

코어샘플을 이용한 질소 등 토양성분 현장 측정방법의 비교평가

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Comparison of In-Field Measurements of Nitrogen and Other Soil Properties with Core Samples

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Abstract

Several methods of in-field measurements of Nitrogen and other soil properties using cores extracted by a hydraulic soil sampler were evaluated. A prototype core scanner was built to accommodate Veris Technologies commercial Vis-NIRS equipment. The testing result for pH, P and Mg were close to RPD (Ratio of Prediction to Deviation = Standard deviation/RMSE) of 2, however the scanner could not achieve the goal of RPD of 2 on some other properties, especially on nitrate nitrogen (NO₃) and potassium (K). In situ NIRS/EC probe showed similar results to the core scanner; pH, P and Mg were close to RPD of 2, while NO₃ and K were RPD of 1.5 and 1.2, respectively. Correlations between estimations using the probe and the core scanner were strong, with $r^2 > 0.7$ for P, Mg, Total N, Total C and CEC.

Preliminary results for mid-IR spectroscopy showed an r^2 of 0.068 and an RMSE for nitrate (N) of 18 ppm, even after the removal of calcareous samples and possible N outlier. After removal of calcareous samples on a larger sample set, results improved considerably with an r^2 of 0.64 and RMSE of 6 ppm. However, this was only possible after carbonate samples were detected and eliminated, which would not be feasible under in-field measurements.

Testing of NO₃ and K ion-selective electrodes (ISEs) revealed promising results, with acceptable errors measuring soil solutions containing nitrate and potassium levels that are typical of production agriculture fields.

Keywords : Soil properties, Nitrogen, Potassium, Ion-selective electrode (ISE), Precision agriculture

1. INTRODUCTION

Growers in the United States, and in developed countries worldwide, apply large amounts of fertilizers to their fields. Fertilizer rates are typically applied in excess of the crop need, since the cost of fertilizer is low relative to the loss in crop yield if a given nutrient is yield-limiting. Nitrogen lost from farm fields contributes to drinking-water quality problems, and nitrous oxide gases from crop production have been identified as a significant contributor of greenhouse gases. One of the main causes of over-application of fertilizers

is the lack of knowledge regarding the optimal fertilizer rate for each area within a field. Knowledge of available nitrate nitrogen would provide growers with a rationale to apply nitrogen site-specifically, provided the information is at a scale that delineates the spatial variability of nitrate accurately.

Current approaches employ conventional soil sampling and lab analysis. Soil nitrate easily moves vertically in the soil, so sampling depths required for nitrate are relatively deep, typically 30 to 120 cm. As a result, nitrate sampling is laborious, time-consuming, and expensive. Because the samples must be submitted to a testing lab for analysis, the

delay in receiving results is a major problem for growers needing to apply fertilizer immediately. As a result of these and other obstacles, many fields that would benefit from improved nitrogen management are not sampled at all, or not sampled with the density required for accurate variable rate prescriptions.

In laboratory analyses, nitrate content of soils is typically determined using an automated spectrophotometric method. In this test, utilizing dried and ground soil samples, nitrate ions are reduced to nitrite by a copper cadmium reductor column. The nitrite ions are then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride. The absorbance is measured at 520 nm (Carter, 1993). Transferring this technology to in-field use is not practical, due to equipment durability, costs, and the cycle times required for various tests.

Alternate methods, which may be feasible for field use, involve the use of various sensor technologies. These sensors are likely not as accurate as equipment used in the lab, yet the measurements can be done more rapidly and at a denser spatial scale than is typically feasible with conventional lab-analyzed soil samples. The use of field sensors to stratify or predict variability patterns, in conjunction with follow-up laboratory calibrations, has the potential to improve overall accuracy of field maps of various soil constituents. An agro-economic analysis of automated pH mapping has shown that higher resolution maps, even with a relatively low accuracy of individual measurements, reduced errors and increased profitability potential of variable rate liming (Adamchuk et al., 2005).

Field-deployable sensors potentially helpful in identifying nitrogen and other nutrients can be divided into three basic categories: 1) Electrical and electromagnetic, 2) Optical, and 3) Electro-chemical (Adamchuk et al., 2004).

Electrical and electromagnetic soil measurements have become commonplace in precision agriculture soil mapping. The predominant soil properties identified by in situ measurements of soil EC are soil texture and soil salinity (Williams and Hoey, 1987; Rhoades and Corwin, 1992). There have been claims of real-time nitrogen measurements by another electrical device (Colburn, 1998). However, these claims have not been verified by independent, published research.

Soil EC measurements integrate multiple factors, which makes it difficult to detect the response due to a single constituent, such as nitrogen. However, in a highly controlled

study than accounted for soil temperature, moisture, and bulk density, soil EC accounted for dynamic changes in plant-available N during the growing season (Eigenberg et al., 2006). In the research, the relationship of soil EC to nitrogen levels will be investigated.

Field mobilization of NIR spectroscopy has been pursued since the late 1980's and results from several systems have been published (Shonk et al., 1991; Sudduth and Hummel, 1993; Shibusawa et al., 1999). NIR wavelengths have shown strong correlation to total nitrogen (Chang et al., 2001), and mineralizable N (Lund et al., 2007), although not as capable of detecting nitrate nitrogen (Islam et al., 2004). Mid-IR appears to offer a more promising potential of detecting nitrate nitrogen, however sample preparation—putting soil into slurry or solution, is required (Jahn and Updadyaya, 2006).

Electro-chemical sensors differ from the sensors described above in that they are designed to directly measure soil chemical characteristics. These sensors include ion-selective field effect transistors (ISFET), ion-selective electrodes (ISE), and an emerging nano-scale technology using a nitrate selective coating of carbon fibers.

Early research into sensing nitrogen availability using ISFET sensors found results were limited by the methodology of extracting the soil, and by instrument drift and hysteresis (Birrell and Hummel, 1997). More recently, an intact core extraction procedure was tested using an extraction solution pushed through a soil core, and an ion-selective field-effect transistor/flow injection analysis (ISFET/FIA) system to sense soil nitrates yielded promising results (Price et al., 2003).

ISE's are commonly used in soil-testing laboratories for pH (Carter, 1993). An on-the-go pH sensing unit, which measures pH using ISE's in direct contact with soil, is commercially available. Results from this unit are well-correlated with laboratory measurements, especially when calibrated with lab-analyzed samples from the field (Staggenborg et al., 2007; Adamchuk et al., 2007).

Unfortunately, the ISE sensing interface for nitrate and potassium are constructed of PVC membranes and are not durable enough to withstand repeated direct soil contact. As a result, in-field research with these ISE's has focused on measuring soil in solution, and with limited success, partly due to the soil sampling mechanism (Adsett and Zoerb, 1991). More recently, the performance of nitrogen ISEs used directly on soil was well-correlated with lab analysis,

however the soil sampling mechanism was still the major problem (Adsett et al., 1999). It has been generally found that nitrate ISE's require frequent re-calibration due to drift.

Nano-scale sensors represent an emerging technology with positive early results. Researchers developed a microsensor using carbon fibers as a substrate for pyrrole electropolymerization, and produced a nitrate sensor that exhibited sensitivity to nitrate at typical field levels, showed rapid response, and experienced less drift when compared with nitrate ISE's (Bendikov et al., 2005). This technology is not commercially available and sensors would need to be constructed in order to conduct field tests. Furthermore, in personal communications with Thomas Harmon of University of California, Merced, he indicated his research revealed durability issues with micro-sensors and he had changed to using nitrate ISEs in his water quality research. Therefore micro-sensor with nitrate selective polypyrrole film will not be tested in this research.

The objectives of this research focused on evaluating several methods of in-field measurement of soil nitrate and other properties. The results of this research will provide a clear direction for the development of an automated in-field soil property sensing system.

2. MATERIALS AND METHODS

To evaluate several methods of in-field measurements of soil properties, cores were extracted from each of 12 barrels inserted in three different fields (sandy, silt loam and silty clay loam) with four different concentrations of ions (zero,

low, medium and high N and K fertilizer applied). Nitrate fertilizer (28% UAN solution) was applied in the barrels based on 30 kg/ha, 60 kg/ha and 90 kg/ha for low, medium and high application, respectively. Kansas soils contain relatively high levels of potassium, consequently K fertilizer application is not required. However to evaluate the function of K ISEs for detecting different concentration of K ions, 50 kg K/ha, 100kg K/ha and 150 kg K/ha from 60% potash for gardening were applied in the barrels.

The order of testing for each location with each sensor proceeded as follows: 1) measured soil in situ using Veris Technologies commercial visible and near-infrared spectroscopy (Vis-NIRS) and soil electrical conductivity (EC) sensor probe, 2) collected 1 meter long cores adjacent to sensor probe insertions and scanned intact core with Vis-NIRS, 3) sensed core with miniaturized four electrode Wenner array EC probe, and 4) segmented core, created soil solutions and measured with ISEs, and EC electrode. Each of the 12 soil cores were segmented for top (0-23 cm) and bottom (24-46 cm) sub samples, and the 24 samples were sent to the Kansas State University Soil Testing Lab for analysis.

A. Core scanner for Vis-NIRS sensor

A prototype core scanner was built with minor modifications of Veris Technologies commercial Vis-NIRS shank equipment (Fig. 1), which includes spectrometers of S4000 (Ocean Optics, Inc., Dunedin, FL, USA) and C9914GB (Hamamatsu Photonics, K.K., Japan) for visible (450-900 nm) and NIR (1100- 2200 nm) ranges. Basic design consists of a table/bed, sized to hold cores that were collected with

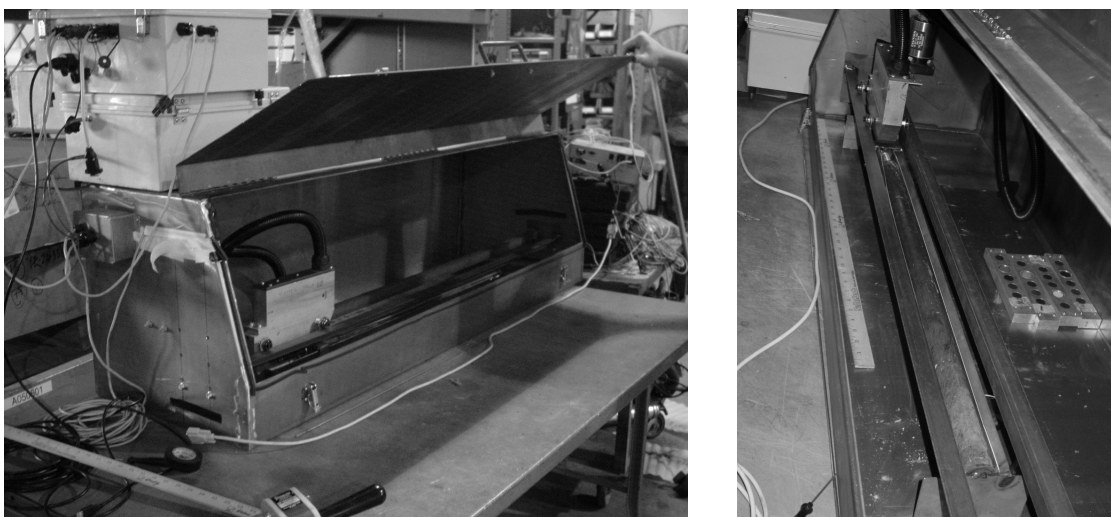


Fig. 1 A prototype core scanner.



Fig. 2 A soil core extracted using a Veris Technologies hydraulic probe unit.

Veris Technologies hydraulic probe, core length 0-120 cm; core diameter 3.2-3.5 cm (Fig. 2). Vis-NIR spectrometers and scanning head were mounted on a transverse arm, positioned in close proximity to soil core. The scanning head moves in relationship to the core, obtaining detailed spectral measurements along the full length of the core. Unlike the commercial Veris Vis-NIR probe spectrophotometer, which collects its measurements through a sapphire window pressed against the soil, allowing negligible interference from ambient light, the core scanning stand was equipped with enclosing apparatus to reduce ambient light effects.

The spectra data were calibrated by PLS regression to predict properties in the soil cores after preprocessing with mean centering and 1st, 2nd Derivative, or SNV. The goal was RPD of 2.

B. Miniaturized four electrode Wenner array EC probe

To evaluate the relationship between soil EC and nitrate levels, a miniaturized four electrode Wenner array EC probe was constructed (Fig. 3). The distance of each electrode was set to 2 cm and the principle of measurement was the same as Veris EC unit. For signal generating and data logging, commercially available Veris instrument was used.

C. Core segment grinding and measuring apparatus

A core segment grinding and measuring apparatus was designed and constructed (Fig. 4). This consists of a soil-solution chamber that core segments were placed into, a soil grinding/blending device, a water-injection unit, a water tank, and a commercial Veris pH controller as an electronic system which processes ISE outputs. After grinding/blending

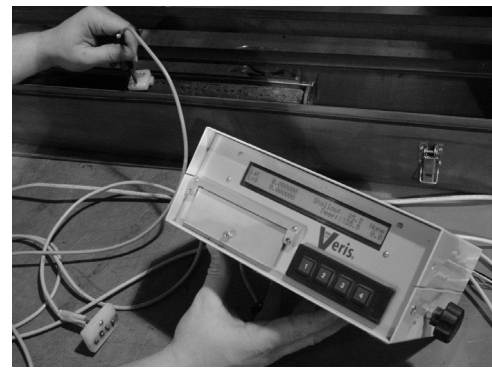


Fig. 3 A miniaturized four electrode Wenner array EC probe.

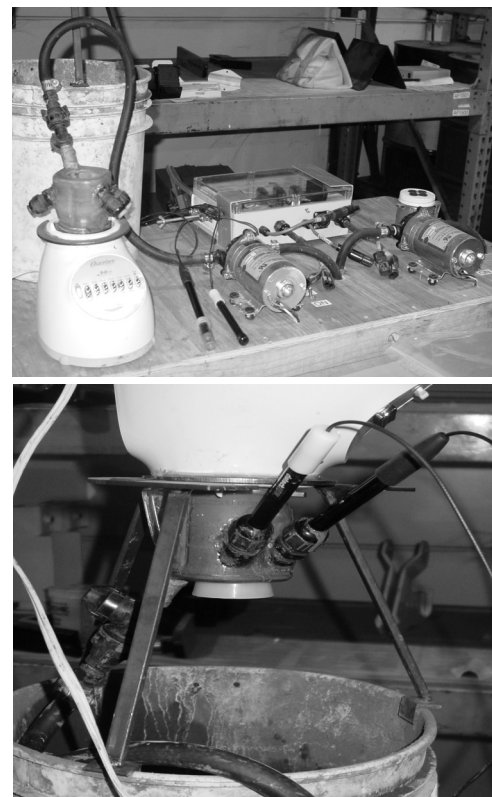


Fig. 4 Core segment grinding and measuring apparatus.

soil core with purified water, the grinding device was inverted to measure soil properties with ISEs and allows easy cleaning of the chamber with water-injection.

D. Ion-selective electrodes for nitrate, potassium and pH measurement

ISEs have been used to directly measure soil chemical properties, unlike other sensors such as a spectrometer, whose data need to be properly processed and calibrated with reference samples. The issues affecting the viability of ISEs, especially nitrate ISEs, in a commercial automated system are: 1) response time to reach steady state output, 2) issues of drift and durability, 3) cost per sample, 4) ion-concentration detection limits and accuracy. In this research, these issues were tested extensively.

For Nitrate measurement, two ISEs were selected. One is NICO 3021BN (Nico Scientific Inc., Huntingdon Valley, PA, USA) and the other is ASI NO43 (Analytical Sensors & Instruments Ltd, Sugar Land, TX, USA).

For Potassium (K) measurement, an ASI KT43 ISE was selected. K ISE only measures water soluble K, not exchangeable K, which is used for fertilizer application recommendations. Therefore exchangeable K should be estimated with K ISE and other soil properties like bulk soil conductivity (ECa) or CEC.

For pH measurement, an antimony metalloid electrode and a glass electrode were selected.

The following calibration equation was used to determine the slope and the intercept for Nitrate and Potassium (Adamchuck et al., 2002):

$$mV = mV_{opN} + mV_{pN} \log(NO_3^- \text{ or } K^+) \quad (1)$$

Where, mV = electrode output (mV)
 NO_3^- = nitrate ion concentration (ppm)
 K^+ = potassium ion concentration (ppm)
 mV_{opN} = electrode output (intercept) at 1 ppm of NO_3^-
 mV_{pN} = mV output increase (slope) due to increase of NO_3^- by 10

E. Mid-IR for nitrate measurement

Mid-IR measurements were made at the sub-contractor laboratory of University of California, Davis. 30 soil samples

obtained from Kansas fields were sent the sub-contractor lab with the soil testing results of ten randomly selected soil samples to check the calibration equation. The soil samples were ground to 75 μm size and then mixed with 1:1 distilled water to create a paste. Each sample was split into ten subsamples before taking the MIR spectra. MIR spectra of each subsample was obtained using a Mattson Galaxy 5020 FTIR spectrophotometer equipped with a ATR crystal and a DTGS (Deuterated Tri Glycine Sulfate) detector with a spectral range of 700 to 3700 wave number (cm^{-1}). The spectra of the background (crystal only) and water spectra were also obtained to implement baseline correction.

The absorbance data corresponding to the wave numbers 1350 cm^{-1} and 1500 cm^{-1} from the baseline corrected spectra were used to predict the nitrate content of soil. Absorbance data at 1350 cm^{-1} should be related to nitrate peak and absorbance data at 1500 cm^{-1} should assist in eliminating the interference from soil carbonate. However, during the sample preparation it was found that two soil samples behaved differently. They were very sticky and the nitrate content appeared to increase with increasing amounts of water. The third soil sample did not have enough soil to create ten subsamples. These samples were removed from the analysis.

3. RESULTS AND DISCUSSION

A. Comparison of the results of Vis-NIRS core-scanner to Vis-NIRS probe

The spectra data were calibrated by PLS regression to predict properties in the soil cores. The goal was RPD (Ratio of Prediction to Deviation = Standard deviation/RMSE) of 2. Several researchers reported that RPD is a useful measure of fit to compare results from datasets with different degrees of variability (Williams, 1987; Hummel et al., 2001; Lee et al., 2009). Chang et al. (2001) categorized RPD ranges as high (> 2.0), medium (1.4-2.0) and low (< 1.4) to classify the ability of NIR to estimate soil properties. A higher RPD indicates a more accurate prediction. As Table 1 shows, Vis-NIRS didn't achieve the goal especially on NO_3 and K. Only pH, P and Mg were close to RPD of 2. Vis-NIRS has the added drawbacks of needing calibration sampling for PLS regression.

Vis-NIRS probing was implemented 10 cm apart from the each coring point. The test showed that P, Mg, Total N, Total C and CEC had high correlation between the

Table 1 Results of chemometrics analysis of Vis-NIR core-scanner and Veris Vis-NIR probe

Soil properties	Range	Vis-NIR Core scanner				Vis-NIR probe insertion			
		RPD	R ²	RMSE	Std dev	RPD	R ²	RMSE	Std dev
pH	5.1-7.9	2.200	0.788	0.490	1.078	1.802	0.693	0.565	1.019
NH ₄	1.4-16.5	0.973	0.077	3.017	2.935	1.060	0.134	2.770	2.935
NO ₃	1.7-32.6	1.635	0.619	5.234	8.556	1.451	0.512	6.059	8.791
P	2.6-222	2.042	0.754	30.470	62.234	2.202	0.789	28.807	63.437
K	143-775	1.334	0.421	142.245	189.684	1.191	0.312	156.736	186.725
Ca	1434-4289	1.710	0.644	584.551	999.699	1.583	0.608	651.426	1031.112
Mg	57-802	1.923	0.725	131.860	253.602	2.053	0.752	120.753	247.926
Total N	0.08-2.29	1.454	0.521	0.016	0.023	1.430	0.493	0.016	0.023
Total C	0.57-2.29	1.577	0.584	0.263	0.415	1.534	0.559	0.278	0.426
CEC	12.5-27.1	1.054	0.142	4.429	4.667	1.213	0.324	3.846	4.667

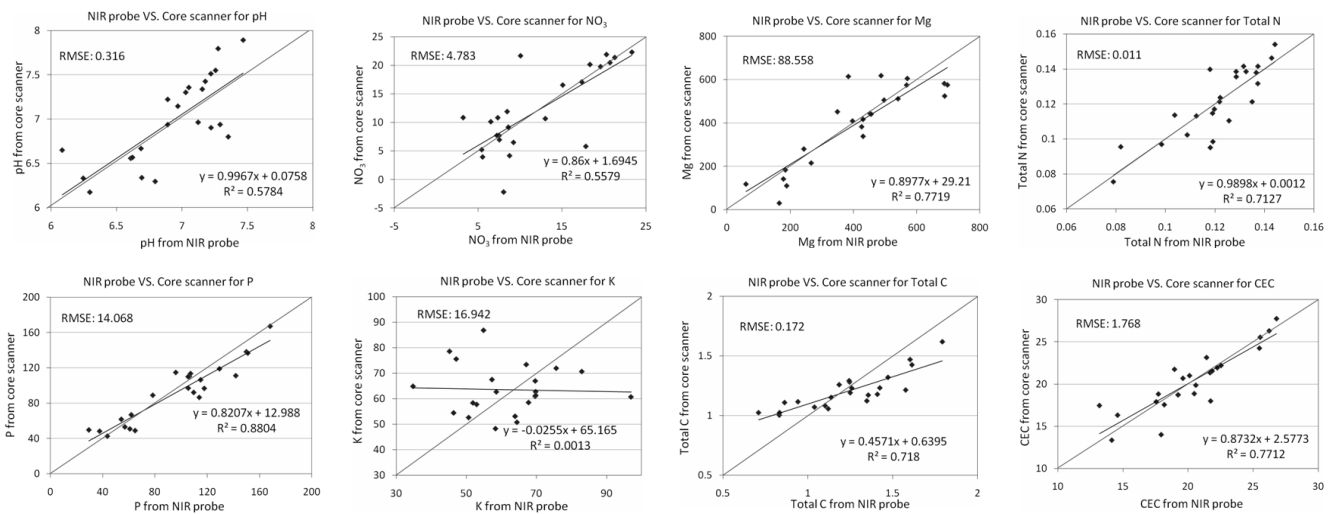


Fig. 5 Relationship between the NIR probe and the core scanner prediction for several soil properties.

probe and the core scanner with $r^2 > 0.7$ (Fig. 5). The core scanner is a feasible alternative to in-situ Vis-NIRS especially for important discovery for deeper (than 1 m) core sampling or where sensor probe usage isn't available. However, neither Vis-NIRS approach was effective at measuring soil nitrate and potassium.

B. Properties of nitrate, potassium and pH ion-selective electrodes

ISEs have been used to directly measure soil chemical properties, unlike other sensors such as a spectrometer, whose data need to be properly processed and calibrated with reference samples. The issues affecting the viability of ISEs, especially nitrate ISEs, in an in-field automated system are: 1) response time to reach steady state output, 2) issues of drift and durability, 3) ion-concentration detection limits and accuracy.

1) Response time

Prior to testing with the 24 soil samples to evaluate the performance of each Nitrate ISE, different N concentration solutions from 0 to 100 ppm were added in a ground soil with very low N concentration, and tested with the ISEs. From Fig. 6 and 7, the NICO ISE had faster response than the ASI ISE, and needed less time to reach a steady state output for detecting lower concentration of Nitrate.

Fig. 8 and 9 show NICO and ASI nitrate electrodes performance with lab results at different reading times for the 24 soil samples with 4 nitrate ranges in 3 soil textures taken from after core scanning. The NICO ISE shows the best correlation in the reading at 5 min ($r^2 = 0.9343$) but the regression coefficient shows greater (1.2799) than 1.

The ISE reading at 90 s shows around 1 of regression coefficient (1.08), which implies no additional calibration is required with lab value to estimate soil nitrate in a field.

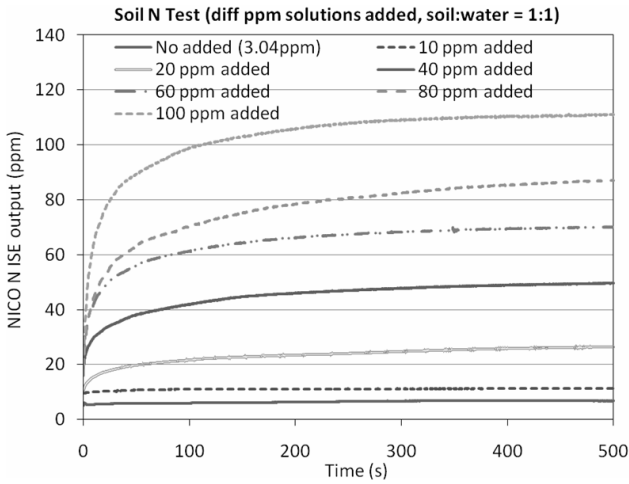


Fig. 6 NICO Nitrate ISE's time response for different concentration N solutions.

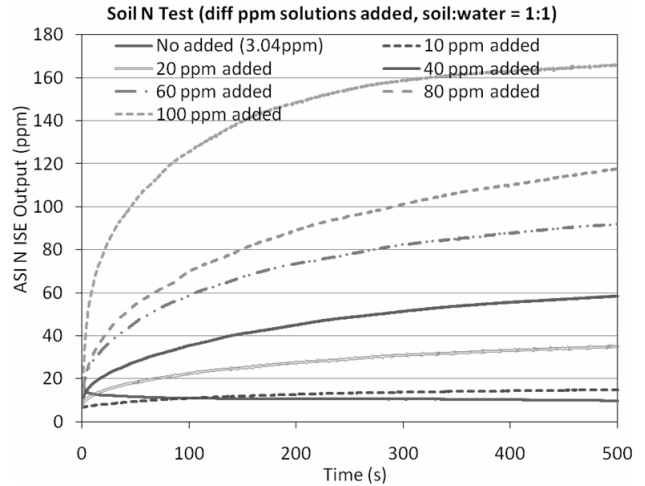


Fig. 7 ASI Nitrate ISE's time response for different concentration N solutions.

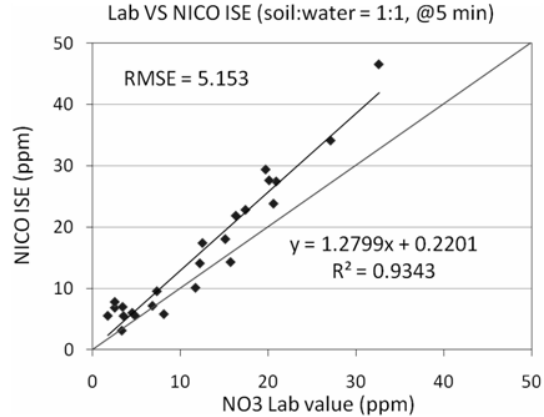
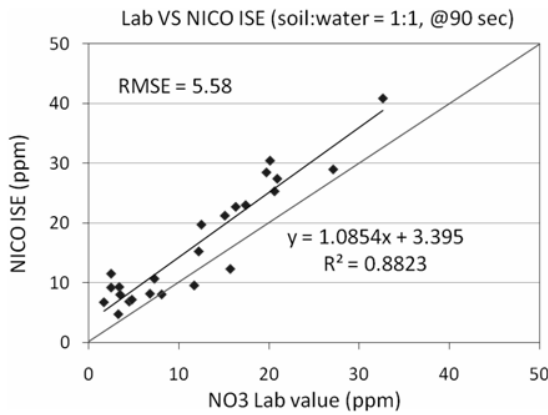


Fig. 8 NICO nitrate ISE performance at 90 s and 5 min reading with 24 soil samples from 4 nitrate ranges in 3 soil textures.

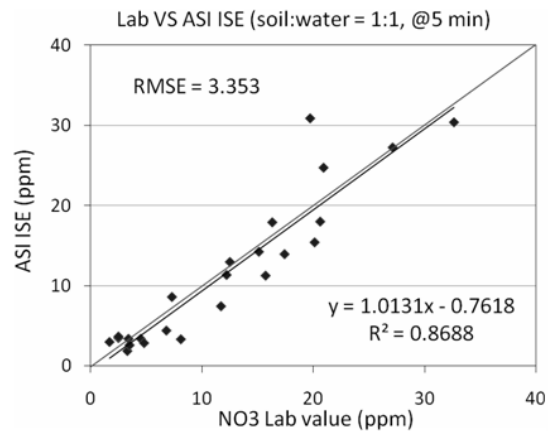
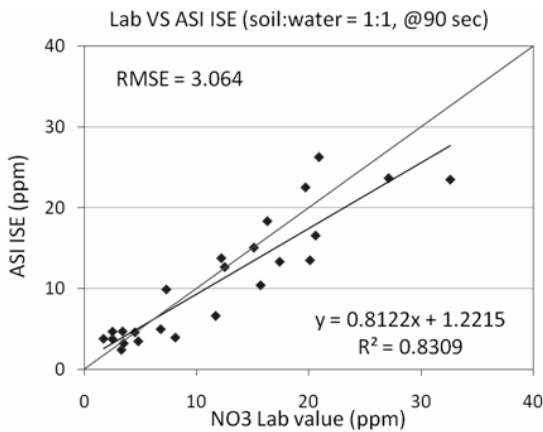


Fig. 9 ASI nitrate ISE performance at 90 s and 5 min reading with 24 soil samples from 4 nitrate ranges in 3 soil textures.

The ASI ISE shows less sensitivity than NICO at the same reading time. Reading at 5 min for ASI shows a regression coefficient around 1, but 5 min reading time may be too long to map one location in a field. ASI test at 90 s also

showed high correlation ($r^2 = 0.8309$). Because NICO ISE showed high correlation with the lab values at 90 s reading ($r^2 = 0.8823$), there may be an option to reduce measuring time in fields by stopping measurement cycle when readings

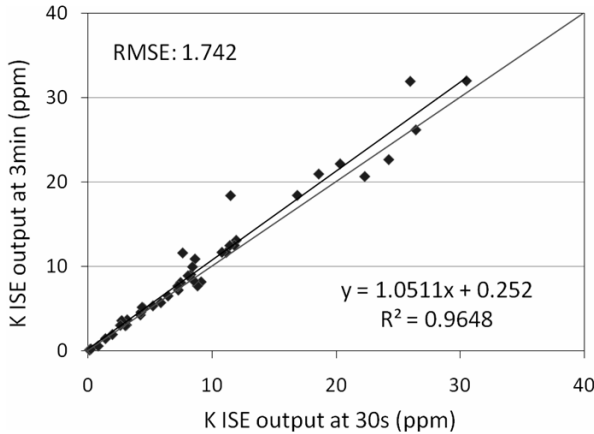


Fig. 10 Comparison of K ISE output at 30s and 3 min.

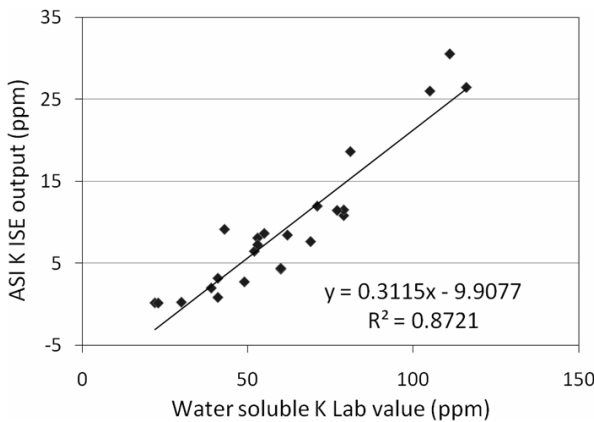


Fig. 11 Plot for water soluble K and ASI K output at 30s.

exceed a critical level in which fertilizer does not need to be applied. As shown in Figure 6, the N solutions of 20 ppm did not need 50 s to reach the steady state output.

For Potassium (K) measurement, an ASI KT43 ISE was selected. The K ISE showed very high correlation between the measurement at 30 s and 3 min with a regression coefficient of 1 and a low offset (Fig. 10). It means the K ISE output is stable within 30 s which is much faster than N ISE. K ISE only measures water soluble K, not exchangeable K, which is used for fertilizer application recommendations. Therefore exchangeable K should be estimated with K ISE and other soil properties like bulk soil conductivity (ECa) or CEC. Fig. 11 shows high correlation between the lab measured water soluble K and K ISE output. Fig. 12 shows the relationship between lab measured exchangeable K and predicted K using multiple linear regression with K ISE and Lab CEC.

For pH measurement, an antimony metalloid electrode and a glass electrode were selected. Both electrodes showed

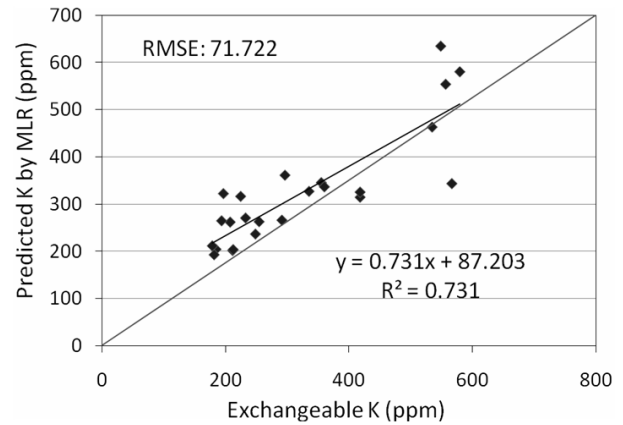


Fig. 12 Exchangeable K prediction using multiple linear regression by lab CEC value and K ISE output.

fast response time within 10 s, and high correlation with lab data ($r^2=0.913$ for antimony and $r^2=0.8672$ for glass).

2) ISE drift and durability

The measured voltage of ISE is proportional to the logarithm of the concentration, and the sensitivity of the electrode is expressed as the electrode slope, which is the difference in millivolt per decade of concentration (1 and 10 ppm or 10 and 100 ppm). Fig. 13 and 14 show offset and slope history from the NICO and ASI N ISE calibration, and the calibration was implemented every cycle before measuring soil nitrate contents. The dates of the experiment were 11/20/09, 11/23/09, 11/24/09 and 11/30/09.

From the first day of the experiment, the offsets decreased significantly as more tests were done. After implementing the first day test, the ISEs were washed, dried and not used until the next test. Three days later (11/23/09), the offset history showed the similar pattern as one in the first test set. One day later (11/24/09) another test was implemented, but the offset did not show the previous trend, in which the first offset returned back to high value and then kept decreasing. This may be because less time was given to the ISEs to recover. Six days later, the last test set showed the offset returned back to 460. The slope history did not show significant loss of sensitivity, and all slope values were higher than 40 during tests. From the above test, it was found that frequent calibration can reduce ISE's drift. Although the calibration parameters were changed by the test repetition and unused duration of ISEs, the measurement was very precise as seen in Fig. 6 and 7. Calibration before each measurement is the best way to measure soil N

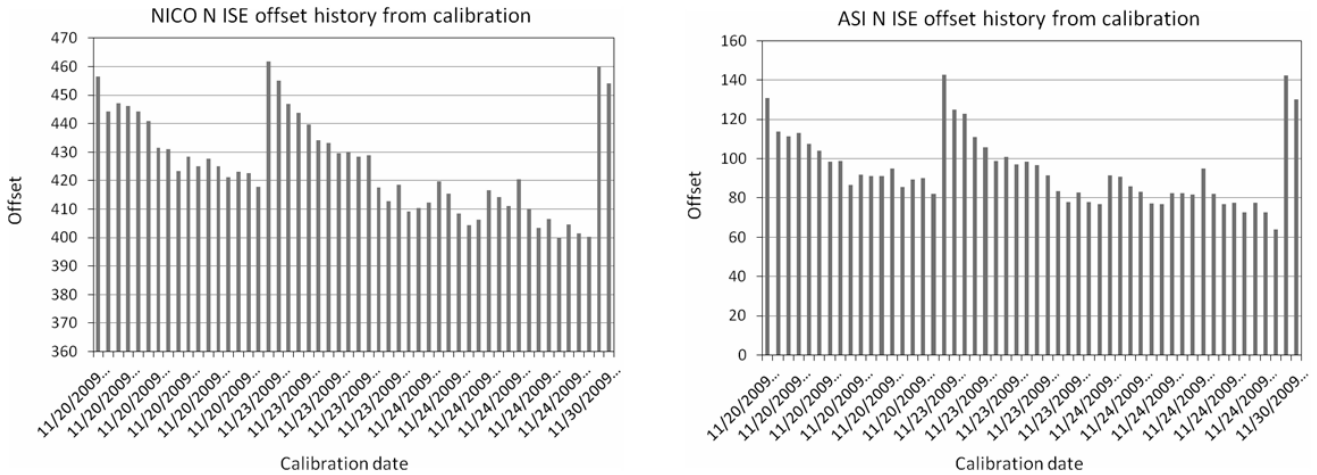


Fig. 13 Offset history from calibration for NICO and ASI N ISEs.

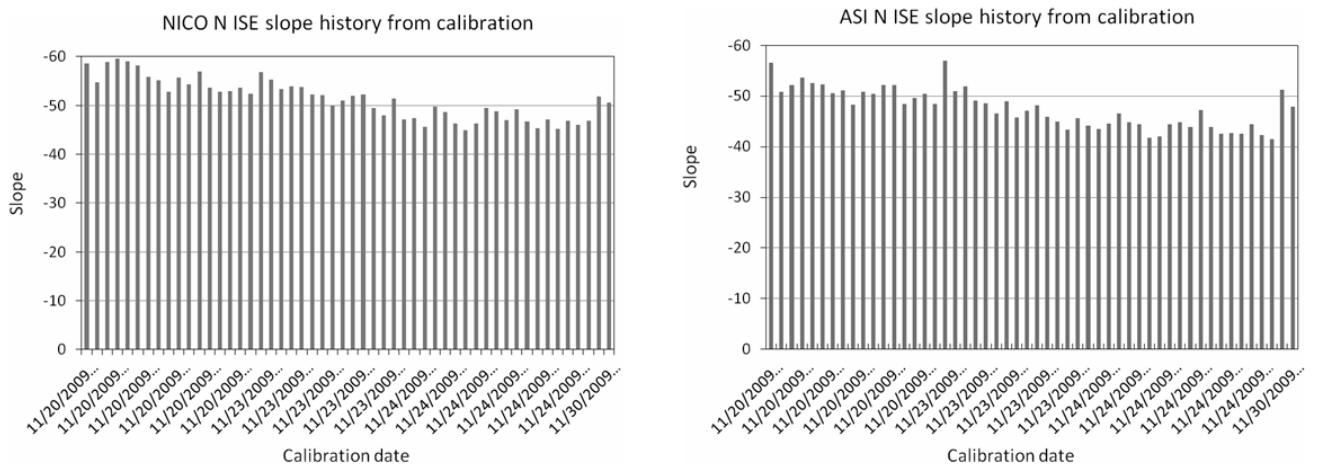


Fig. 14 Slope history from calibration for NICO and ASI N ISEs.

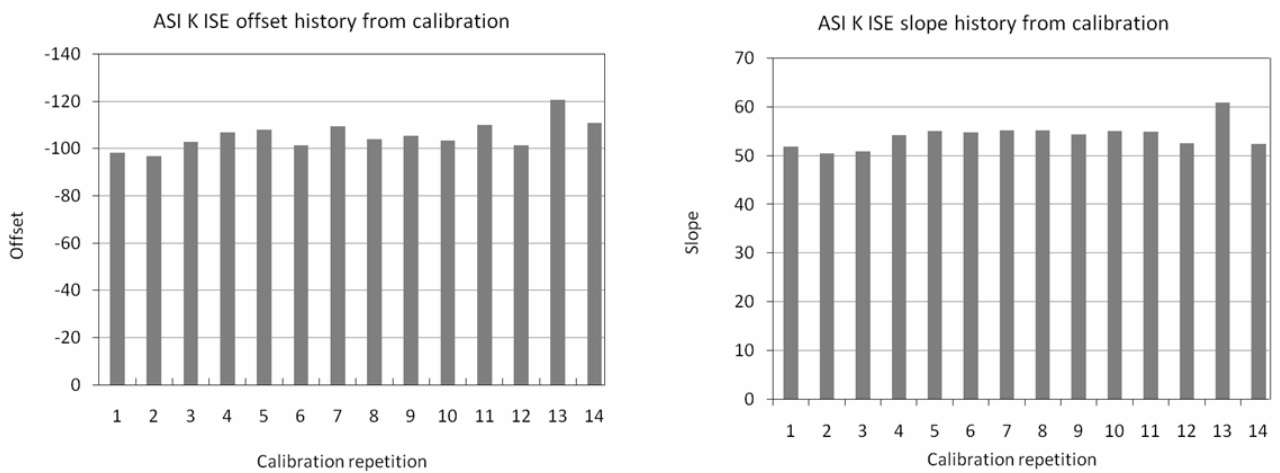


Fig. 15 Offset and slope history from calibration for ASI K ISE.

precisely. Unlike the calibration for N ISE, ASI K ISE did not show any decreasing trend for offset or slope in the calibration history as shown in Fig. 15.

Both of the ISEs have polyvinyl chloride (PVC) sensitive membranes which is less durable than glass or metal electrodes. To reduce ISE's mechanical damage from contacting the

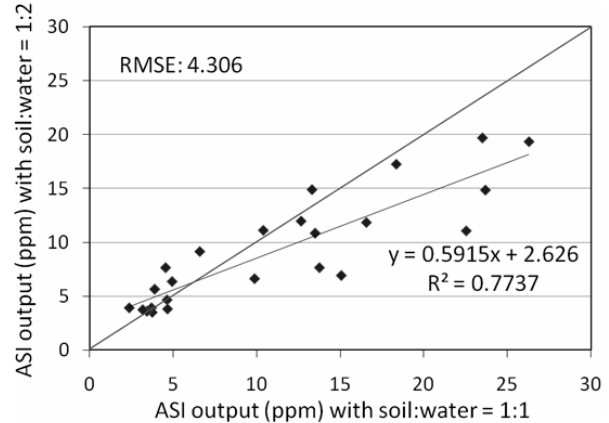
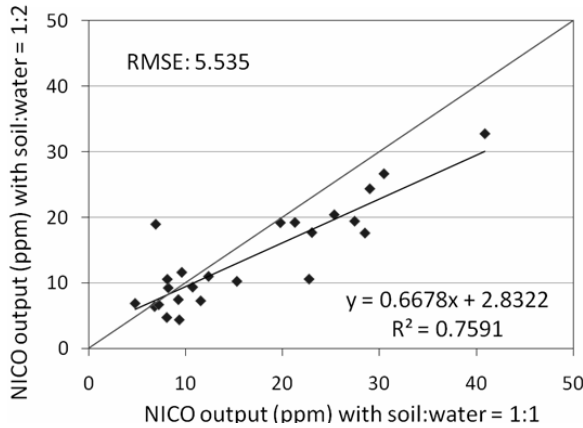


Fig. 16 Soil to water ratio plots for NICO (left) and ASI (right) Nitrate electrodes.

sensitive surface to soil, measurement was implemented in soil slurry. To evaluate ISE’s durability in slurry, 200 soil samples were measured with ISEs for each N and K. Each measurement was recorded for 5 min, and calibration was implemented between every measurement using 10 and 100 ppm solutions. An ISE with slope lower than 40 and permanent loss of sensitivity may be considered as failed and needing replacement. According to the history of calibration, severe sensitivity loss has not yet appeared, and the ISEs still work properly after 300 measurements.

Another test was implemented to evaluate N ISEs’ sensitivity for continuing measurement without rest. N ISEs were inserted in soil slurry with known ion concentration for 60 s and washed for 5 s, then kept the routine until ISEs lose the sensitivity. After about 50 times of continuous reading, the ISEs showed severe drift during measurement and never stabilized. The ISEs’ sensitivity was returned to a normal condition in distilled water after an hour later. However this sensitivity loss may not happen in field measurement, because rest time can be given to the ISE after each measurement during sequence of washing slurry chamber and ISEs, taking sub cores, preparing slurry and calibration.

3) Ion-Concentration Detection

As the results in Figures 8 and 9 show, the ISEs from both vendors were able to accurately measure field-typical nitrate and potassium concentrations, from contrasting soil textures, using 1:1 soil water ratios. To allow easier cleaning of the slurry chamber, the soil to water ratio anticipated was 1:2 or higher. According to our tests, performance for NICO and ASI N ISEs at 1:2 for soil to water ratio showed much lower readings than 1:1 ratio (Fig. 16). These reductions

are due to dilution of soil slurry. K ISE also showed lower regression coefficient than 1 (0.74).

Low concentrations of N and K ions may require using ion strength adjusters for faster response; however it was found that their use was unnecessary for the test soils with higher than 3 ppm concentration of N and K ions.

C. Determination of Nitrate content of soil using Mid-IR

The mid-IR spectroscopy consultant initially encountered difficulty using a preliminary set of 10 soil samples with field-typical range of nitrate (<100 ppm). After calcareous samples were removed from the set, calibration improved slightly, but not enough samples remained to be valid. Calibration was attempted on a second set using 20 samples, with similar results. Even after several calcareous samples were removed, calibration to NO₃ was not successful (Fig. 17). The RMSE was nearly 30 ppm, and even with a high

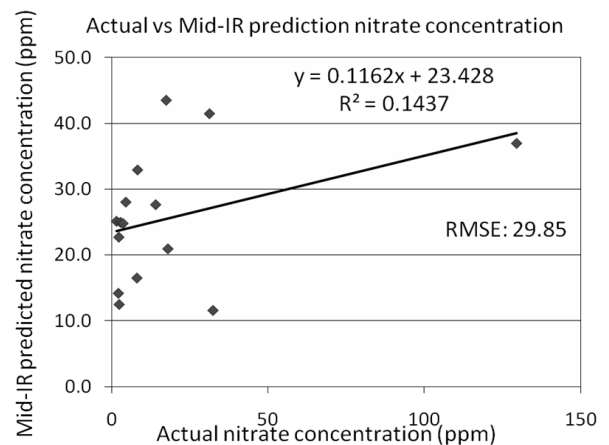


Fig. 17 Prediction of nitrate concentration in 20 soil samples.

nitrate sample removed, the RMSE remained over 18 ppm. After removal of calcareous samples on a larger sample set, results improved considerably with an R^2 of 0.64 and RMSE of 6 ppm. However, this was only possible after carbonate samples were detected and eliminated, which is not feasible under in-field measurements.

D. Evaluation of the relationship between soil EC and nitrate levels

Soil EC sensing of soil cores was accomplished by the following technologies: 1) a miniaturized four electrode Wenner array EC probe was constructed, with signal and logging from commercially available Veris instrument, and 2) a commercial EC electrode meter (WD-35607, Oakton instruments, Vernon Hills, IL, USA) to measure conductivity of soil solution and/or soil core.

Fig. 18 shows very high correlation between a commercial conductivity meter and a Veris mini EC probe though the mini EC probe readings show two times higher than the commercial conductivity meter.

Table 2 shows comparison of Lab CEC, Nitrate level, and EC from probing insertion, Mini-probe and EC meter. Table 3 shows correlation matrix among nitrate level and several EC readings. Lab CEC value shows correlation close to 0.6 with all the EC readings, but correlation between nitrate and all the three EC devices was low.

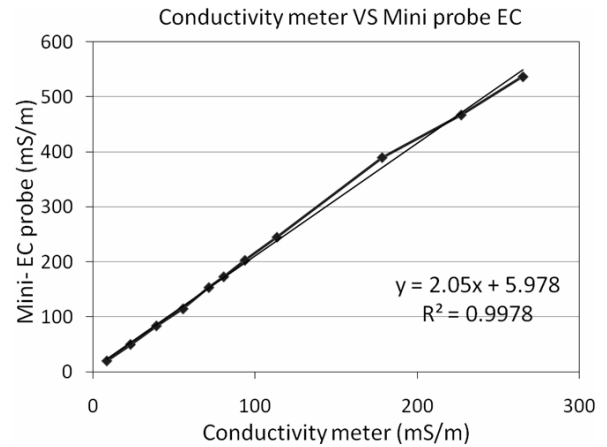


Fig. 18 Correlation between a commercial conductivity meter and a mini EC probe.

Table 2 Comparison of Lab CEC, Nitrate level, and EC from probing insertion, Mini-probe, and EC meter

Sample ID	Nitrate level (ppm)	Lab CEC	EC from a probing insertion (ms/m)	Mini-EC from core (ms/m)	EC meter from slurry (ms/m)
Clay #1 0-9	11.7	25.2	18.0	85.5	45.0
Clay #1 9-18	2.5	22.0	33.9	85.9	42.0
Clay#2 0-9	12.5	27.1	37.7	77.7	46.0
Clay #2 9-18	2.5	22.4	47.8	81.4	40.7
Clay #3 0-9	16.3	24.9	41.3	88.4	38.0
Clay #3 9-18	3.3	22.3	43.9	89.3	36.0
Clay Control 0-9	7.3	26.2	31.7	82.5	37.0
Clay Control 9-18	1.7	22.0	50.2	89.3	35.0
Silt #1 0-9	20.6	20.0	31.2	45.9	34.0
Silt #1 9-18	17.4	26.7	33.2	55.6	36.0
Silt #2 0-9	19.7	20.1	34.6	41.0	31.2
Silt #2 9-18	15.1	14.8	34.0	36.3	31.0
Silt #3 0-9	32.6	19.1	20.1	49.8	40.0
Silt #3 9-18	20.1	14.9	15.6	44.4	30.5
Silt Control 0-9	27.1	17.0	14.8	47.6	38.6
Silt Control 9-18	15.7	17.9	15.8	77.4	40.5
Sand #1 0-9	4.5	12.9	16.3	50.6	25.6
Sand #1 9-18	3.4	23.3	27.8	33.3	37.5
Sand #2 0-9	12.2	12.5	19.6	37.6	37.0
Sand #2 9-18	4.8	21.8	37.5	43.1	35.0
Sand #3 0-9	20.9	13.3	22.2	55.1	34.5
Sand #3 9-18	6.8	22.6	38.4	43.6	38.0
Sand Control 0-9	8.1	14.6	20.1	46.2	25.0
Sand Control 9-18	3.5	23.3	37.5	69.4	31.0

Table 3 Correlation matrix among nitrate level and several EC readings

	Nitrate level (ppm)	Lab CEC	EC from in situ probing (mS/m)	Mini-EC from core (mS/m)	EC meter from slurry (mS/m)
Nitrate level (ppm)	1.00				
Lab CEC	-0.28	1.00			
EC from in situ probing(mS/m)	-0.51	0.59	1.00		
Mini-EC from core (mS/m)	-0.35	0.55	0.43	1.00	
EC meter from slurry (Ms/m)	0.07	0.57	0.15	0.48	1.00

4. CONCLUSIONS

This study evaluated frequently cited several methods of in-field measurement of soil properties using cores extracted by a hydraulic soil sampler. Cores were extracted from each of 12 barrels inserted in three different fields (sandy, silt loam and silty clay loam) with four different concentrations of ions (zero, low, medium and high N and K fertilizer applied). Major findings were:

- (1) A prototype core scanner was built to accommodate Veris Technologies commercial Vis-NIRS equipment. The test result for pH, P and Mg were close to RPD of 2, however the scanner could not achieve the goal of RPD of 2 especially on NO₃ and K.
- (2) In situ NIRS/EC probe measurement showed that pH, P and Mg were close to RPD of 2, while NO₃ and K were RPD of 1.5 and 1.2, respectively. Correlation between the probe and the core scanner showed high with $r^2 > 0.7$ for P, Mg, Total N, Total C and CEC.
- (3) The mid-IR spectroscopy measurement showed that RMSE for nitrate was 18 ppm even with calcareous samples and possible N outlier removed.
- (4) Soil EC sensing of soil cores was accomplished with the in-situ sensor probe, and with a miniaturized four electrode Wenner array EC probe and a commercial EC electrode meter. The results showed Lab CEC value has correlation around 0.6 with the EC readings from all three EC devices; however nitrate level did not show any correlation to EC.
- (5) Testing of nitrate and potassium ion-selective electrodes (ISEs) has revealed promising results, with acceptable errors measuring soil solutions containing nitrate and potassium levels that are typical of production agriculture

fields. The NICO N ISE had a faster response than ASI N ISE, yet both showed high correlation with the lab values at 90 s reading ($r^2 = 0.88$ and $r^2 = 0.83$). A K ISE showed much faster response than N ISEs and settled in stable status within 30 s. The correlation between Lab measured exchangeable K and predicted K showed high using multiple linear regression with the K ISE and Lab CEC ($r^2 = 0.731$).

This study results showed that ion-selective electrodes were the only sensors tested that are currently feasible to use in an automated system. When clean, recently calibrated ISEs were brought into contact with soil core segments dispersed in a 1:1 soil water ratio, and allowed 1-2 minutes to settle, the result was a nitrate measurement with an error of 5 ppm or less. Further research will be focused on developing an automated in field measurement system for soil nitrates and potassium with ISEs.

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