradient inducing saturated water flow through the flow cells. A 500 mg L⁻¹ NO₃-N strength potassium nitrate solution source was connected at the inflow end and the nitrate concentration change with time was monitored along the length of the flow cells by soil solution sampling and analyzing it in the laboratory for NO₃-N concentration. At the time of sampling, Time Domain Reflectometry (TDR) wave forms were recorded using the TDR mini-probes inserted at regular intervals along the length of the flow cells. The bulk soil electrical conductivity and the water content values extracted from the TDR wave forms were used to predict the nitrate concentrations at different locations. The nitrate concentration values predicted from the TDR data correlated well with the nitrate concentrations obtained through soil solution sampling method indicating the possibility of using TDR for monitoring nitrate movement in the groundwater non-destructively.

Keywords: nitrate contamination, TDR, electrical conductivity, non-destructive measurement

INTRODUCTION

The problems associated with groundwater contamination have gained prominence during the past two decades. Nitrate contamination of soils and the remediation of such soils have attracted research in the recent past. Laboratory flow experiments studying nitrate contamination and remediation require nitrate concentrations be measured at regular space and time intervals. However, such nitrate monitoring can be expensive and tedious. In situ monitoring of nitrate movement may lead to large savings of money and time. Real-time monitoring of nitrate concentration change in the soil may also enable researchers to make timely decisions during the course of an experiment.

Time Domain Reflectometry (TDR) measures the apparent dielectric constant of the media in which the wave guide is inserted. Topp et al. (1980) and Topp and Davis (1985) used time domain reflectometry (TDR) for measuring the volumetric water content of soils. They established a strong relationship between the volumetric water content and dielectric constant of the soil for different soils. Since then, changes in soil water content have been successfully monitored non-destructively using TDR probes.

A measure of soil electrical conductivity can be obtained from TDR waveforms by analyzing the change in voltage signal toward the tail-end of the waveform as a function of travel time. The bulk or apparent soil electrical conductivity (EC_b) can be found by analyzing the change in voltage level of the waveform (Dalton et al., 1984; Topp et al., 1988; Zegelin et al., 1989; Noborio 2001). However, estimation of concentration of solutes from EC_b requires determination of a direct relationship between EC_b and the concentration or an intermediate step of secondary calibration such that concentration can be determined from soil solution electrical conductivity (EC_w).

A two-step process is involved in obtaining solute concentration from EC_b . First, EC_w is obtained from EC_b using a functional relationship between the two. The solution concentration is then estimated from EC_w . Relating EC_w to EC_b requires independent calibration.

There are different methods available to obtain EC_w from EC_b . Rhoades et al. (1976) and Nadler (1982) developed models that require empirical constants to relate EC_b to EC_w . Mualem and Friedman (1991) and Heimovaara et al. (1995) used physical parameters that can be obtained by measuring soil properties. These models can be used where such soil properties have already been determined. Rhoades et al. (1989) used a three-pathway model that partitions soil water into mobile and immobile fractions and used these fractions to relate EC_b to EC_w .

Kachanoski et al. (1992) showed linear relationship between TDR-measured EC_b and EC_w under constant soil water conditions. Working with various models for the estimation of EC_w from EC_b in sandy soils, Amente et al. (2000) concluded that there is no benefit in using soil hydraulic properties than using simpler models. Hameed et al. (2003) compared the estimation of EC_w using two different dielectric techniques as measured by a TDR and a Sigma Probe and concluded that TDR measurements were superior to the Sigma Probe measurements.

Ebrahimi-Birang et al. (2006) looked at the possibility of using MP917 Moisture Point instrument (ESI Environmental Sensors, Inc.) for soil electrical conductivity measurements. They reported MP917 provides suitable accuracy in relative measurements of soil electrical conductivity.

The aim of this study was to determine the feasibility of using TDR miniprobes in in-situ monitoring of the soil nitrate concentration in a laboratory flow experiment.

Methods and Materials

The measurements taken for this study were from an experiment conducted to test the effectiveness of a treatment procedure to remediate nitrate contamination in the soil. The data were obtained from three control flow cells which were not subjected to the remediation treatment.

Three Plexiglas flow cells (replicates) were used in the experiment. The flow cells were 0.30 m long and had 0.03 m long spacers at both inflow and outflow end to provide influent and effluent reservoirs, respectively. The length of the soil in the flow cell was thus 0.24 m having an internal diameter of 45 mm. Each flow cell had two removable endplates that had one port each for solution inflow to the column and outflow from the column. An O-ring kept the seal between each endplate and the flow cell. In order to take pore fluid samples, each flow cell had

four ports spaced 0.060 m apart along the length of the flow cell starting at 0.045 m from the inflow end. Four additional holes of 14 mm internal diameter were located 0.060 m apart, along the length starting at 0.015 m from the inflow end to insert Time Domain Reflectometry (TDR) mini-probes to monitor water content and EC_b . A schematic diagram of the flow cell is shown in Fig. 1.

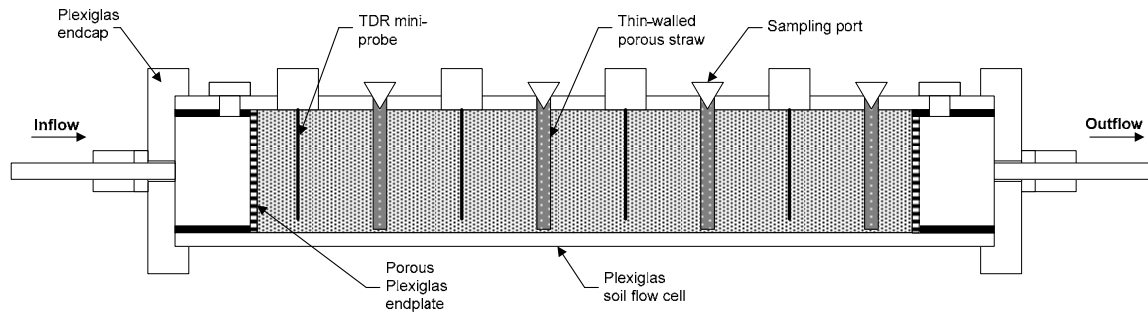


Fig. 1 Schematic diagram of the flow cell used in the laboratory experiment.

Four holes of 14 mm internal diameter were located 0.060 m apart, along the length starting at 0.015 m from the upstream to insert TDR mini-probes to monitor water content and bulk electrical conductivity of the soil. A TDR mini-probe consists of three 1.5 mm diameter stainless steel of 0.035 m length. A two metre coaxial cable was used to connect the TDR mini-probe to the TDR cable tester. A Tektronix® 1502B metallic TDR cable tester (Tektronix, Beaverton, OR) was used to obtain waveforms from TDR mini-probes for water content and EC_b determination.

Soil used for the laboratory-scale experiment was obtained from the Manitoba Crop Diversification Centre in Carberry, Manitoba. The soil was collected from a depth of 0.40 - 0.60 m. The collected soil was air dried and the clods were broken using a mallet. The dry soil was then sieved through a 2 mm sieve and the soil retained on the 2 mm sieve was discarded. Soil passing through the 2 mm sieve was used as the test soil for the laboratory experiment. The particle size distribution was found to be 20% sand, 54% silt and 26% clay. Based on the textural triangle of the USDA classification scheme, the soil can be classified as a silt loam.

In packing the flow cells, care was taken to ensure a uniform bulk density across the columns. The columns were packed, with air-dried soil that had passed through a 2 mm sieve, in 10 mm sections to achieve uniformity. The soil was tamped using a tamping device. After packing each section, the surface was scarified to prevent the formation of any distinct and denser layers in between. A thin piece of nylon mesh material was placed between the soil in the column and the perforated spacer to prevent soil being washed out. The quantity of soil packed was used to determine the bulk density. The bulk densities of the soil in the flow cells were in the range of $1.20 - 1.47 \times 10^3 \text{ kg m}^{-3}$.

The flow cells were saturated using de-ionised and de-aired water. The flow cells were mounted vertically on a specially designed flow cell holder. While saturating the flow cells, care was taken not to trap air that may hinder the saturation process. To avoid the formation of air pockets, the flow cells were flushed with carbon dioxide for two days so as to displace the air from pore spaces. This would prevent the formation of air pockets as carbon dioxide is more soluble in water than air. After two days, the flow cells were connected to a tank of de-ionized and de-aired water supply with the inflow at the bottom. The movement of the wetting front was maintained at less than 10 mm h^{-1} by controlling the flow into the soil flow cells. After complete saturation, the orientation of the flow cells was changed to the horizontal position. TDR mini-probes were then inserted, sealed in place using silicone and connected to their coaxial cables. Reservoirs were created for pore fluid extraction. Thin walled perforated plastic tubes were inserted into the reservoir to prevent the collapse of soils into these reservoirs. The flow cells continued to receive water for a week to stabilize the system.

The changes in the water content (θ) and EC_b were monitored daily by connecting the TDR mini-probes individually to a TDR cable tester. The individual waveforms were stored in a computer and a Quick Basic Computer program was used to extract θ and EC_b values from these waveforms

Once the flushing of the columns with de-ionized water was completed, the experiment was started by introducing a 500-mg NO₃-N L⁻¹ potassium nitrate solution at the upstream end in place of the de-ionized water. A constant hydraulic gradient of 1.25 was maintained throughout the experiment in all the columns

To monitor changes in nitrate concentration during the experiment, pore water samples were extracted from the ports that were located 0.060 m apart along the length of the column starting at 0.045 m from the upstream end. A one-mL syringe was used to extract the fluid sample. To avoid cross-contamination while sampling, syringes were assigned to each port and were not interchanged. After every sampling each syringe was thoroughly rinsed with de-ionized water. The sampling was done before the start of the experiment (Day 0), one day after the start of the experiment (Day 1) and thereafter every other day until the end of the experiment. A sample of 0.4 mL was extracted and diluted by 15 times using an electronic scale. Samples showed varying degrees of opaqueness because of the fine soil particles present in them. Because nitrate analyses were based on colorimetric principles, these particles may interfere with their determination. Therefore, the samples were centrifuged at 10000 rpm for ten minutes to remove these particles. The supernatant was then stored in a refrigerator prior to nitrate analysis. Nitrate content of the diluted samples were analyzed using a Technicon® autoanalyzer II Colorimeter (Technicon Instruments Corporation, Tarrytown, NY). Measured values were first multiplied by a constant to convert the values to NO₃-N mg L⁻¹ units. Then they were multiplied by appropriate dilution factor to obtain actual nitrate concentration in the pore water.

For the data analysis, the average of the EC_b from the first and the third TDR probes from the inflow end of the flow cell were considered to represent the nitrate concentration of the first sampling point from the inflow end. The nitrate concentration at the second sampling port was considered to be represented by the average EC_b values of the second and third TDR probes. In the same way, the nitrate concentration at the third sampling port was considered to be represented by the average EC_b values of the third and the fourth TDR probes.

First, the nitrate concentrations in ppm were converted to dS m⁻¹ unit using a calibration equation as the EC_b by TDR were measured in dS m⁻¹ units. The converted nitrate concentration (EC_w), bulk electrical conductivity (EC_b), and water content (θ) data from the first set of experiments was analyzed using nonlinear regression model to develop EC_b as a function of EC_w and θ. The regression model developed was validated using the data from the second set of experiments.

Results and Discussion

The following calibration equation ($R^2 = 0.99$) was developed by measuring the EC_w of solutions that had varying nitrate concentrations (Fig. 2).

$$EC_w = 0.027NC + 4.524$$

where,

EC_w = Electrical conductivity of solution (dS m⁻¹)

NC = Nitrate concentration (ppm)

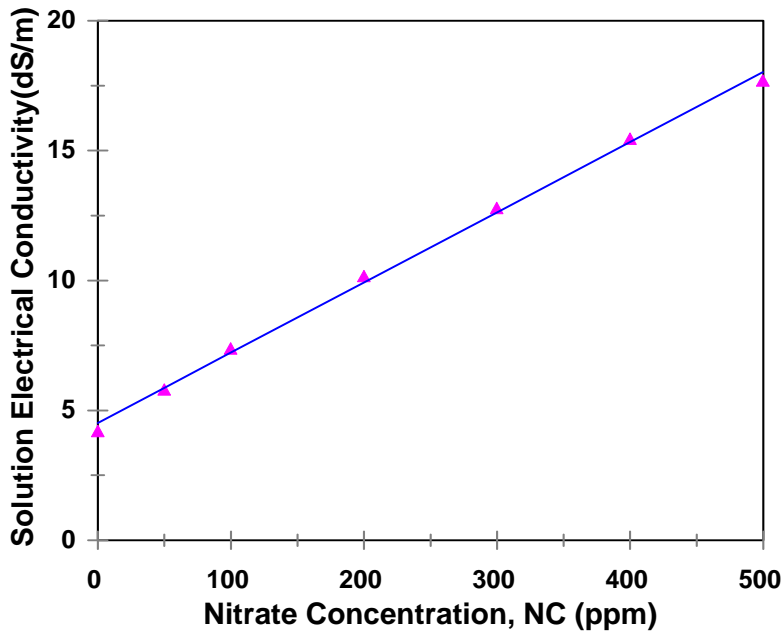


Fig. 2 TDR Calibration curve for potassium nitrate solution.

Using the EC_w and θ from the first set of experiments, a nonlinear regression model was developed having EC_b as a function of EC_w and θ .

$$EC_b = 11.046 - 0.556EC_w\theta^2 + 0.835EC_w\theta$$

where,

EC_b = Bulk electrical conductivity of the soil ($dS\ m^{-1}$)

EC_w = Electrical conductivity of pore-water solution ($dS\ m^{-1}$)

θ = Water content of the soil ($m^{-3}\ m^{-3}$).

The constant 11.046 represents the electrical conductivity of the soil solids. The EC_b and θ data from the second set of experiments were used for the prediction of EC_w during the second set of experiments. These predicted EC_w were converted to nitrate concentration in ppm using the calibration equation. Figure 3 shows the predicted

nitrate concentration values against the measured nitrate concentrations.

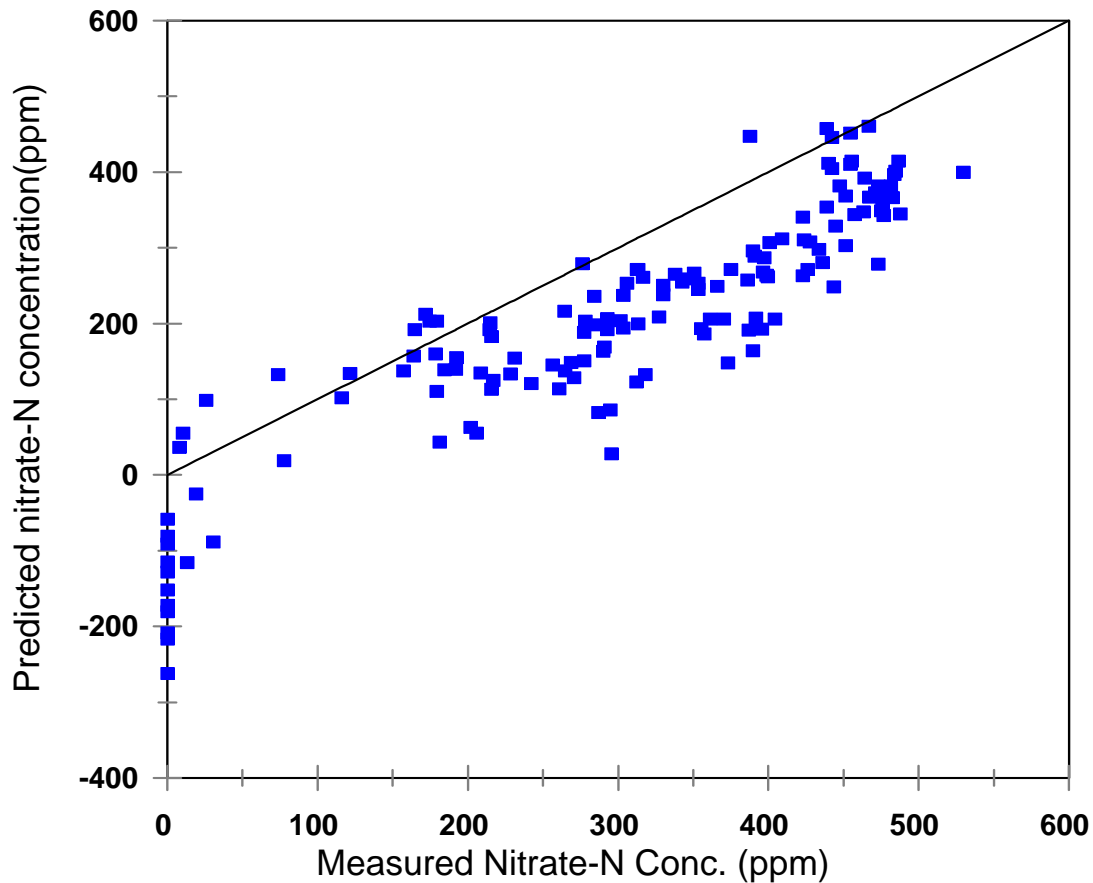


Fig. 3 Prediction of nitrate concentrations using soil bulk electrical conductivity and soil water content.

Figure 3 shows that the nonlinear-model predicted nitrate concentrations in the soil linearly increases as the nitrate concentration in the soil increases. Therefore, the TDR detects the changes in the nitrate concentration in the soil. However, the precision is low due to the high variability. As shown in Fig. 3, the predicted nitrate concentration values clearly fall short of the 1:1 reference line. This may limit the use of TDR for nitrate measurement where a high degree of accuracy is needed for nitrate concentration determination. Because the conventional method of “sample and analyze” is tedious and expensive, TDR can well be used for monitoring the changes in nitrate concentrations as an exploratory technique before one decides to extract porewater samples for later analysis.

Conclusions

The TDR detected the changes in the nitrate concentration of the flow cells. Although the TDR is sensitive to the changes in nitrate concentration, typically TDR under-predicts nitrate concentration. For this reason, the TDR can be used for monitoring the changes in nitrate concentration although the exact nitrate concentration may not be determined by using TDR. Because the conventional method of “sample and analyze” for nitrate concentration is tedious and expensive, TDR probes can be useful in detecting the changes in nitrate concentration in the soil in a flow experiment as an exploratory technique before expensive nitrate analysis is done for nitrate determination. Employing TDR for monitoring nitrate concentration changes in the soil as a non-destructive, in situ technique can

lead to large savings of money especially in nitrate-contamination remediation experiments where repeated flow experiments are required to be run frequently. Further experimentation is needed to improve the accuracy of detection of nitrate by TDR.

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