

Development and use of an automated on-the-go soil nitrate mapping system

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Development and use of an automated on-the-go soil nitrate mapping system

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Abstract

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An on-the-go soil nitrate mapping system (SNMS) has been developed that automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyzes it electrochemically for nitrate (NO_3^-) concentration in real-time (6 s) using a nitrate ion-selective electrode (NO_3^- -ISE) as the analysis instrument. Additionally, global positioning system (GPS) geo-referenced position data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field being sampled.

The SNMS overcomes many of the impediments, roadblocks, and serious obstacles cited by many researchers of measuring and assessing soil $\text{NO}_3\text{-N}$ variation using conventional methods in terms of sample analysis lag time, high labor requirements, and high costs. Soil $\text{NO}_3\text{-N}$ measurements using the SNMS can be obtained on a fine scale and with lab-grade accuracy. These data can be used for (i) linking soil $\text{NO}_3\text{-N}$ variation to crop growth, (ii) environmental monitoring of soil $\text{NO}_3\text{-N}$, (iii) developing site-specific crop management practices, and (iv) assessing soil nitrate variation.

It was determined that a NO_3^- -ISE could be used in a soil-slurry solution. Lab tests using a Chaswood clay loam soil indicated that measured NO_3^- concentrations did not vary significantly with soil:extractant ratio or extract clarity. Using normalized response time curves, a field (soil) calibration method was developed that enables sample NO_3^- concentration to be predicted with 95% accuracy after 6 s of measurement time.

Performance testing of the soil sampler was conducted in five fields. Coefficient of uniformity (CU) for sample bulk density was 92.9%, which produced less than a 5.5% deviation in sample delivered weight (DW) in 83.6% of the cases. Mean DW error was 10.9% and DW CU was 82.0%, mostly due to localized high clay content in three of the fields. Mean pocket fullness (PF) was 89.9%, and PF CU was 83.6%. Pocket fullness was linearly correlated with DW ($R^2 = 0.979$, $n = 140$). It was concluded that the sampler's 'uniform bulk density' design principle was validated for all intents and purposes of field use. Delivered weight uniformity, particularly when sampling in clayey soils, should be increased by further improving the design.

Extensive field-scale validation testing of the SNMS' nitrate extraction and measurement sub-assembly in wheat (*Triticum aestivum* L.) and carrot (*Daucus carota* L.) production systems was performed. Field conditions included conventional tillage vs. no tillage, inorganic vs. organic fertilization, four soil groups, and three time points throughout the season. It was found that: (i) the level of agreement, as measured by Root Mean Squared Error (RMSE), Mean Absolute Error (MAE) and Coefficient of Efficiency (CE), between SNMS soil $\text{NO}_3\text{-N}$ and standard lab soil $\text{NO}_3\text{-N}$ measurements was excellent; (ii) at the field-scale, there was little practical difference when using either integer math or whole math data processing; (iii) regression equations can be used to enable field measurements of soil $\text{NO}_3\text{-N}$ using the SNMS to be obtained with lab-grade accuracy; (iv) future designs of the SNMS' control system can continue to use cheaper integer math chip technology for processing the NO_3^- -ISE readings; and (v) future designs of the SNMS would not need a soil moisture sensor, ultimately saving on manufacturing cost and keeping the system simpler.

The SNMS can be used as an effective tool to assist soil scientists with experimental investigations of the spatial and temporal aspects of soil $\text{NO}_3\text{-N}$. Using data collected by the SNMS and a combination of classical and geostatistical analytical techniques and tools, the spatial and

temporal aspects of NO₃-N variation in wheat at several time points covering pre-seeding, growing season, and post-harvest soil conditions, as well as the intrinsic spatial structure of NO₃-N present in the field, were assessed. Posted values (contour) maps were generated that gave excellent visual pictures of the spatial variation. The means for each sampling date varied between 4.38–28.80 mg kg⁻¹, and coefficients of variation ranged between 24.1–71.2%. A very strong ‘proportional effect’, and significant positive autocorrelation at separation distances ≤20 m were found. Variograms of spatial structure for each sampling date were highly similar with nuggets between 0.291–0.510, ranges between 27–68 m, and nugget-to-sill ratios between 0.280–0.439. Spatial dependency was found overall to be moderate. The intrinsic spatial structure of NO₃-N variation was determined to be temporally stable over the study period. A scaled averaged variogram model representing the intrinsic spatial structure had a sill of 1.005, a nugget of 0.331, and a range of 44 m.

The SNMS can be used as an effective tool for assisting plant scientists with the conduct of agronomic experiments. Soil NO₃-N, plant nitrogen, and yield responses in (i) wheat under liquid dairy manure (LDM) management with conventional tillage (CT) and no tillage (NT) treatments, and (ii) carrot under CT management with inorganic fertilizer (IF) and LDM fertility treatments were determined at seven time-points over a growing season. In wheat, mean soil NO₃-N level varied with sampling date, but not between treatments except early in the season when it was nearly two times higher for CT. Mean plant tissue-sap NO₃-N, grain yield, and grain Total N showed no difference between treatments. In carrot, mean soil NO₃-N level varied with sampling date and between treatments. Early in the season, it was nearly three times higher for IF and then dropped to remain at two times higher during the remainder of the season. Mean plant tissue-sap NO₃-N and tissue Total N varied with sampling date but not between treatments, except for Total N at the end of the season. Fresh root yield and root Total N showed no difference between IF and LDM.

The SNMS offers the potential to assist researchers working in *precision agriculture* to develop better soil nitrogen practices for agricultural production. It offers farmers the potential to more intensely and precisely analyze variations in soil NO₃-N levels throughout the growing season in correlation with environmental and crop response data in order to make the most sound and site- and time-specific management decisions possible. As well for farmers, it offers the potential for them to measure and document soil NO₃-N levels in their fields thus improving traceability and their ability to be compliant with any current and future legislation requiring control of nitrogen fertilizers. It offers regulators the potential to conduct environmental monitoring of NO₃⁻ levels in agricultural fields and water sources. Ultimately as a result of its use, the public may be assured that soil nitrogen management practices in agriculture are being conducted in the most environmentally friendly way.

Keywords: Ion-selective electrode, precision agriculture, soil sampling, geostatistics, nitrate variation, liquid dairy manure, tillage, wheat, carrot.

Preface

The initial work on the development of the soil nitrate mapping system (SNMS), originally called a nitrate monitoring system (NMS) began with the PhD program of my colleague and dear friend Dr. John Adsett. When I came to the Nova Scotia Agricultural College (NSAC) as a faculty member in 1989, John was on leave of absence doing his PhD work at the University of Saskatchewan. We corresponded by letter and I offered to work on continued development of the system with him when he returned to the NSAC in 1990. So began a research partnership spanning 17 years until his retirement in 2007. Work on developing the system was intermittent over the years for a variety of reasons, but always with vision and purpose. The results of our work were not always published. Being very hands-on and practical-minded types of individuals, we were both just happy to be “doing things” rather than “writing about what we were doing”. Readers of this thesis, therefore, may sometimes wonder “something seems to be missing here?” I have done my best to write this thesis so ‘apparent gaps’ are minimal. Readers can rest assured that the work conducted during this program has been very, very detailed and methodical. Dr. Adsett also is one of my co-promotors at the NSAC and I wish to fully acknowledge his significant contribution to the research. Thank you, John!

To my other co-promotor at the NSAC, Dr. Kris Pruski, I also wish to extend a sincere thank you for your assistance with this research work. Your guidance, moral support, and friendship have been a great help to me.

I no doubt will be forever grateful to my promotor at Wageningen University, Dr. Paul Struik for giving me the opportunity to pursue this PhD degree under his guidance. From a professional perspective, Paul is an exceptional researcher and thesis supervisor. Working with him has been fabulous. He knew when and how much to push to get the best out of me. He was always respectful of my situation of doing this degree while continuing to fulfill my work responsibilities at the NSAC. We had some great discussions about the research both in person and via e-mail. Paul was always prompt with his reviews of the data files and results, journal papers, and thesis manuscript. From a personal perspective, Paul and his wife Edith have been gracious hosts during my visits to the Netherlands. We enjoyed many visits together, tours around the Netherlands, fine dining, and good Scotch. I am truly blessed to have had Paul as my supervisor. I look forward to many more years of collaboration and friendship. Thank you, Paul! Thank you, Edith!

To my remaining chapter papers co-authors Jacob Thottan, Cathy MacLeod, Dr. Tess Astatkie, Dr. Gordon Brewster, and Dr. Raj Lada, please know that I am grateful

for your contributions to the research. It has been a pleasure to work with you.

I am indebted to Dr. Jerzey Nowak a former colleague at the NSAC and still a friend who was the one who originally gently pushed me to pursue this degree. Thank you, Jerzy.

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The contributions of the Nova Scotia Water Quality Research Group (NSWQRG) and NSAC's Processing Carrot Research Program (PCRP) group are gratefully acknowledged.

The advice of Dr. Claude Caldwell and Dr. Glenn Stratton, NSAC faculty colleagues, regarding certain field and lab procedures is also appreciated.

On the personal side, I extend my heart-felt thanks to several of my close friends: Jay Brenton, Susan Dunn, and Judy Milne in Canada, and Annemie Hanssen and Lucy Platvoet in the Netherlands. Your support when I needed friendship and spiritual uplifting to keep trudging onward was a saving grace.

My family has also given me great support. I expect it is inconceivable to many people what a family goes through when one member is heavily engaged in the pursuit of a PhD degree while working full-time. It has not been easy on them or me. They know I love them dearly, but I would like to publicly acknowledge that love. It is for them that I live. I cannot make up for lost family time. I can only say "I love you" to my children Andrew, Jennifer, Allison, and Nicole, and my dear, dear wife Lynn. Thank you for your support and love.

Lastly, I would like to thank God. It is through His will and grace that I have been blessed with the skills and knowledge to complete this work. He provided me as

well with a little ‘study buddy’ named Bentley, a Lhasa Apso puppy, to keep me company during the many hours of aloneness sitting in front of my computer in my home office.

Kevin J. Sibley

Nova Scotia, May 2008

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Frequently used abbreviations

AIC	Akaike information criteria
BD	bulk density
CE	coefficient of efficiency
CT	conventional tillage
CU	coefficient of uniformity
CV	coefficient of variation
DAP	days after planting
DC	direct current
DOY	day of year
DPM	data processing methods
DTGS	deuterated triglycine sulfate
DW	delivered weight
FIA	flow injection analysis / flow injection autoanalyzer
GPS	global positioning system
IF	inorganic fertilizer
IM	integer math
IMFits	integer math regression fit values
ISA	ionic strength adjustor
ISE	ion-selective electrode
ISFET	ion-selective field effect transistor
LDM	liquid dairy manure
MAE	mean absolute error
MC	moisture content
MCC	moisture content correction
MCT	mercury cadmium telluride
MIR	mid-infrared
NIR	near-infrared
NMS	nitrate monitoring system
NSAC	Nova Scotia agricultural college
NSERC	Natural Sciences and Engineering Research Council
NSWQRG	Nova Scotia water quality research group
NT	no tillage
PCRCP	Processing Carrot Research Program
PF	pocket fullness
RMSE	root mean squared error
RSS	residual sum of squares
SBC	Schwartz's Bayesian criteria
SNMS	soil nitrate mapping system
SSCM	site-specific crop management
UMVUE	uniformly minimum variance unbiased estimators
WM	whole math
WMFits	whole math regression fit values

CHAPTER 1

General introduction

Soil nitrate links to crop growth and yield

Crop growth and yield are affected by the ability of the plants to take up and utilize available inorganic soil nitrogen. Nitrate is the pre-eminent form of inorganic soil nitrogen which is taken up and utilized by plants and is the major nutrient factor determining crop yield (Hay and Walker, 1989). Some of the soil nitrate arises from natural soil processes, whereas farmers also apply nitrogen to the crop in the form of inorganic fertilizer or manure to the soil, or through irrigation water or foliar applications. The presence or absence of $\text{NO}_3\text{-N}$ in the topsoil is often an indicator of how thoroughly the plants have been able to take it up and whether the plants would respond to the addition of fertilizer (Fox et al., 1989), as most $\text{NO}_3\text{-N}$ is taken up from the top 30 cm of soil (Schröder et al., 2000).

Soil nitrate is an environmental issue

The importance of dealing with environmental issues associated with the use of nitrogen fertilizers will continue to increase as modern agriculture scrambles to provide the world's rising population with high-quality, safe, and nutritious food. Water sources contamination and associated socio-economic costs indicate a great need for precise soil fertility management practices – using the right form of fertilizer, applied at the right time, in the right amount, and in the right way (Power and Schepers, 1989; Dinnes et al., 2002). The anion nitrate (NO_3^-) is highly soluble in water. Thus, it is contained in interstitial water within the soil matrix. There it is readily available for plant uptake. But, it can also move freely with water flow, eventually leaching into surface-water and groundwater bodies. Therefore, it has been found to cause many of the environmental issues in water sources associated with inorganic fertilizer and manure use (Spalding and Exner, 1993; Jemison and Fox, 1994; MacDonald, 2000; Dinnes et al., 2002).

The seriousness and extent of NO_3^- contamination of water sources and its effect on drinking water quality has been documented and discussed by many researchers in Canada, the United States, and the European Community (USEPA, 1990; Addiscott et al., 1991; Reynolds et al., 1995; Oenema et al., 1998; Henkens and Van Keulen, 2001). As a result, policy makers are revising laws to ensure the safety of public water supplies. These include amendments to the Water Pollution Control Acts in Canada and the United States, the European Community Nitrate Directive, and the

Mineral Policy in the Netherlands.

Nitrate leaching from soil into groundwater is dependent on many soil and environmental factors and soil and crop management practices. Most of the cases where agriculture has been implicated for causing NO_3^- pollution have been attributed to poor soil nitrogen management practices involving inorganic and manure fertilizer inputs (Mudahar and Hignett, 1987; Follett, 1989; Geron et al., 1993; Campbell et al., 1994; Patni et al., 1998; Koroluk et al., 2000; Astatkie et al., 2001; Randall and Mulla, 2001; Dinnes et al., 2002). As such, better soil nitrogen management practices, including more accurate fertilizer recommendations and placement, could help minimize the contribution by agriculture to the NO_3^- pollution problem.

Precision agriculture and site-specific crop management

For farmers, the profitability of their crops can be severely affected if poor nitrogen management practices are used. This is due to the extra input costs involved, the negative effects on crop performance (growth, yield and quality) experienced, and possible penalties for excessive use, leaching or surplus at the end of the growing season.

Precision agriculture offers an exciting opportunity to use highly advanced technology for developing better management practices in agriculture. The ultimate goal of such technology is to enable farmers to more intensely and precisely analyze variations in field conditions throughout the growing season, in correlation with environmental and crop response data, in order to make the most sound, and site- and time- specific management decisions possible. *Precision agriculture* seeks to use this knowledge of variation to develop site-specific crop management (SSCM) practices which offer the potential for increased production efficiencies to farmers, while at the same time offering assurances to the public those practices are being conducted in the most environmentally friendly way (Birrell and Hummel, 2000; Ehsani et al., 2001; Adamchuk et al., 2004a; Bongiovanni and Lowenberg-DeBoer, 2004; Bourenanne et al., 2004).

One of the gaps which remain to be filled in *precision agriculture* technologies is the availability of an economical, automated, on-the-go mapping system that can be used to intensely and accurately collect information on the current status of nitrate in the soil. The inability to assess soil and plant data rapidly and inexpensively in the field remains one of the biggest limitations of precision agriculture (Ehsani et al., 2001; Adamchuk et al., 2004b). In particular the lack of a soil nitrate ($\text{NO}_3\text{-N}$) measurement system is a major roadblock (Ehsani et al., 1999). If this roadblock could be overcome, a positive contribution toward achieving the ultimate goal of *precision agriculture* technology would be made.

Variation in soil nitrate links to crop growth and yield

Soil NO₃-N levels in agricultural fields, as well as other chemical and soil physical properties, exhibit high variation spatially and temporally and at different measurement scales and levels of aggregation (Heuvelink and Pebesma, 1999). Much research has been dedicated to assessing and characterizing this variation to improve our understanding of the effects of soil NO₃-N on crop growth and yield within agroecosystems (Almekinders et al., 1995).

Growing plants utilize varying amounts of soil NO₃-N during different phenological (growth) stages and its availability should ideally be in response to the need. In wheat, for example, the utilization of soil NO₃-N is high during tillering and a sharp rise occurs shortly before stem extension. By the time of anthesis, the level of available soil NO₃-N during early plant growth has already determined yield for the most part by influencing population density and the degree of stimulation of tiller fertility, spikelet initiation, and floret fertility. Ultimately, final grain weight, however, depends upon source-sink relationships and, in particular, upon leaf-area duration while grain filling takes place (Hay and Walker, 1989). Soil NO₃-N uptake is greatly reduced shortly after anthesis, and nitrogen is re-translocated from leaves primarily, and other vegetative organs secondarily, to the ears to meet the need of the filling grains (Simpson et al., 1983). The reduction in soil NO₃-N uptake during grain filling varies with weather conditions, disease pressures, and subsequent management practices (i.e. irrigation or chemical applications) which put stress on the plants, causing varying levels of nitrogen re-translocation from the leaves. This re-translocation of nitrogen, along with other elements, is a natural part of a leaf's senescence, but is accelerated when the rest of the plant is unable to supply nitrogen (Hay and Walker, 1989). Physiologically, soil NO₃-N and crop yields are linked via nitrate uptake and its conversion into proteins and chlorophylls during plant growth (Engel et al., 1999; Schröder et al., 2000) and photosynthesis buffering against soil nitrogen deficits by an abundance of RuBP carboxylase that serves as a reserve of protein in the leaves during unfavorable weather conditions (Hay and Walker, 1989).

The availability and distribution of NO₃-N in the soil depends on many soil forming, chemical, microbial, plant growth, environmental, and management factors that influence soil nitrogen dynamics. These factors include soil erosion, soil weathering, soil texture, soil organic matter content, soil temperature, soil pH, relative rates of N-uptake by plants, several N-transforming processes (e.g., mineralization, immobilization, and (de-)nitrification), precipitation, evaporation, tillage, drainage, and fertilizer inputs (Addiscott, 1983; Wagenet and Rao, 1983; Trangmar et al., 1985). Because the effects of these factors and their interactions are distributed and highly variable (Almekinders et al., 1995), they also lead to the characteristic behavior of

NO₃-N being distributed and highly variable within the soil matrix.

Nitrate measurements made in the field during fertilizer application would ensure that only the amount needed by the plants is applied. Using this concept, the fertilizer application rate could be adjusted on-the-go in direct response to the available soil NO₃-N. This process would require an automated, reliable method for soil NO₃-N measurement, as well as agronomic interpretation of those measurements which consider the needs of the plants (Adsett and Zoerb, 1991).

As well, studying the levels of nitrogen in plants at the various phenological stages in correlation with availability and distribution of soil NO₃-N levels at the same times, and on a small-scale, could be useful information for researchers developing better site-specific nitrogen management practices. Collecting this information at the required sampling intensity, however, is very tedious and generally cost and time prohibitive using current methods (Engel et al., 1999; Birrell and Hummel, 2000; Ehsani et al., 2001; Adamchuk et al., 2004a).

Assessing soil nitrate variation

Classical parametric statistics, although useful to a certain degree, are not fully adequate for assessing and quantifying spatially dependent variables such as soil NO₃-N (Journel and Huijbregts, 1978; Vieira et al., 1981; Trangmar et al., 1985; Hamlett et al., 1986; Isaaks and Srivastava, 1989; Cressie, 1991; Cambardella et al., 1994; Webster and Oliver, 2001; Ruffo et al., 2005; Jung et al., 2006; and others).

Thus, geostatistical techniques have been developed to provide practically useful mathematical tools for assessing the spatial and temporal of variation and spatial structure of soil properties including soil NO₃-N (Journel and Huijbregts, 1978; Burgess and Webster, 1980; Webster and Burgess, 1984; Isaaks and Srivastava, 1989; Webster and McBratney, 1989; Cressie, 1991; Van Noordwijk and Wadman, 1992; McBratney and Pringle, 1997, 1999).

Research applying these tools on a field-scale, such as through SSCM-experimentation (Pringle et al., 2004), has led to the development of a multitude of methods for determining minimum soil sample spacing, sampling grid layout and cell size (Vieira et al., 1981; Russo, 1984; Webster and Burgess, 1984; Han et al., 1994; Van Meirvenne, 2003; Lauzon et al., 2005), optimum number of samples (Webster and Burgess, 1984), sampling schemes and protocols for pre-planning experimental designs (Trangmar et al., 1985; Chang et al., 1999; Ruffo et al., 2005) and sample bulking strategies (Webster and Burgess, 1984).

However, when using these methods for implementing *precision agriculture* practices related to soil nitrogen management, the “most serious obstacles” are still the need to know the spatial structure in advance and the cost of obtaining this information

even though the sampling effort required is much less than for full-scale sampling (Webster and Burgess, 1984; Lark, 1997; McBratney and Pringle, 1999; Jung et al., 2006).

Concept of a soil nitrate mapping system

Development of a soil nitrate mapping system (SNMS) would be a technology that can contribute to *precision agriculture* by providing a way to quickly, accurately, and affordably collect the data necessary to analyze small-scale variation in soil nitrate in time and space while crops are being grown, thus enabling this variation to be linked to crop growth and yield. Ideally while on-the-go in the field, a SNMS would automatically collect a soil sample and directly analyze it for nitrate concentration in real-time using a nitrate ion-selective electrode (NO_3^- -ISE) as the analysis instrument. Additionally, global positioning system (GPS) geo-referenced data could be simultaneously recorded at each sampling location to enable a nitrate map to be created for the field. A SNMS, thus, would overcome many of the impediments, roadblocks, and serious obstacles cited above of measuring and assessing soil NO_3^- -N variation using conventional methods in terms of sample analysis lag time, high labor requirements, and high costs.

Measuring soil nitrate directly with an ion selective electrode

The ion-selective electrode (ISE) provides a rapid and reliable method for quantitative chemical analysis of soil nitrate. Nitrate ISEs, which are highly selective to NO_3^- ions in solution, were first used around 1967 as quick and reliable alternatives to chemical-based laboratory methods for nitrate measurement (Dahnke, 1971). The NO_3^- -ISE electrochemically generates a voltage that varies with ionic strength (molarity) according to the Nernst equation (Morf, 1981). Through calibration with known standards, the logarithm of solution molarity is related to NO_3^- -ISE output voltage to determine a linear response relationship (i.e. calibration curve) for determination of nitrate concentration (mg L^{-1} or ppm) of subsequent soil sample measurements. Measurement of nitrate concentration of a soil sample then proceeds by mixing together a known 'weight' (mass) of soil with a known volume of deionized or distilled water (e.g. soil:extractant ratio) and measuring the molarity of the solution with the NO_3^- -ISE. The resulting voltage output is mathematically converted to concentration via the calibration curve, and subsequently to content (mg kg^{-1}) via the soil:extractant ratio.

Many researchers over the years have studied various aspects of NO_3^- -ISE performance (accuracy, repeatability, stability, reliability), the potential for measurement interference by other ions, solution ionic strength, and use of deionized or distilled water as an extractant, for a multitude of use conditions, and in comparison with other

chemical-based methods of soil nitrate determination (Myers and Paul, 1968; Mahendrappa, 1969; Milham et al., 1970; Onken and Sunderman, 1970; Dahnke, 1971; Mack and Sanderson, 1971; Morf, 1981; Yu, 1985; Robbins, 1989; Adsett, 1990; Adsett and Zoerb, 1991; Sah, 1994). As a result, NO_3^- -ISEs have enjoyed wide acceptability because the results obtained are comparable to other chemical-based methods' results, and they are quick and simple to use. Today, several types of NO_3^- -ISE are manufactured commercially, and they are widely used in laboratories around the world for water quality monitoring and plant tissue sap nitrate measurement in addition to soil nitrate measurement.

It is because of their well-defined operating characteristics, reliability, and commercial availability that a NO_3^- -ISE was chosen as the analysis instrument for the soil nitrate mapping system (SNMS).

Review of other on-the-go soil nitrate measurement systems

Over the last 20 years or so, attempts to develop an on-the-go soil $\text{NO}_3\text{-N}$ measurement system by other researchers have been based on three types of sensors: (i) ion-selective field effect transistor (ISFET), (ii) ISE, and (iii) spectrophotometer. The majority of this research work has not progressed past laboratory feasibility studies and testing in soil-bins, and none has resulted in a fully-functioning prototype used for conducting field experiments demonstrating their practical usefulness as has been done with the SNMS as part of the research of this thesis (presented in Chapters 6 and 7). A brief review of these works is presented below. Details can be obtained by reviewing the cited papers directly, or the summaries contained in the comprehensive review paper recently published by Adamchuk et al. (2004a) who concluded "sensor prototypes capable of accomplishing this task are relatively complex and still under development." It is interesting to note that my early research on the SMNS conducted with my esteemed colleagues (presented in Chapters 2 and 3 and published in 1994 and 1999, respectively), and the work of Adsett and Zoerb (1991) developing the first prototype, has been cited by most of these researchers.

Ion-selective field effect transistor sensor based systems

Loreto and Morgan (1996) developed a prototype on-the-go soil $\text{NO}_3\text{-N}$ measurement system that consisted of a soil core-sampling wheel, indexing and processing table, and a data acquisition and control system. This system was quite similar to that of Adsett and Zoerb (1991); however it used a specially developed prototype ISFET as the NO_3^- analysis instrument. In soil bin tests, correlations between ISFET measurements with a NO_3^- -ISE and laboratory colorimetric analysis measurements had an R^2 between were 0.65 and 0.43, respectively. The system worked reasonably

well as a first attempt, but issues with the ISFET's response characteristics and calibration drift were apparent. Work has continued focusing on the development of ISFET technology and its use in combination with novel soil extraction and flow injection analysis (FIA) systems as a potential method of real-time measurement of NO_3^- in filtered soil extracts (Birrell and Hummel, 1997, 2000, 2001; Price et al., 2003). This work has resulted in the development of a promising combination ISFET/FIA system that gives reasonable results compared to a cadmium reduction method using a Lachat FIA (Slope 1:1, $R^2 = 0.779$) with a measurement time ranging between 3–5 s (Price et al., 2003), but it is still at the laboratory level.

Ion-selective electrode sensor based systems

As part of an investigation into the feasibility of an on-the-go soil K and $\text{NO}_3\text{-N}$ mapping system, Adamchuk et al. (2002a) performed laboratory tests on four commercially available NO_3^- -ISEs to simulate the direct soil measurement technique used in an automated soil pH measurement system developed by Adamchuk et al. (1999, 2002b). In the laboratory, manually remoistened previously air dried soil samples were pressed into contact with the sensing membrane of each NO_3^- -ISE to determine NO_3^- concentration (liquid basis of mg L^{-1} reported as ppm). These results were compared to a standard cadmium reduction laboratory analysis technique to give an indication of the accuracy of the NO_3^- -ISEs. For individual soil samples, R^2 values ranging 0.38–0.63 were obtained, depending on the ISE, while averaging of three repeated measurements yielded R^2 values ranging 0.57–0.86. It was concluded that it is feasible to use a NO_3^- -ISE for measuring soluble nitrate concentration of naturally moist soil samples, but one of the main limitations of the proposed method reported was difficulty in maintaining high quality contact between soil and electrode. It should also be noted that use of the proposed method in the field in combination with the pH measurement system's soil sampling mechanism would not enable the $\text{NO}_3\text{-N}$ content (mg kg^{-1}) of the sample to be directly computed since the 'weight' (mass) of the soil sample would not be known.

Spectrophotometer sensor based systems

Laboratory testing and field-based experimentation of a near-infrared (NIR) spectrophotometer conducted by Ehsani et al. (1999) using soils samples spiked with ammonium sulfate, ammonium nitrate, and calcium nitrate (10–100 ppm) revealed that soil $\text{NO}_3\text{-N}$ could be detected with R^2 ranging 0.764–0.996 using partial least squares regression with each data point being an average of 10 sub-samples. However, the calibration equation must be derived from samples taken from the same location. Otherwise, the analysis procedure developed fails. Further laboratory-based research

work (Ehsani et al., 2001) using soil samples spiked with ammonium nitrate and calcium nitrate (400–3000 ppm) and a spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) sensor showed that the ratio of area under the nitrate peak to area under the water peak in the mid-infrared (MIR) spectra is proportional to NO_3^- concentration ($R^2 = 0.811$), and that the analysis technique is not dependent on the time of measurement, soil type, or nitrate source. However, as the authors themselves note, the range of NO_3^- concentration in agricultural soils is usually less than 100 ppm so the practicality of this sensing method is questionable unless a more sensitive mercury cadmium telluride (MCT) type sensor can be used.

Use of a real-time portable spectrophotometer using a multi-spectral approach has been investigated by Shibusawa et al. (1999, 2003). They reported that NIR reflectance could be used to detect soil $\text{NO}_3\text{-N}$ with an R^2 of 0.5.

Christy et al. (2003) have conducted preliminary field testing of a prototype soil reflectance mapping unit utilizing a NIR spectrophotometer for simultaneously measuring total N, total carbon, pH, and moisture content. Results from testing in a single field indicated the system could repeatably produce clear definition of patterns in these soil parameters related to spectral reflectance with an R^2 of 0.86, 0.87, 0.72, and 0.82, respectively.

Description of the soil nitrate mapping system developed and presented in this thesis

The SNMS (Fig. 1), as developed and presented in this thesis, is an electro-mechanical machine that automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyzes it electrochemically for nitrate concentration in real-time (6 s) using a nitrate ion-selective electrode (NO_3^- -ISE) as the analysis instrument. Additionally, global positioning system (GPS) geo-referenced position data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field being sampled.

The SNMS consists of six sub-assemblies: (1) soil sampler, (2) soil metering and conveying, (3) nitrate extraction and measurement, (4) auto-calibration, (5) control, and (6) GPS. Prior to use, the NO_3^- -ISE is calibrated using pre-prepared reagent-grade NO_3^- standards placed into the holding chambers of the auto-calibration sub-assembly. As well, a field (soil) calibration is completed to enable rapid measurements of NO_3^- concentration to be taken during system operation. As the tractor moves forward, the SNMS collects a soil sample via the combination of soil sampler and soil metering and conveying sub-assemblies. During sampling, the hydraulic-powered wood-saw blade is lowered into the soil by the carrying frame. Over a travel distance of approximately 0.5 m, the blade cuts a 15-cm deep slot and

throws a spray of finely chopped soil onto the head-end area of an automatically positioned flat-belt transfer conveyer. This action creates a sample of uniform bulk density and finely-granulated particles to facilitate the subsequent nitrate extraction process. The conveyor belt has an oblong fixed-volume pocket milled into its surface to collect a sample from the soil landing on the conveyor. A specially designed scraper placed above the belt levels the soil sample in the pocket without compaction and removes excess soil from the belt as the belt moves to deliver the soil sample to the nitrate extraction and measurement sub-assembly of the SNMS. During delivery, the pocket stretches lengthwise as it passes around the conveyor's tail-end roller to facilitate complete emptying of the pocket (like emptying an ice-cube tray).

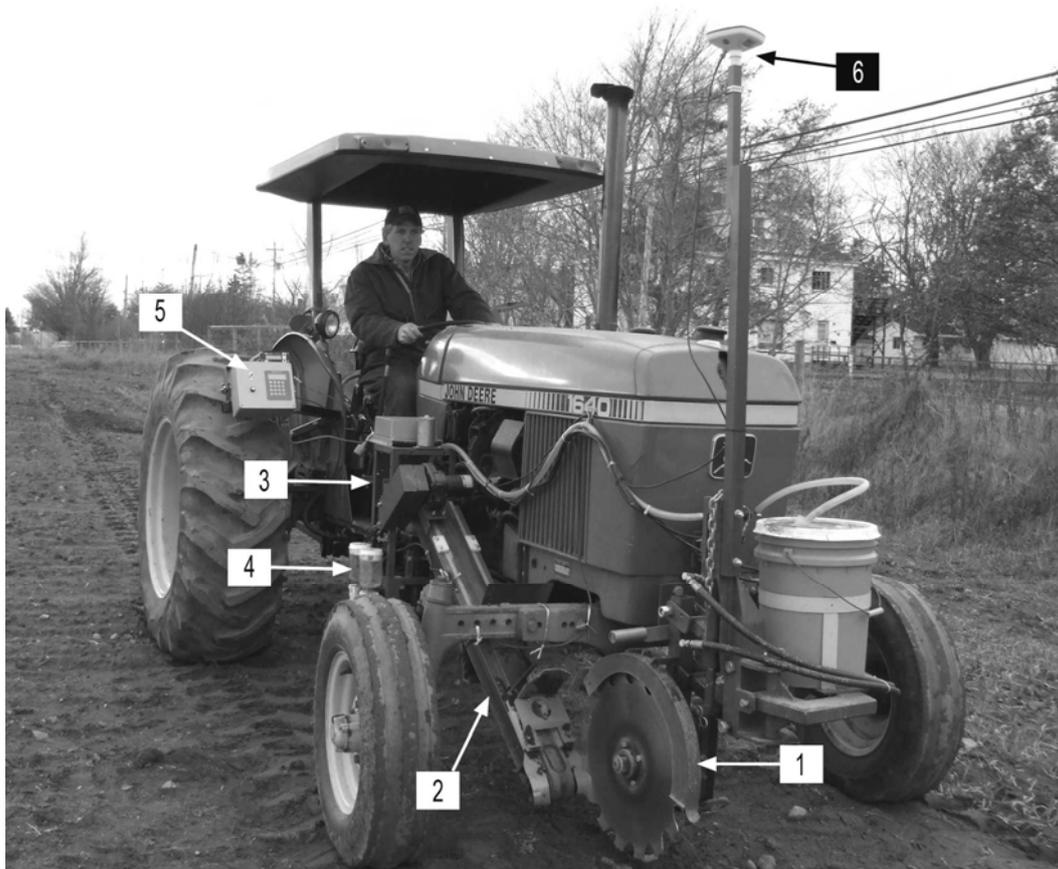


Fig. 1. Tractor-mounted soil nitrate mapping system with six sub-assemblies: (1) soil sampler, (2) soil metering and conveying, (3) nitrate extraction and measurement, (4) auto-calibration, (5) control, (6) GPS.

Just prior to soil sample delivery, water for NO_3^- extraction is pumped into the nitrate extraction and measurement chamber to completely submerge the sensing module of the NO_3^- -ISE and the stirrer is activated. The soil sample is received into the chamber where vigorous mixing takes place creating a soil-slurry solution and rapidly extracting NO_3^- into solution. The NO_3^- concentration of the solution is measured by the NO_3^- -ISE and stored in the control system's computer memory. Geo-referenced position data are simultaneously recorded by the GPS sub-assembly at each sampling location to enable a nitrate map to be subsequently created for the field. All data collected are downloaded to a computer for post-sampling processing via the computer-interface facility built into the control system.

The SNMS can be used to analyse soil samples automatically while on-the-go, or manually while stationary by hand-placing samples into the nitrate extraction and measurement sub-assembly. It is envisioned that two configurations of the system will eventually be used in practice – a tractor-mounted version (as shown in Fig. 1) and a 'suitcase' (portable) version.

Research program and major objectives

The research work presented in this thesis, for a variety of reasons, was conducted over a period of 16 years, beginning in 1991 with laboratory experiments aimed at refining the initial nitrate monitoring system prototype (Adsett, 1990; Adsett and Zoerb, 1991) and culminating in 2006–07 with extensive field-scale validation testing of a fully-functioning prototype and the conduct of soil science and plant science field experiments demonstrating its practical usefulness. The major steps taken and milestones achieved in the research program are outlined in Fig. 2. The major objectives of the research program were to:

- Determine if a NO_3^- -ISE could be used in a soil-slurry solution and under what operating variables.
- Develop a method for speeding up the nitrate extraction and measurement process.
- Develop new soil sampler, nitrate extraction, and control units. Integrate units into a second-generation prototype and conduct preliminary field testing.
- Perform design refinements. Construct and test new prototypes.
- Test performance of soil sampler on a field scale.
- Validate the accuracy of the nitrate extraction and measurement capabilities of the SNMS on a field scale.
- Demonstrate that the SNMS can be a useful tool to assist soil scientists

with experimental investigations of the spatial and temporal aspects of soil NO₃-N.

- Demonstrate that the SNMS can be a useful tool to assist crop scientists with experimental investigations of plant and soil nitrate responses under a variety of field management conditions.

Specific objectives for meeting the major objectives are presented below in the thesis structure section and in the individual chapter introductions.

The research work was conducted at the Nova Scotia Agricultural College (NSAC) Truro, Nova Scotia, Canada (45°22'N 63°16'W). The major field experiments demonstrating the usefulness of the SNMS were conducted in spring wheat (*Triticum aestivum* L.) and carrot (*Daucus carota* L.), two crops having high economic importance to the Atlantic region of Canada in particular, and internationally in general. Overall field conditions in which the performance of the SNMS was tested included four soil groups, conventional tillage vs. no tillage, and inorganic vs. organic fertilizer application.

Thesis structure

The major works conducted during the research program form the basis of the chapters in this thesis, as described below.

Chapter 1. General introduction

Chapter 1 gives a brief introduction to the issues associated with soil nitrate from both an environmental prospective and a crop production perspective, and proposes that if poor production practices are the cause of the issues, then the issues should be able to be corrected by improving those practices. It is further proposed, generally, that *precision agriculture* technology will enable farmers to more intensely and precisely analyze field conditions throughout the growing season, in correlation with crop response data and environmental data, in order to make the most sound management decisions possible. And specifically it is proposed that an automated soil nitrate mapping system will be one such technology that can contribute to *precision agriculture* as it will provide a way to collect the small-scale data necessary to analyze the variation in soil NO₃-N and link this variation to crop performance. A brief discussion of the most important aspects considered for development and use of the system are presented and discussed. These include: (i) soil nitrate links to crop growth and yield, (ii) soil nitrate is an environmental issue, (iii) precision agriculture and site-specific crop management, (iv) variation in soil nitrate links to crop growth and yield, (v) assessing soil nitrate variation, (vi) concept of a soil nitrate mapping system,

(vii) measuring soil nitrate directly with an ion selective electrode, and (viii) review of other on-the-go soil nitrate measurement systems. Finally, a description of the soil nitrate mapping system (SNMS) is presented and the major objectives, steps taken, and milestones achieved during the research program are delineated.

1988–90 First tractor-mounted prototype designed and built by John Adsett as part of his PhD thesis, Univ. of Saskatchewan, Canada. Many problems with its functioning were identified, but overall it was proved that the concept was sound and feasible.



1991 Lab testing of non-traditional use of ISE in a soil-slurry solution occurred at the Nova Scotia Agricultural College (NSAC), Canada with new team led by John Adsett and Kevin Sibley.

1992 New nitrate extraction unit bench-model developed and lab tested.

1993–94 New soil sampler developed and preliminarily field tested.

1994–96 Second generation tractor-mounted prototype built. Experienced unforeseen problems with nitrate extraction and control units.

1996 Third generation prototype incorporating changes to the extraction and control units. Successfully controlled fertilizer spreader application rate in response to soil nitrate measurements while on-the-go. Shipped SNMS to the Netherlands for demonstration to Greenland Nieuw-Vennep BV



2000–01 Fourth generation prototype incorporating GPS. Fully automated data collection and computer interface capabilities were developed. SNMS successfully used to map soil nitrate levels in NSAC fields.

2006–07 Extensive field-scale validation testing and proof-of-concept use for conducting soil science and plant science in-field research experiments demonstrated.



Fig. 2. Major steps taken and milestones achieved in the research program for developing and testing the soil nitrate mapping system (SNMS). (a) First tractor-mounted prototype (1990). (b) Demonstration of third-generation prototype to Greenland Nieuw-Vennep BV and European researchers in the Netherlands (1996). (c) Demonstration of the fourth-generation prototype to precision agriculture class students at the Nova Scotia Agricultural College (2006).

Chapter 2. Laboratory evaluation of the ion selective electrode for use in an automated soil nitrate monitoring system

As a first step in the research program, Chapter 2 explores the use of the NO_3^- -ISE for measuring NO_3^- in a soil-slurry solution. Typically in the laboratory, these electrodes were inserted into a clarified extract solution during NO_3^- measurement. As such, the first prototype SNMS, developed by Adsett (1990), used a specially designed unit wherein the soil was mixed with deionized water and then the solution was clarified before being presented to the electrode for NO_3^- measurement. Difficulties in getting a clear solution often caused clogging of the unit. When we began our work together, I posed the question: “could this electrode be used in a soil-slurry solution?” Supplemental questions followed: “if so, at what soil/extractant ratios and at what solution clarity?” and “what would the electrode response time be like, and would its response be stable? These are the fundamental questions answered in this chapter.

Chapter 3. Development of an automated on-the-go soil nitrate monitoring system

Success with the use of the NO_3^- -ISE in a soil-slurry solution in the laboratory (Chapter 2) led to the development of bench-top models and testing of the various components (units) needed for a fully-functioning second-generation prototype. These units included a soil sampler unit, a soil metering and conveying unit, a nitrate extraction unit, and a programmable electronic control unit complete with an electrode auto-calibration routine. Chapter 3 presents the steps taken in the development, integration, and preliminary field testing of the second prototype. This research work also included development of a field (soil) calibration method for speeding up the measurement process to facilitate on-the-go use of the system.

Chapter 4. Field performance testing on an on-the-go soil sampler for an automated soil nitrate mapping system

The preliminary field testing of the SNMS (Chapter 3) revealed several problems with the nitrate extraction and control units that were not obvious during development. The preliminary tests of the soil sampler unit (data never reported), however, revealed that it worked well enough to enable re-development of other units experiencing problems to continue. Once this work was completed (prototypes three and four), the soil sampler was subjected to extensive field performance testing, which is the work being presented in Chapter 4. This testing was carried out in five field conditions in order to determine (i) the validity of the sampler’s ‘uniform bulk density’ design principle, (ii) the uniformity of pocket fullness, (iii) the relationship between pocket fullness and delivered ‘weight’ (mass), and (iv) the uniformity of delivered weight.

Chapter 5. Field-scale validation of an automated soil nitrate measurement system

Also with completion of the redevelopment work, a next step was extensive field-scale validation of the nitrate extraction unit. Chapter 5 presents the work conducted to determine the level of agreement between SNMS soil NO₃-N measurements and standard lab soil NO₃-N measurements for a variety of field conditions and the development of regression equations to enable field measurements using the SNMS to be obtained with lab-grade accuracy. As well, the use of cheaper integer math chip technology, as opposed to more expensive whole math chip technology, in the electronic control unit for processing the NO₃⁻-ISE measurements was validated. The question of whether a soil moisture content sensor was necessary for achieving accurate results in the field was also explored. Field conditions included conventional tillage vs. no tillage, inorganic vs. organic fertilization, four soil groups, and three time points throughout the season.

Chapter 6. Using an automated on-the-go mapping system to assess the spatial and temporal aspects of soil nitrate

With the SNMS now working quite well, the next steps in its development were to put it through its paces in the field to demonstrate its usefulness. In Chapter 6, the proof-of-concept use of the SNMS as an effective tool to assist soil scientists with experimental investigations of the spatial and temporal aspects of soil NO₃-N is presented. Using data collected by the SNMS on a fine-scale sampling grid and a combination of classical and geostatistical analytical techniques and tools, the spatial and temporal aspects of NO₃-N variation in a wheat production system at several time points covering pre-seeding, growing season, and post-harvest soil conditions, as well as the intrinsic spatial structure of NO₃-N present in the field, were assessed.

Chapter 7. Using an automated on-the-go soil nitrate mapping system to investigate plant and soil nitrate responses in wheat and carrot production systems

In Chapter 7, the proof-of-concept use of the SNMS as an effective tool to assist crop scientists with experimental investigations of plant and soil nitrate responses under a variety of field management conditions is presented. Using data collected by the SNMS on small-scale sampling grids before, during, and after crops were being grown enabled the variation in soil NO₃-N levels over time to be linked to crop performance. Soil NO₃-N, plant nitrogen, and yield responses in (i) wheat under liquid dairy manure management with conventional tillage and no tillage treatments, and (ii) carrot under conventional tillage management with inorganic fertilizer and liquid dairy manure fertility treatments were determined at seven time-points over a growing season.

Chapter 8. General discussion

Chapter 8 wraps up the thesis with a discussion integrating the findings of the various aspects of the work conducted during the research program, reflecting on the original objectives and suggesting potential benefits of using the SNMS in the field. As well, suggestions for future research are presented.

CHAPTER 2

Laboratory evaluation of the ion-selective electrode for use in an automated soil nitrate monitoring system¹

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Abstract

Environmental pollution partly caused by excessive use of nitrogen fertilizer is focusing the attention of the agricultural industry towards prescription farming. It has been suggested that fertilizer application rates should be varied in response to the *in situ* nutrient concentrations of the soil. The time consuming nature of present methods of soil nitrate testing limits their suitability for *in situ* use. The nitrate ion-selective electrode was tested in the lab for its suitability for use in an automated soil nitrate monitoring system. Tests were conducted to evaluate the parameters of soil:extractant ratio, extract clarity, and electrode response time. Results indicate that with proper calibration, the electrode is suitable for *in situ* measurement of soil nitrate concentration and reliable readings may be obtained in less than 4 s.

Keywords: Nitrate, soil nitrate, ion selective electrode, ISE.

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Introduction

Environmental pollution caused by excessive use of agricultural fertilizers and pesticides will have to be dealt with as we approach the year 2000. Direct effects such as ground water and soil contamination and increasing socio-economic costs call for improved cropping and soil management practices. Success of these practices depends in part on ways to reduce the incidence of excessive soil nitrate.

Nitrate, a key form of nitrogen for plants, is leachable in some soil types if present in a quantity larger than required by the growing crop. Nitrate is now found in increasing concentrations in drinking water and rivers and lakes (Addiscott et al., 1991). Efficient nitrogen management, including more accurate nitrogen fertilizer recommendations, could help to minimize the contribution by agriculture to the nitrate problem.

According to Fox et al. (1989), the nitrate concentration in the top 30 cm of soil is a good indicator of whether growing plants would respond to additional N fertilizer. Nitrate measurements made in the field during fertilizer application would ensure that only the amount needed by the plants is applied. Using this concept, fertilizer application rate could be adjusted on-the-go in direct response to the concentration of available nitrate in the soil. This process would require an automated, reliable method for nitrate determination, as well as an interpretation of the measured nitrate concentration which considers the needs of the growing plant.

Work done by Myers and Paul (1968) and Mack and Sanderson (1971) indicates that the nitrate ion-selective electrode (ISE) offers a convenient and rapid method of determining nitrate directly in soil extracts.

This chapter presents a laboratory evaluation of the nitrate ISE for use in an automated soil nitrate monitoring system (NMS). A tractor-mounted NMS will require a dependable sensor to determine varying nitrate concentrations across a field, so that a fertilizer spreader can be controlled accordingly.

Materials and methods

Soil samples

Soil samples of sandy loam, silty clay loam, and clay loam were taken in mid September from the surface layer (15 cm) of fields in Cumberland and Colchester counties of Nova Scotia, Canada. All fields were on farms serviced by the Land Evaluation and Planning Service (LEAPS) for the Nova Scotia Department of Agriculture and Marketing. A clayey soil is considered to be more difficult to work with in an automated system than coarser textured soils. The tests reported in this

chapter relate to Chaswood clay loam, of the gleysolic order, of the subgroup RegoGleysol. Particle size analysis revealed a composition of 34% sand, 37.9% silt, and 28.1% clay. The sampled A horizon was a fine textured alluvial formation which had been deposited above loamy sand.

The soil samples were not dried, ground or cooled, but were maintained to resemble field conditions as much as possible. They were stored in sealed plastic containers at room temperature. Each comparative set of tests was performed within a one or two day period.

Nitrate ion-selective electrode measurements

Soil nitrate concentrations were determined using an electrochemical cell with a nitrate ISE (Orion Model 93-07, Orion Research Inc., USA) and a sleeve-type Ag/AgCl double-junction reference electrode (Orion Model 90-02). Ammonium sulphate (0.04M) was used as the outer filling solution of the reference electrode. The cell generates an electric potential which is related to the nitrate concentration in the soil extract by the Nernst equation:

$$E = E_0 + S \log (A) \quad [1]$$

where E is the electrochemical cell potential (mV), E_0 is the standard potential (mV) in a 1M solution, ideally a constant, S is the electrode slope (–mV per decade of concentration), and A is the nitrate activity (effective concentration moles L^{-1}) in the solution.

The nitrate calibration standards were prepared one decade apart in concentration to bracket the expected soil nitrate concentrations. Analytical grade potassium nitrate was used for preparation of standards. Recalibration was performed every 10–30 sample readings in order to compensate for changes in temperature or in the condition of the nitrate sensing membrane itself.

Nitrate extraction

Nitrate extractions were performed in 100 mL beakers by mixing together known masses of soil and extractant. The electrodes were connected to an Orion EA940 Ion/pH meter.

Nitrate extraction was accelerated by magnetic stirring. When the electrode potential became steady (drift $< 1\text{mV min}^{-1}$), the meter indicated the nitrate concentration in moles L^{-1} . Deionized water was used as the extractant, since comparative testing in the lab indicated no advantage in using an ionic strength adjustor (ISA). Also water requires no preparation time and does not add additional

chemicals to the sample as would occur if solutions such as ammonium sulphate were used for extraction. Adsett (1990), Myers and Paul (1968), Mack and Sanderson (1971) and Dahnke (1971) all used deionized water as an extracting medium.

Comparison of soil:extractant ratios

To determine the effect of soil:extractant ratio on final indicated soil nitrate concentrations, nitrate extractions were performed at mass ratios of 1:15, 1:5 and 1:3. Time to reach a stable electrode potential and the final molarity readings were recorded.

Effect of extract clarity on electrode response

This test was performed to determine whether the clarity of the soil extract had any effect on the final nitrate concentration indicated by the electrode. Twelve soil extracts were prepared and the nitrate concentrations were measured. Six of the prepared samples were filtered through Whatman No. 5 filter paper and the clear extracts were collected and tested for nitrate concentrations. The remaining six samples were covered with plastic to restrict evaporation, and the soil particles were allowed to settle. After 24 hours the supernatant was decanted, and tested for nitrate concentrations.

Electrode response time

Since the electrode will be required to perform rapid analysis in the field, tests to determine the minimum acceptable measurement time were conducted. A criterion for speeding up the measuring process in the field was sought.

Six samples of clay loam soil were used to generate data on electrode response time. The electrodes were placed in a beaker containing distilled water being stirred at a uniform speed. When the electrode potential became steady, the soil sample was dumped quickly into the beaker, and nitrate measurements were continuously taken until 100% extraction was indicated. The electrodes were stored in deionized water between samples.

Normalized response curves of measurement time versus percentage of final indicated nitrate level were prepared for each sample. A 95% confidence interval of the mean time required to obtain a certain percentage (i.e. 10%, 20%, ...100%) of the final reading was determined.

Results and discussion

Calibration

The electrode calibration slopes ranged from -51 to -63.1 mV dec^{-1} , and the standard potential ranged from -38 to -56 mV . Fig. 1 shows a typical calibration curve for the nitrate electrode. Calibration curves were found to change from day to day and often differed from the theoretical slope value of -59.16 mV dec^{-1} .

Calibration slope changes are attributable to several factors including temperature, condition of reference electrode filling solutions, and condition of the nitrate sensing membrane. The reference electrode solutions were changed every few days as specified by the manufacturer (Orion Research Inc., 1986). Regular calibration of the electrode was required to maintain reliability. Therefore, a method of calibrating the electrode easily in the field must be designed as an integral part of the operation of an automated nitrate monitoring system.

Comparison of soil:extractant ratios

Testing of the soil:extractant ratio revealed that there was no significant difference ($\alpha = 0.05$) between the final nitrate concentrations for the three ratios tested. The mean nitrate nitrogen concentrations determined at soil:extractant ratios of 1:15, 1:5 and 1:3 were 18.6, 18.6, and 19.3 ppm, respectively.

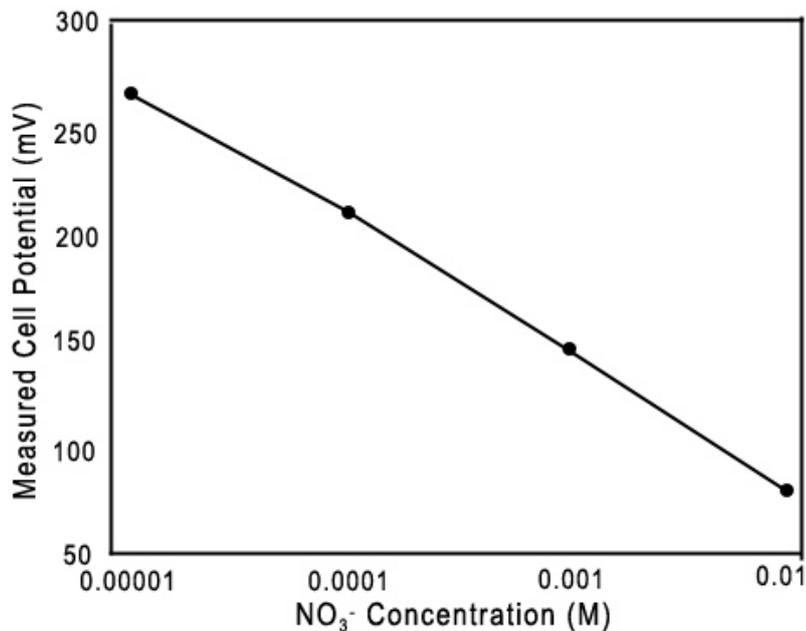


Fig. 1. Typical calibration curve for the nitrate ion-selective electrode.

Effect of extract clarity on electrode response

In terms of mechanical extractor design, these results indicate that any of the three ratios may be used in the field with equal results. The electrode, however, responds faster to high concentrations of nitrate (Orion Research Inc., 1986), and in order for readings to be within the linear range of the electrode, it would be preferable to design the extractor to use a high soil:extractant ratio in soils having a low nitrate concentration. The tests to determine the effect of clarity on electrode performance showed that there was no significant difference ($\alpha = 0.05$) between final nitrate concentration indicated in either decanted, filtered, or soil/extractant suspension samples. Mean nitrate nitrogen concentrations determined for the suspension, decanted, and filtered samples were 34.1, 32.0, and 33.8 ppm, respectively. The higher nitrate levels in the clarity tests, compared to the ratio tests reported in the previous subsection, are not surprising. The clarity tests were performed 27 days later than the ratio tests.

The uniformity of results with suspensions, and decanted and filtered samples, supports the use of the ISE for in-field use where time consuming filtering of soil extracts required by other nitrate determination methods would complicate system design and slow down operation. Using an ISE, Paul and Carlson (1968), Myers and Paul (1968), Dahnke (1971) and Yu (1985) also found that there was no significant difference between nitrate determinations made in soil/extractant suspensions or filtrates. Our results confirm that local Chaswood clay loam soils exhibit similar behaviour in this respect to soils elsewhere and separation of the extract from the soil is not necessary when using the ISE to make nitrate measurements. An advantage of clarifying the extract, however, would be reduced soil particle abrasion of the electrode membrane and other sensitive components of an extractor.

Electrode response time

Figure 2 shows a typical response curve of the ISE. The electrode potential dropped sharply indicating a rapid release of nitrate into solution. It was found that the electrode detected a large percentage of the nitrate concentration in less than 20 s, but it took up to two minutes to detect the total nitrate concentration in the soil. The final reading time (total nitrate concentration) was based on a signal drift of less than 1 mV min^{-1} . It was also found that the electrode had very consistent response time curves.

Normalizing the data for time to indicate a certain percentage of final concentration (Fig. 3) showed that 80% of the final nitrate concentration was consistently indicated within 12 s, 40% was indicated within 6 s, and 20% was indicated within 4 s. Therefore, is not necessary to wait until 100% of the nitrate in a soil sample is extracted before taking a measurement. Reliable estimates of the

sample's total nitrate concentration can be made in less than 4 s, which is within the range required for rapid in-field measurements.

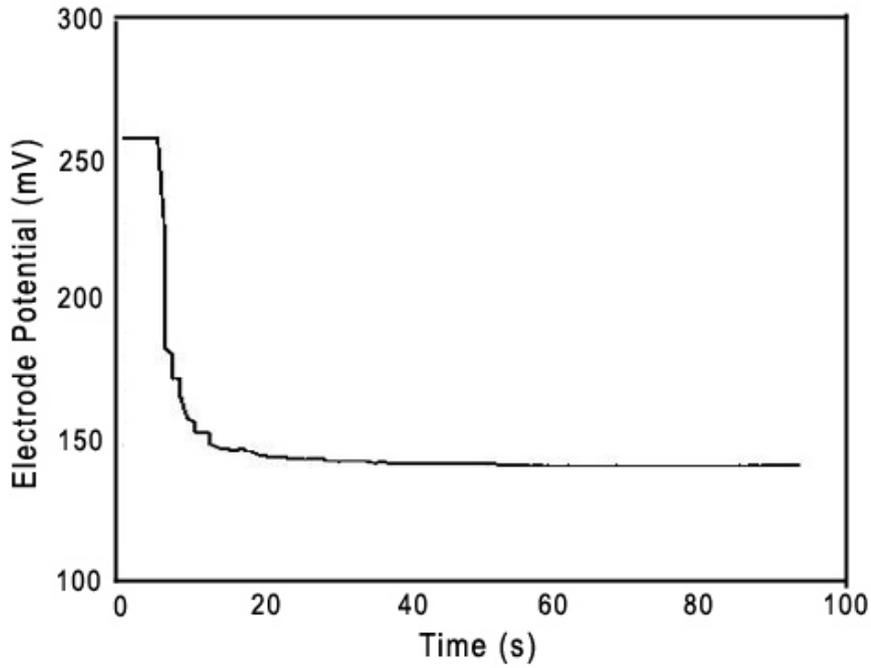


Fig. 2. Electrode response in soil suspension with nitrate extraction.

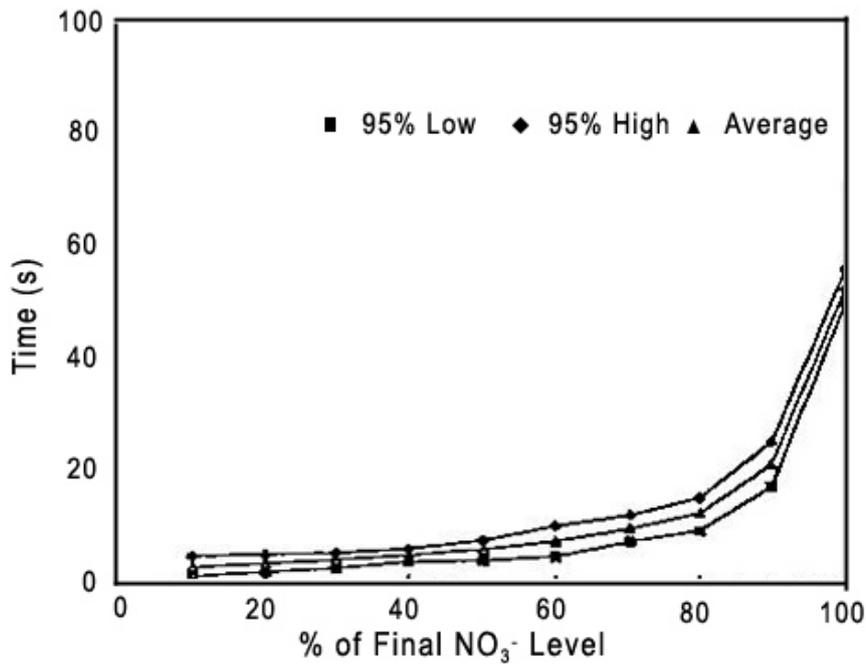


Fig. 3. A 95% confidence interval on time required for nitrate detection in a clay loam soil.

Summary and conclusions

The usefulness of the nitrate ion-selective electrode for measuring nitrate in soil extracts was investigated with a view to its adaptation to an automated field soil nitrate monitoring system (NMS).

Regular ISE calibration was required for reliable results. Electrode response time and repeatability in the laboratory were determined to be acceptable for adaptation of the electrode to an automated NMS.

In Chaswood clay loam, indicated soil nitrate concentrations did not vary significantly with soil:extractant ratio or extract clarity. Reliable estimates of total nitrate concentration were made in less than 4 s using normalized response time curves.

The ISE appears to be well suited for adaptation into an automated soil NMS. A successful NMS will depend, however, not only on properly functioning electrochemical and mechanical components. Work must be done on the interpretation of nitrate electrode signals with respect to seasonal soil nitrogen transformations and plant nutrition. Optimum variable fertilizer rates can then be determined and applied under the direction of an automated nitrate monitoring system.

CHAPTER 3

Development of an automated on-the-go soil nitrate monitoring system¹

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Abstract

An automated, on-the-go, soil nitrate monitoring system (NMS) was built and tested, making use of a nitrate ion-selective electrode (NO_3^- -ISE) which offers a convenient and quick method for in-field soil nitrate measurement. The system consists of a soil sampler which collects a representative soil sample at regular intervals, a soil metering and conveying unit which meters a known amount of soil into an extraction unit, a nitrate extraction unit which extracts the soil nitrate using deionized water and analyzes for nitrate using an Orion NO_3^- -ISE, and an electronic control unit that measures nitrate concentration and provides the control signals to operate the system. The overall operation of the system was controlled using a Micromint BCC52 computer. A field calibration process was used to enable prediction of soil nitrate levels within 10 s after soil sampling. Results from lab testing indicate that for a silty clay loam soil, the actual, or final, nitrate level could be predicted with 95% accuracy after 6 s of measurement.

Keywords: Soil nitrate, ion selective electrode, field measurement, fertilizer application.

¹ Published as: Adsett, J.F.^b, J.A. Thotton, and K.J. Sibley^b. 1999. Development of an automated on-the-go soil nitrate monitoring system. *Applied Engineering in Agriculture* 15(4):351–356. ^b Authors contributed equally.

Introduction

Nitrate (NO_3^-), a key form of nitrogen (N) for plants, is susceptible to significant leaching losses in some soil types particularly if present in a quantity larger than required by the growing crop. The leached NO_3^- can end up in groundwater and in rivers where it causes eutrophication (Addiscott et al., 1991). Unacceptable levels of NO_3^- in drinking water sources can, to an extent, be prevented by improving the efficiency of chemical fertilizer usage. Several countries have set a maximum limit of 10 mg L^{-1} of NO_3^- in drinking water (Addiscott et al., 1991).

In most cases where fertilizer has been pinpointed for causing NO_3^- pollution, it has been due to poor soil and plant management practices (Follett, 1989 in Campbell et al., 1994). Efficient N management, including more accurate N fertilizer recommendations and applications, could help minimize the contribution by agriculture to the NO_3^- pollution problem. In a 10 year research effort (Owens et al., 1994), when N fertility was provided by fertilizer at 224 kg ha^{-1} , concentrations of NO_3^- in subsurface flow exceeded drinking water standards. When alfalfa replaced the chemical fertilizer as a nitrogen source, NO_3^- concentrations decreased to 30% of the earlier levels. Nitrate measurements made in the field during N fertilizer application would be one way to ensure that only the amount needed by the plants is applied. Using this concept, the fertilizer application rate could be adjusted on-the-go in direct response to the concentration of available NO_3^- in the soil. This process would require an automated, reliable method for NO_3^- determination, as well as an interpretation of the measured NO_3^- concentration which considers the needs of the growing plant (Adsett and Zoerb, 1991). This system will then become an important tool in precision farming where, for example, side-dress fertilizer input could be based on the soil nutrient level and crop need.

This chapter presents steps taken in the development and testing of an automated soil nitrate monitoring system (NMS). The NMS concept and details of an initial prototype of the system are discussed in detail by Adsett (1990).

Equipment and methods

Preliminary lab testing of the nitrate ion-selective electrode

Prior to the development of the nitrate monitoring system, the suitability of the NO_3^- ion-selective electrode (NO_3^- -ISE) for use in an automated system was investigated in the lab. The results of this work are discussed in detail by Thottan et al. (1994). The results of the study included response characterization of the NO_3^- -ISE which enables the prediction of NO_3^- levels as early as 6 s from the start of measurement. Work done

by Myers and Paul (1968), and Mack and Sanderson (1971) indicate that the NO_3^- -ISE offers a convenient and rapid method for determining NO_3^- directly in soil extracts. One major drawback of the NO_3^- -ISE is the interference caused by other ions such as chloride and bicarbonate. These interfering ions become a problem if they are present in large concentrations and may rule out the use of the NO_3^- -ISE to measure NO_3^- in such soils.

Development of the nitrate monitoring system

The NMS consists of a soil sampler, soil metering and conveying unit, nitrate extraction and measurement unit, and a control unit. The overall operation of the NMS is controlled using a Micromint BCC52 (Micromint Inc., USA) computer system. During the operation of the NMS, the soil sampler and the other components of the NMS are attached to the front of a tractor. A variable rate fertilizer spreader may be attached to the rear of the tractor. As the tractor travels forward, the soil sampler collects a soil sample which is then moved into the nitrate extraction and measurement unit where it is mixed with deionized water to remove the NO_3^- ions. It should be noted that this process will only remove the readily available NO_3^- ions from the soil matrix. A fair percentage of NO_3^- ions will be attached to the soil colloidal surfaces or to the root hairs. The NO_3^- concentration, which is a good correlation of the available nitrogen in soil moisture, is then measured using a NO_3^- -ISE. To increase the frequency of soil sampling and measurement, the NO_3^- readings are taken for a short time (less than 10 s), and the NO_3^- reading obtained at this time is used to predict the final NO_3^- concentration, making use of the response characteristics of the NO_3^- -ISE. Depending on the measured NO_3^- concentration and the crop need, the fertilizer application rate can then be regulated by sending a control signal to the fertilizer spreader.

Soil sampler

The soil sampler (Fig. 1) used with the system employs a woodsaw blade powered by a hydraulic motor. The blade is mounted on a frame that can be hydraulically raised for transport or lowered for intermittent sampling. During sampling, the frame is allowed to float to follow ground contours. To obtain a sample, the blade is brought to a speed of about 250 rpm and then lowered into the soil. The blade cuts through the top 15 cm of the soil as it travels forward and throws a spray of finely divided soil onto a properly positioned soil conveyer.

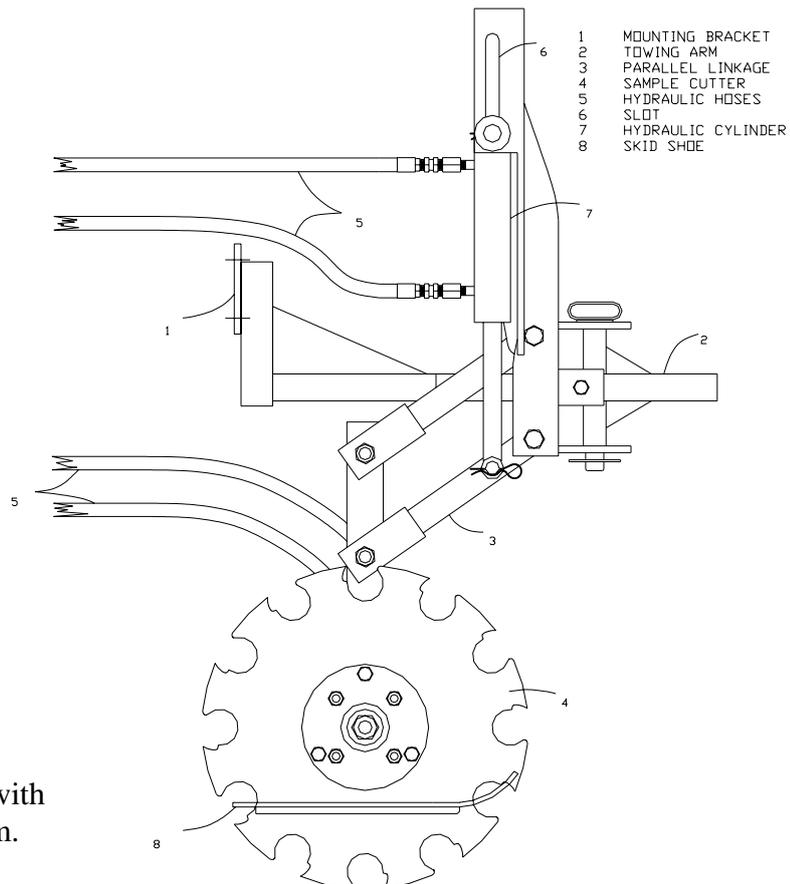


Fig. 1. Soil sampler used with the nitrate monitoring system.

Soil metering and conveying unit

The soil metering and conveying unit provides the bridge between the soil sampler and the nitrate extraction unit. It consists of a vulcanized rubber belt (Fig. 2) with a recess (pocket) cut into it to collect a sample of known volume and uniform density from the 'spray' of soil exiting the soil sampler. A specially designed scraper placed above the belt levels the soil sample in the pocket without compaction and removes excess soil from the belt. The belt is installed on a frame with steel roller supports at either end and driven by a 12 Vdc gear motor. The conveyer is positioned such that when the pocket passes over the roller at the upper end, it drops the soil sample into the extraction chamber. The flexing action of the belt as it passes over the roller causes complete emptying of the soil from the pocket, provided the soils are at field workable moisture levels.

Positioning of the conveyer belt pocket is achieved using a microswitch to detect the location of a notch cut in the side of the belt. An electronic circuit using a FLIP-FLOP provides the signals to activate the relays which control the conveyer drive motor. The use of the microswitch and the notch to position the conveyer ensures that any slippage of the belt will have no adverse effect on positioning the pocket at the correct location.

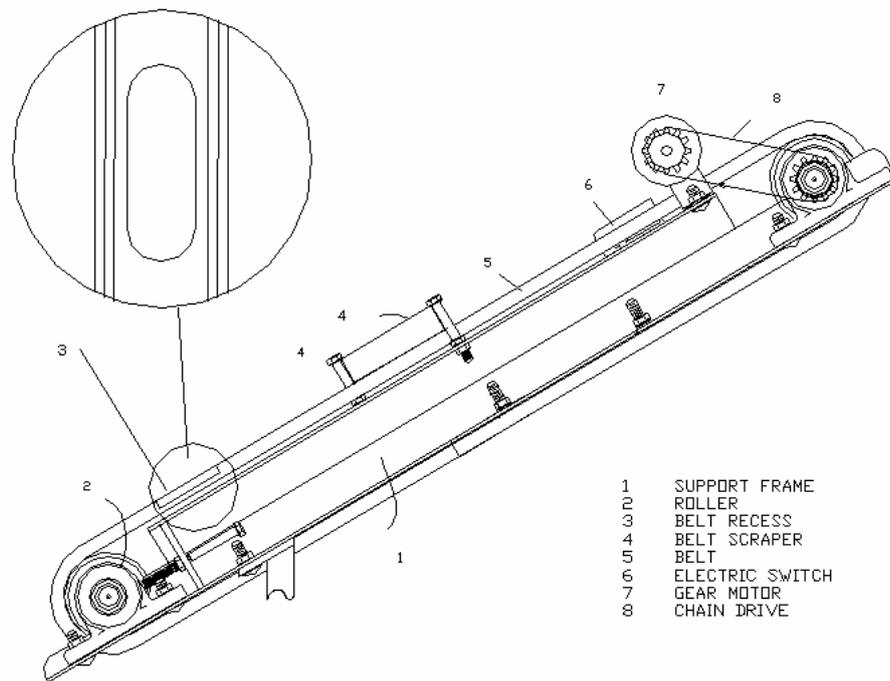


Fig. 2. Soil metering and conveying unit.

Nitrate extraction and measurement unit

The nitrate extraction and measurement unit (Fig. 3) consists of an extraction chamber, an impeller for mixing, and the NO_3^- -ISE (Orion Model 93-07, Thermo Electron Corp., USA) and reference electrode (Orion Model 90-02). The two electrodes and the sample, plus the associated circuitry, comprise an electrochemical cell. The extraction chamber was constructed using rigid acrylic tubing so that the extraction process could be viewed. The base of the chamber was constructed using a tapered acrylic block for ease of cleaning. An opening was machined in the middle of the base and a mechanical valve was attached to serve as the cleaning outlet valve. The valve was controlled using a 12 Vdc solenoid. In normal position, the extractor outlet is kept closed by the valve. When the solenoid is powered, it opens the extraction chamber outlet. The extraction chamber was electrically isolated from other components to eliminate any stray voltages that may interfere with the NO_3^- -ISE signal.

The added advantage of having the extraction chamber outlet normally closed was that the extraction chamber could be used as a storage unit for the electrodes in a dilute NO_3^- standard solution when not being used. To the lower end of the valve, a 3.5-cm diameter polyvinyl chloride (PVC) pipe was connected. The PVC pipe provided structural support and electrical isolation for the extraction chamber, as well as being an extension of the extraction chamber outlet.

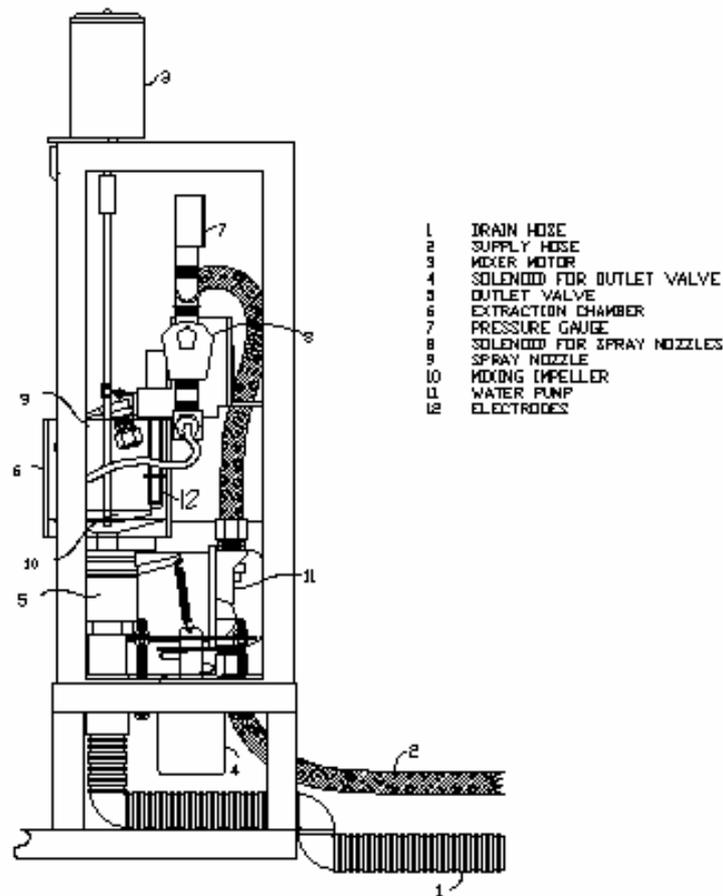


Fig. 3. The nitrate extraction and measurement unit.

A full cone spray nozzle (Delavan 33974-3) was placed just above the extraction chamber for supplying the extractant and also for cleaning purposes. The nozzle was connected to a pump and a solenoid valve was fitted in between the nozzle and the pump to allow on/off flow control and also to meter in the exact amount of extractant under computer control.

The mixing mechanism consisted of a fibreglass shaft with an acrylic impeller attached to one end. The fibreglass shaft was used in order to eliminate the possibility of any stray voltage being conducted into the extraction chamber. The shaft was powered using a variable speed 12 Vdc motor and was operated at 300 rpm.

Electronic control unit

The heart of the control unit (Fig. 4) was the Micromint BCC52 BASIC Computer/Controller (Micromint Inc., 1988). The BCC52 computer contains an Intel 8255 chip which provides three software configurable parallel input/output (I/O) ports. Each port

provides eight inputs or outputs for a total of 24 I/O lines. The advantages of the BCC52 system include the ability to program it in BASIC and its erasable programmable read only memory (EPROM) capability. The EPROM support makes it a stand alone unit and on power-up the program stored in the EPROM is initiated.

All the controls used in the nitrate extraction and measurement unit are simple ON/OFF type and are controlled by the BCC52 computer. The switching of all the devices (pumps, solenoids, DC motors) is performed using 12 Vdc relays. A relay driver chip, ULN2803A, is used to energize the relays. The measurement and control circuit developed to interface with the BCC52 computer is shown in Fig. 4.

Nitrate measurement circuitry

The NO₃⁻-ISE signal was conditioned using a field effect transistor operational amplifier (LF353N) for impedance matching. A 12 bit analog to digital converter, Micromint BCC30 (Micromint Inc., 1990), which has the capability of converting 16 single ended inputs or eight differential inputs was used for measuring the electrode voltage. The BCC30 board plugs into the motherboard of the BCC52 system.

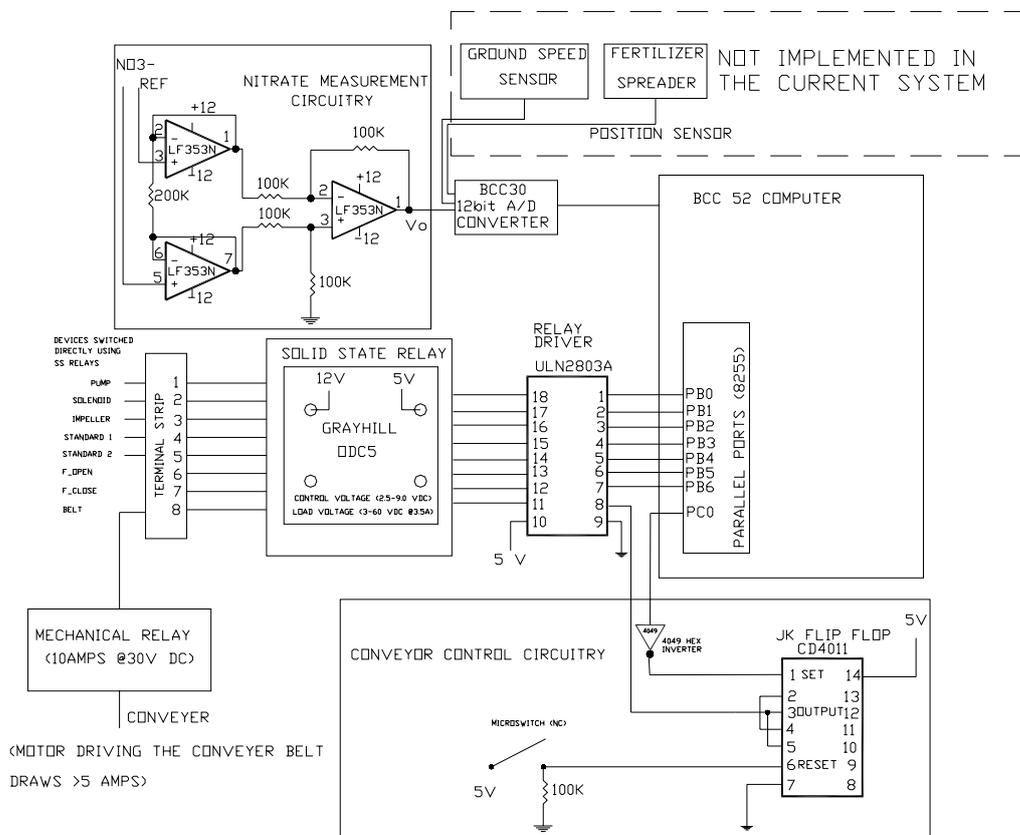


Fig. 4. Electronic control unit measurement and control circuit.

Operation of the nitrate monitoring system

The operation of the NMS includes the following procedures:

1. Electrode (NO_3^- -ISE) Calibration
2. Field Calibration
3. Soil NO_3^- -N analysis

The electrode calibration procedure is important since the reliability of the NO_3^- measurements depends entirely upon proper calibration of the NO_3^- -ISE. The calibration procedure provides a relationship between electrode potential and NO_3^- concentration. Two NO_3^- standard solutions of known concentrations are used for calibration. The NMS monitoring system software provides an autocalibration routine which performs a calibration under computer control. The electrode calibration provides the coefficients for the Nernst equation (Morf, 1981) from which the NO_3^- concentration is calculated. Thottan et al. (1994) describes the calibration theory and process in detail. The current control system calls for a calibration check every hour. Extended field testing is required before deciding on the required frequency of electrode calibration.

Once the electrode calibration is completed, a field (soil) calibration is required to determine a scaling factor which allows the prediction of the final NO_3^- concentration within the first 10 s of measurement. Field calibration is necessary due to variations in soil properties in different fields and changes in the speed of response of the NO_3^- sensing membrane with prolonged usage. A field calibration must be done by measuring soil NO_3^- -N using a sufficient number of samples so as to determine the response characteristics of the NO_3^- -ISE for the particular soil type in the field being sampled. The field calibration procedure uses a simple statistical procedure which is programmed into the NMS control software (Thottan, 1995). This routine determines the quickest time at which the NO_3^- prediction can be made with sufficient accuracy and the scaling factor to predict the final NO_3^- concentration. After field calibration, soil samples can be collected at regular intervals and analyzed for NO_3^- .

Testing

The NMS was first tested in the lab. The system was cycled repeatedly through the steps of soil conveying, NO_3^- extraction, and NO_3^- measurement; all under computer control. Silty clay loam soil samples were placed in the pocket of the conveyer manually, since there was no facility to use the soil sampler in the lab. Deionized water (100 mL) was added to the extraction chamber, with the impeller turning. The electrode potential readings were then started and the soil conveyer was activated. The

NO_3^- readings were each obtained for about 1.5 min and were stored in data files for later analysis.

A field test was then conducted with the system mounted on a tractor. Data were collected successfully and stored using an NEC 486SX/33 portable computer for five soil samples. The field testing was performed in sandy loam soil near the edge of a field containing agronomic experimental plots.

Results

The results from the lab test are shown in Figs. 5 and 6. Figure 5 shows NO_3^- -ISE response for samples with varying $\text{NO}_3\text{-N}$ ($\text{NO}_3\text{-N} = \text{NO}_3^- \times 14/62$) concentrations (LABTEST I), while Fig. 6 shows $\text{NO}_3\text{-N}$ concentrations for 16 identical and well mixed soil samples (LABTEST II). The results from LABTEST II indicate that repeatable NO_3^- measurements can be obtained using the NO_3^- -ISE. The results from the lab tests were used in developing a criterion for speeding up the $\text{NO}_3\text{-N}$ measurement in the field. The $\text{NO}_3\text{-N}$ data were normalized by using the percentage levels of 'final' $\text{NO}_3\text{-N}$ detected as a function of time (procedure discussed in Thottan et al., 1994). A 95% confidence interval (CI) on the normalized electrode response curves (Fig. 7) shows that 95% of the time, 80% of the final $\text{NO}_3\text{-N}$ concentration was consistently indicated within 12 s, 70% was indicated within 6 s, and 20% was indicated within 4 s. This result was used to develop the field calibration routine which provides the measurement time and scaling factor to make an early prediction of the actual $\text{NO}_3\text{-N}$ concentration. The early prediction of $\text{NO}_3\text{-N}$ concentration will allow a quick adjustment of the N fertilizer application rate required for the sampled location and also helps to increase the sampling frequency. In other applications of the system such as mapping of $\text{NO}_3\text{-N}$ concentrations for later use, early prediction is not as necessary.

The operation of the field calibration routine was simulated using NO_3^- extraction data files created during the lab test of the NMS and a BASIC computer program. This program read the data files and computed the ratio between final $\text{NO}_3\text{-N}$ concentration and the $\text{NO}_3\text{-N}$ concentration indicated during the first 40 s of extraction. The process was repeated for several data files. The program then computed the mean, standard deviation, and coefficient of variation of the ratios at each time interval ($t = 2, 4, \dots, 40$ s). The results from the simulated field calibration tests are shown in Table 1.

The results from Table 1 were used to predict the final $\text{NO}_3\text{-N}$ concentration using the $\text{NO}_3\text{-N}$ reading obtained at 6 s. A scaling factor of 1.43 was used to predict ($R^2 = 0.99$) the $\text{NO}_3\text{-N}$ concentration based on the $\text{NO}_3\text{-N}$ concentration indicated at

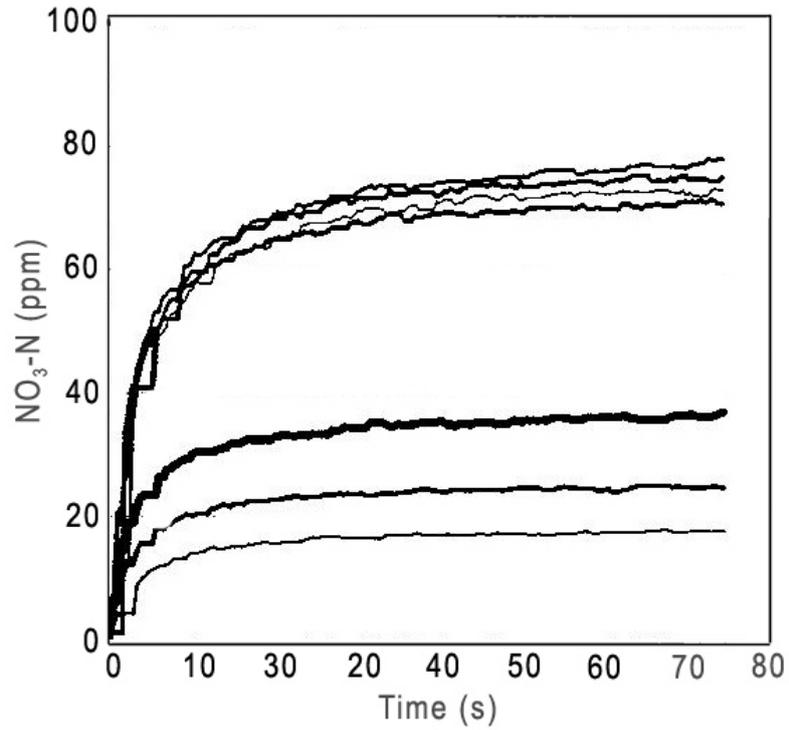


Fig. 5. The NO₃⁻-ISE response curves for soils with varying NO₃-N levels (LABTEST I).

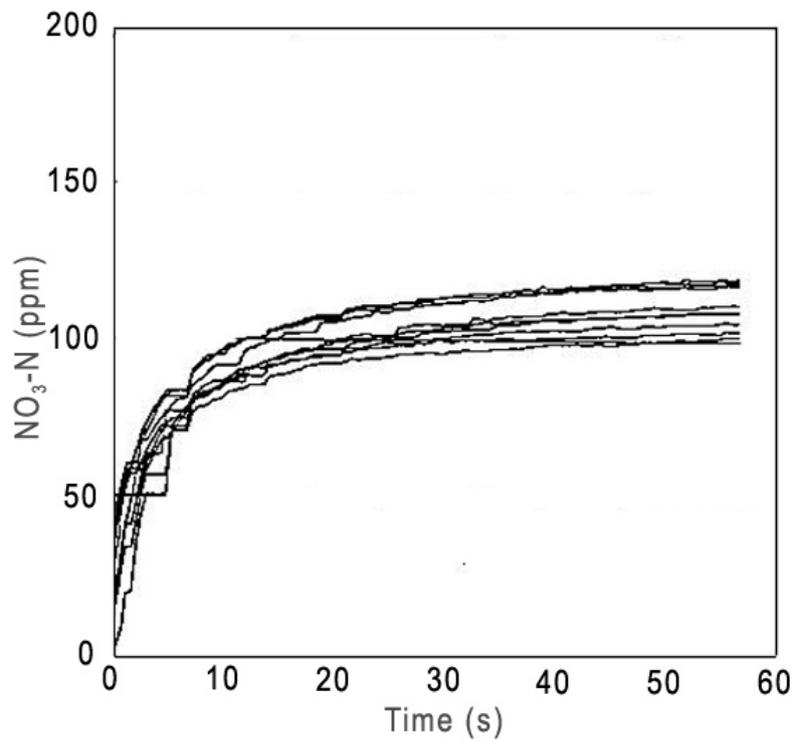


Fig. 6. The NO₃⁻-ISE response curves for soils with similar NO₃-N levels (LABTEST II).

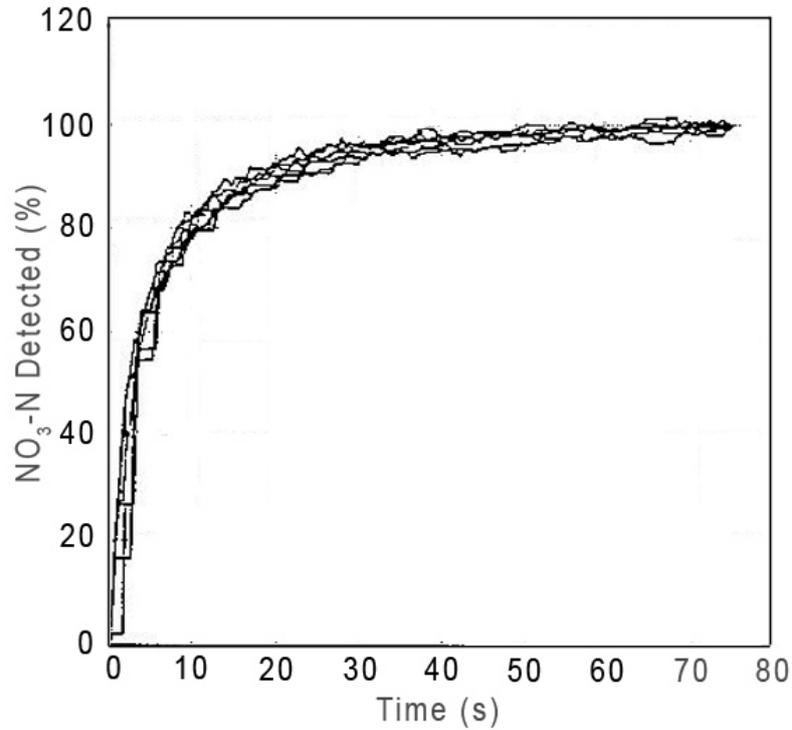


Fig. 7. Normalized NO_3^- -ISE response curves for LABTEST I.

Table 1. Results from the field calibration routine.

Prediction time t (s)	Actual $\text{NO}_3\text{-N} / \text{O}_3\text{-N} (t)$	Standard deviation	Coefficient of variation
2	3.05	1.44	47.20
4	1.69	0.09	5.84
6	1.43	0.05	3.33
8	1.33	0.04	3.11
10	1.24	0.03	2.14
12	1.21	0.04	2.91
20	1.11	0.02	1.77
30	1.05	0.01	1.32
40	1.05	0.01	1.31

6 s. The actual, or final, $\text{NO}_3\text{-N}$ concentration and the predicted $\text{NO}_3\text{-N}$ levels are shown in Fig. 8. The results indicate that the error in predicted $\text{NO}_3\text{-N}$ levels is less than 10%, which should be adequate for calculating fertilizer application rates.

Field testing revealed several mechanical and electrical problems that were not obvious during the lab test. One problem detected during the field test was the

clogging of the extraction chamber outlet with plant residue and small stones present in the sample. Also there were unacceptable levels of noise in the electrode signals. Ongoing work is addressing these problems. The limited results from the field tests are presented in Fig. 9, which shows typical NO_3^- -ISE response curves.

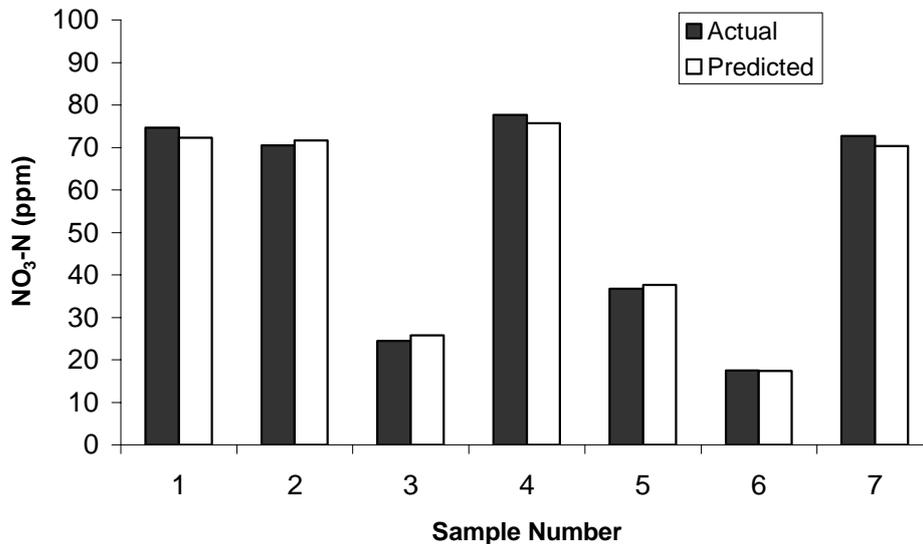


Fig. 8. Actual and predicted nitrate levels for LABTEST I.

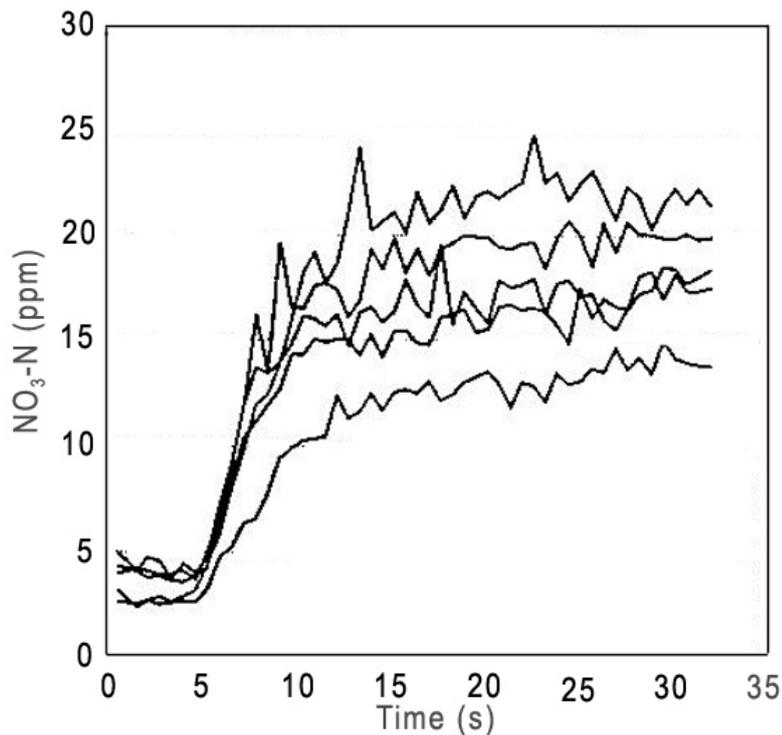


Fig. 9. NO_3^- -ISE response curves from the field test of nitrate measurement system.

Conclusion

The overall performance of the NMS in the lab was very satisfactory, however, more work needs to be done before using the system in the field. The lab testing shows that the NO_3^- -ISE is suitable for rapid in-field soil $\text{NO}_3\text{-N}$ measurement with proper calibration procedures. The criterion developed for speeding up the measurement process show that in silty clay loam soil, the actual, or final, $\text{NO}_3\text{-N}$ concentration can be sufficiently predicted within 6 s of the commencement of extraction. The repeatability of the NO_3^- -ISE was found to be excellent for use in an automated soil nitrate measurement system.

CHAPTER 4

Field performance testing of an on-the-go soil sampler for an automated soil nitrate mapping system¹

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Abstract

An automated on-the-go soil sampler was developed as part of a soil nitrate mapping system that collects data for precisely analyzing small-scale variation in soil NO₃-N. An essential requirement of the sampler is the ability to reliably collect a soil sample of known 'weight' (mass). It was hypothesized that if a uniform bulk density sample could be collected in a device of fixed volume, then the mass of the sample would be known and constant. The sampler employs a woodsaw blade to cut a 15-cm deep slot in the soil at a sampling location as it travels forward and to throw a spray of finely chopped soil into a fixed-volume pocket milled into the surface of an automatically positioned flat-belt transfer conveyer. Performance testing of the sampler was conducted in five fields. Coefficient of uniformity (CU) for sample bulk density was 92.9%, which produced less than a 5.5% deviation in sample delivered weight (DW) in 83.6% of the cases. Mean DW error was 10.9% and DW CU was 82.0%, mostly due to localized high clay content in three of the fields. Mean pocket fullness (PF) was 89.9%, and PF CU was 83.6%. Pocket fullness was linearly correlated with DW ($R^2 = 0.979$, $n = 140$). It was concluded that the sampler's 'uniform bulk density' design principle was validated for all intents and purposes of field use. Delivered weight uniformity, particularly when sampling in clayey soils, should be increased by further improving the design.

Keywords: Soil sampling, soil nitrate measuring, ion-selective electrode, precision agriculture.

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Introduction

Precision agriculture offers an exciting opportunity to use highly advanced technology for better agriculture. The ultimate goal of such technology is to enable farmers to more intensely and precisely analyze variations in field conditions throughout the growing season, in correlation with environmental and crop response data, in order to make the most sound and site-specific management decisions possible. This ability is offering new production efficiencies to farmers, while at the same time offering assurances to the public that agricultural practices are being conducted in the most environmentally friendly way.

A soil nitrate mapping system (SNMS) (Fig. 1) will be one such technology that can contribute to *precision agriculture* as it provides a way to collect the data necessary to analyze the variation in soil $\text{NO}_3\text{-N}$. The SNMS consists of six sub-assemblies: (1) soil sampler sub-assembly, (2) soil metering and conveying sub-assembly, (3) nitrate extraction and measurement sub-assembly, (4) auto-calibration sub-assembly, (5) control sub-assembly, (6) GPS sub-assembly. The system automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyses it electrochemically for nitrate concentration in real-time (6 s) using a nitrate ion-selective electrode (NO_3^- -ISE) as the analysis instrument. Additionally, global positioning system (GPS) geo-referenced data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field. The system can be used to analyse soil samples automatically while on-the-go, or manually while stationary by hand-placing samples into the nitrate extraction and measurement sub-assembly. It is envisioned that the SNMS will eventually be used in practice as (i) a tractor-mounted version (as shown in Fig. 1) and (ii) a 'suitcase' version.

From its beginnings as a first prototype (Adsett, 1990; Adsett and Zoerb, 1991), the SNMS has undergone several developmental iterations. The use of a NO_3^- -ISE in this type of application has been extensively lab tested (Thottan et al., 1994; Thottan, 1995; Brothers et al., 1997). Development and preliminary field testing of the five initial sub-assemblies and their integration into one complete system followed (Thottan, 1995; Adsett et al., 1999). In 2001, a completely new electronics and control system that incorporated the GPS sub-assembly was added.

Preliminary field testing during design and development of the 'soil sampler' (combination of sub-assemblies 1 and 2) in 1994 (data never reported) revealed that it worked well enough to enable development of other sub-assemblies of the SNMS experiencing difficulties to continue. A next step in the soil sampler's development was extensive field performance testing, which is the work being reported in this chapter.

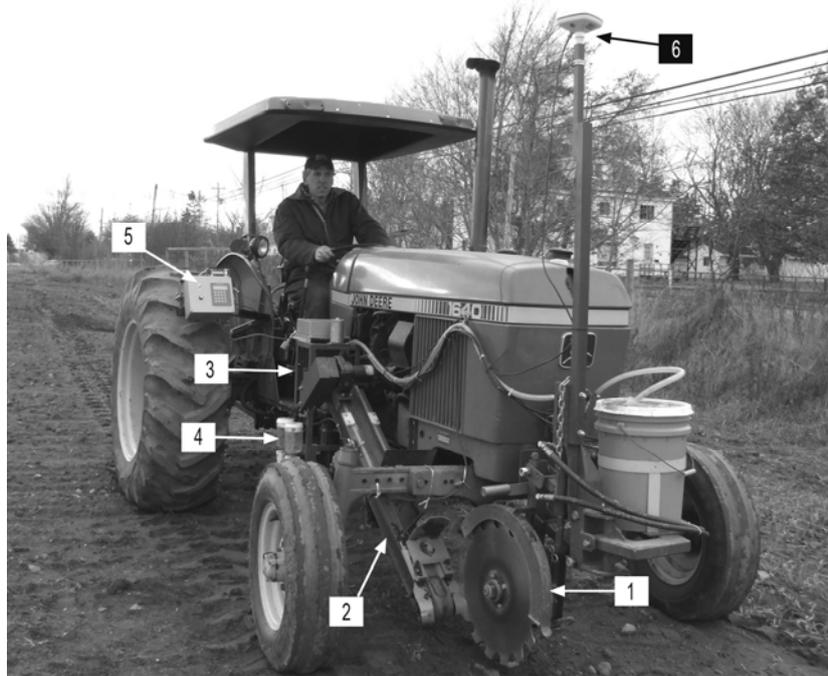


Fig. 1. Soil Nitrate Mapping System (SNMS) with six sub-assemblies.

Review of existing soil samplers

Many vehicle-mounted soil sampling devices are mentioned in the literature, all having varying degrees of success. Most are based on the traditional soil coring concept. Schickendanz et al. (1973), Ginn et al. (1978), Chandler and Savage (1979), and White (1982) all describe hydraulically activated coring devices mounted to either the front, side, or rear of a tractor. These devices all collect undisturbed individual core samples, but the tractor must be stopped, their sampling rate is slow, and they often eject incomplete cores. Wrenn et al. (1982) describes a tractor-mounted sampler that collects a core and releases it on the ground for manual collection. We note none of the devices have any mechanism for automatically transferring the samples onward for analysis, as is required for automated on-the-go soil analysis.

Devices for collecting continuous samples consist of rotating tines (Johnson, 1981), sub-soiler type blades with elevators (Behringer, 1982), slotted discs and powered augers (Sneath et al., 1989), and chain cutters (Sneath et al., 1989; Adsett, 1990). These devices generally sample the 30- to 100-cm zone, have high draft requirements (45–75 kW), have problems with clogging in wet and clayey soils, are susceptible to stone damage, are subject to jamming due to silicates glazing from heat generation during sampling, or have problems coping with surface trash.

Lütticken (2000) developed a GPS-equipped, auger-type system that enables automatic control of precise depth under varying field conditions when collecting soil

samples. The system was reported to work well. However, we note, like the coring devices, it must also stop at each sampling location and soil is collected in a container for later analysis.

As part of an investigation into the feasibility of an on-the-go soil K and $\text{NO}_3\text{-N}$ mapping system, Adamchuk et al. (2002a) performed laboratory tests on four commercially available NO_3^- -ISEs to simulate the direct soil measurement technique of an automated soil pH measurement system developed by Adamchuk et al. (1999, 2002b). The soil pH measurement system uses a toolbar-mounted shank with an attached sampling mechanism to scoop soil (approximately 5–10 g at a 10-cm depth) and bring it into firm contact with the sensing membrane of the electrode being used for analysis. During sampling the mechanism is positioned 5 mm below the shank to enable soil collection while leaving a small gap to reduce interference by large soil particles and small rocks. A GPS is used to geo-reference the sampling location. In the laboratory, Adamchuk et al. (2002a) manually re-moistened previously air dried soil samples and pressed them into contact with the sensing membrane of each NO_3^- -ISE to determine NO_3^- concentration (liquid basis of mg L^{-1} reported as ppm). These results were compared to a standard cadmium reduction laboratory analysis technique to give an indication of the accuracy of the NO_3^- -ISEs. For individual soil samples, R^2 values ranging 0.38–0.63 were obtained, depending on the ISE, while averaging of three repeated measurements yielded R^2 values ranging 0.57–0.86. It was concluded that it is feasible to use a NO_3^- -ISE for measuring soluble nitrate concentration of naturally moist soil samples, but one of the main limitations of the proposed method reported was difficulty in maintaining high quality contact between soil and electrode. We note as well, that use of the proposed method in the field in combination with the pH measurement system's soil sampling mechanism would not enable the $\text{NO}_3\text{-N}$ content (mg kg^{-1}) of the sample to be directly computed since the 'weight' (mass) of the soil sample would not be known.

Kataoka et al. (2004) developed and lab-tested an on-the-go soil sampling system which consists of three parts: (i) roto-tiller, (ii) soil transport conveyor, and (iii) soil can collection apparatus. This system is quite similar to ours. As the tractor moves forward, the roto-tiller throws pulverized soil rearward onto a flighted plastic soil-transport conveyor which subsequently dumps the soil into cans being moved transversely beneath its outlet end with a typical canning factory type round-belt conveyor. Sampling depth is up to 20 cm. Sampling location is recorded with a GPS mounted on the tractor. The system was reported to have good performance in generating pulverized soil. However, there were issues with the soil conveyer becoming blocked because too much soil was thrown onto the conveyor to be adequately handled at certain conveyor speeds. The system was only tested in a soil

bin containing pre-roto-tilled silt-loam soil having a moisture content of 21.1% and a wet density of 1.32 g cm^{-3} . The study was conducted to understand the performance of the system at various combinations of forward travel speeds, roto-tiller rotational speeds, and transport conveyor speeds. The ability and performance of the soil collection apparatus to collect soil was not tested. We also note that the system does not mass the samples and that the samples are intended to be taken to a laboratory for analysis.

Design principle of the soil nitrate mapping system's soil sampler

An essential requirement of the SNMS is the ability to reliably collect a soil sample of known 'weight' (mass) for analysis while on-the-go. This is the job of the soil sampler. During calculation of $\text{NO}_3\text{-N}$ content (mg kg^{-1}) of a soil sample analyzed by the SNMS, a constant soil to extractant (water) ratio representing the dilution factor during nitrate extraction and concentration measurement is used (Thottan, 1995). Thus, it is required to know the mass of the soil sample in addition to the volume of the extractant. Directly massing (weighing) a very small soil sample in the range 10–15 g accurately on-the-go is extremely difficult, if not virtually impossible. The fact that none of the samplers reviewed above have the capability to collect a sample of known 'weight' (mass) is a testament to this difficulty. Therefore, it was decided to utilize the simple physics relationship between mass, volume, and density (Eqn. 1) in order to estimate the mass of a sample:

$$m_s = \rho_s \times V_s \quad [1]$$

where m_s = mass of sample (g), ρ_s = bulk density of sample (g cm^{-3} wet basis), and V_s = volume of sample (cm^{-3}).

It was hypothesized that if a uniform bulk density sample could be collected in a device of fixed volume, then the mass of the sample would be known and constant. This is the principle upon which the design of the SNMS' soil sampler is based.

Design concepts and description of the soil nitrate mapping system's soil sampler

To overcome many potential mechanical complexities during construction and operation of the soil sampler, two design concepts of (i) breaking the sampling cycle into three linear processing step (chop, collect, transfer) and (ii) mechanically separating soil engagement from collection and transfer were conceived.

The soil sampler (Fig. 2(a)), originally reported by Thottan (1995) and Adsett et al. (1999), employs a woodsaw blade powered by a hydraulic motor. The blade is mounted on a frame that can be hydraulically raised and lowered automatically and

intermittently while on-the-go for sampling. During sampling, the blade is lowered into the soil and the frame is allowed to float to follow ground contours while the blade is allowed to swivel horizontally up to $\pm 10^\circ$ to accommodate slight deviations in travel path. A travel distance of approximately 0.5 m is required to collect a sample. The blade cuts a 15 cm deep slot as it travels forward, and throws a spray of finely chopped soil onto the head-end area of an automatically positioned flat-belt transfer conveyer (Fig. 2(b)). This action is intended to create a sample of uniform bulk density and finely-granulated particles to facilitate the subsequent nitrate extraction process. The conveyor belt has an oblong fixed-volume pocket milled into its surface to collect a sample from the soil landing on the conveyor. A specially designed scraper placed above the belt levels the soil sample in the pocket without compaction and removes excess soil from the belt as the belt moves to deliver the soil sample to the nitrate extraction and measurement sub-assembly of the SNMS. During delivery, the pocket stretches lengthwise as it passes around the conveyor's tail-end roller to facilitate complete emptying of the pocket (like emptying an ice-cube tray). The GPS antenna is mounted directly above the blade on a pole. The operation of the sampler is controlled via an electronic control system.

The soil sampler can be operated in either fully automatic or semi-automatic mode. While operating in fully automatic mode, the distance between sampling locations is determined by a pulse counter mounted to the tractor's front-right wheel hub. The operator sets the desired distance by adjusting the electronic control system. While operating in semi-automatic mode, the operator drives to a desired sampling location and manually activates the control system to take a sample.

Objectives and scope

In this study, field testing of the SNMS' soil sampler was conducted with the objectives of determining (i) the validity of the sampler's 'uniform bulk density' design principle, (ii) the uniformity of pocket fullness, (iii) the relationship between pocket fullness and delivered 'weight' (mass), and (iv) the uniformity of delivered weight. The scope of this study was limited to testing in five locally available field conditions, as described below.

Materials and methods

Field sites

In late-Fall of 2006, field testing was conducted in five fields on the Nova Scotia Agricultural College (NSAC) farm, Truro, Nova Scotia, Canada (45°22'N 63°16'W). These fields were Banting Field (Banting), Field #207 South (F207S), Field #207

North (F207N), Field #206, (F206), and Field #102 (F102). There were three soils groups, Pugwash 52 (PGW52), Debert 22 (DRT22) and Truro 52 (TUO52), present in these fields. The PGW52 soil group is a well to moderately-well drained soil having 50–80 cm of friable, coarse loamy solum over firm, coarse-loamy lower subsoil material with an average in-situ bulk density of 1.25 g cm^{-3} in the Ap horizon. The DRT22 soil group is an imperfectly drained soil having 20–50 cm of friable, coarse loamy solum over firm, coarse-loamy lower subsoil material with an average in-situ bulk density of 1.41 g cm^{-3} in the Ap horizon. The TUO52 soil group is a well drained soil having 50–80 cm of friable, coarse-loamy solum over loose, fine-sandy lower soil material with an *in situ* bulk density of 1.50 g cm^{-3} in the Ap horizon. Full descriptions of these soils are well documented by Webb and Langille (1996).

The surface conditions of the fields ranged from bare soil to high-residue wheat stubble. Moisture content (0–15-cm depth) in the fields ranged between 13.3–27.6% wet basis. The field-specific conditions are shown in Table 1.

Soil sampling strategy and analyses

It was planned to sample at five random locations in each of the five fields, with six repeated samples at each location, for a total 150 samples. However, only 140 samples were collected and analyzed. F207S had one bad sample due to a data processing error. In F207N, seven samples were not collected due to mechanical breakage of the PTO shaft driving the sampler's hydraulic system and two samples collected for weighing were inadvertently lost.

Table 1. Field conditions description.

Date	Field	Soil group [†]	Crop	Surface condition	Moisture content [‡] (% wet basis)
10 Oct. 2006	Banting	PGW52	Fallow	Bare to slightly weedy	13.3–17.2
17 Oct. 2006	F207S	DRT22, PGW52	Wheat	Stubble, high residue	20.1–27.6
18 Oct. 2006	F207N	PGW52	Wheat	Stubble, high residue	20.9–22.9
31 Oct. 2006	F206	TUO52	Switchgrass	Fresh plowed, disced	21.2–23.2
5 Nov. 2006	F102	PGW52	Rye	Bare, newly planted	16.3–20.3

[†] PGW52, Pugwash 52; DRT22, Debert 22; TUO52, Truro 52.

[‡] Moisture content range at sampling locations for 0–15-cm depth.

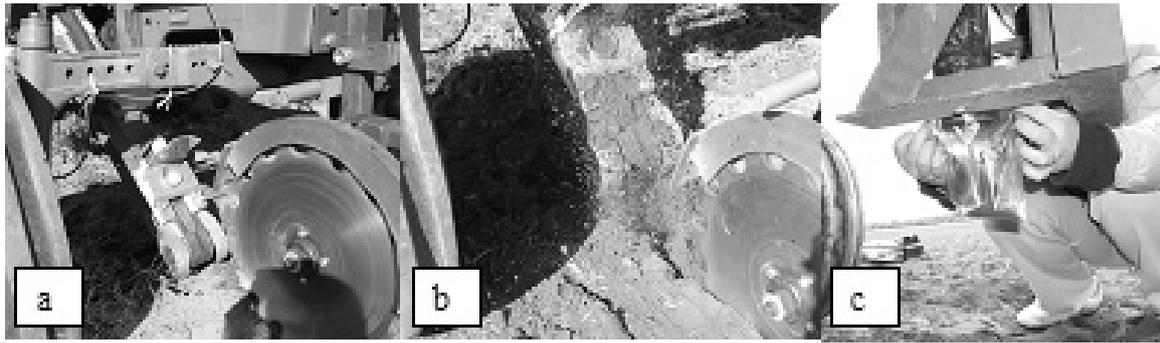


Fig. 2. Soil sample collection procedure. (a) Soil sample collection apparatus set-up. (b) Soil sampler in action. (c) Delivered soil sample being collected into plastic bag for weighing.

A special apparatus was designed and installed immediately above the conveyor pocket to hold one standard 125.5 mL aluminum gravimetric moisture analysis can (Fig. 2(a)). During sample collection, the sampling blade was run through the soil, creating a spray of finely chopped soil particles landing on the conveyor in the pocket area and filling the can (Fig. 2(b)). A sample collected in the can was hand-leveled off without compression using a flat wooden stick, then sealed with the can's cover. These samples were transported to the lab and immediately weighed, then placed into a drying oven at 105°C for 24 hours. Bulk density (BD) and moisture content (MC) were determined from these samples. A sample collected in the conveyor pocket was dumped through a plastic tube into a plastic bag and then sealed with the bag's zip-lock feature (Fig. 2(c)). These samples were transported to the lab and immediately weighed to determine delivered weight (DW).

Pocket fullness assessment

To assess pocket fullness (PF), digital photographs were taken of each sample collected in the conveyor pocket. As the conveyor moved to deliver a sample, it was stopped by manually tripping the position switch. The photograph was then taken by manually holding the camera square to the conveyor surface. A typical photograph is shown in Fig. 3(a). Each photograph was then cropped close around the pocket, enhanced (brightness and contrast) using photo editing software (Camedia Master 4.1, Olympus America Inc., USA) to improve visual clarity, then saved and printed in color on high-brightness white paper (Fig. 3(b)).

Each photo was then analyzed visually by eye to determine PF according to equation 2:

$$PF = ((V_{pc} + V_{bc} + V_{pof} - V_{puf}) / V_p) \times 100\% \quad [2]$$

where V_p = unit volume of pocket, V_{pc} = unit volume of pocket filled with soil, V_{bc} = unit volume of belt area covered with soil, V_{puf} = unit volume of pocket under-filled with soil, and V_{pof} = unit volume of pocket overfilled with soil.

Individually, each cropped photo was overlaid with a 1.0 cm² grid-embossed transparent film (Fig. 3(c)). Each grid on the film contained 100 units (1 mm² block). Measures of pocket area (A_p), pocket cover area (A_{pc}), belt cover area (A_{bc}), pocket under-filled area (A_{puf}), and pocket over-filled area (A_{pof}) on a unit basis were then made by counting and summing the number of blocks corresponding to each area. Each unit area was then multiplied by a corresponding estimated number of unit-layers of depth (D_i) to determine unit volume according to equations 3 through 7:

$$V_p = A_p \times D_i \quad [3]$$

$$V_{pc} = A_{pc} \times D_i \quad [4]$$

$$V_{bc} = A_{bc} \times D_i \quad [5]$$

$$V_{pof} = A_{pof} \times D_i \quad [6]$$

$$V_{puf} = A_{puf} \times D_i \quad [7]$$

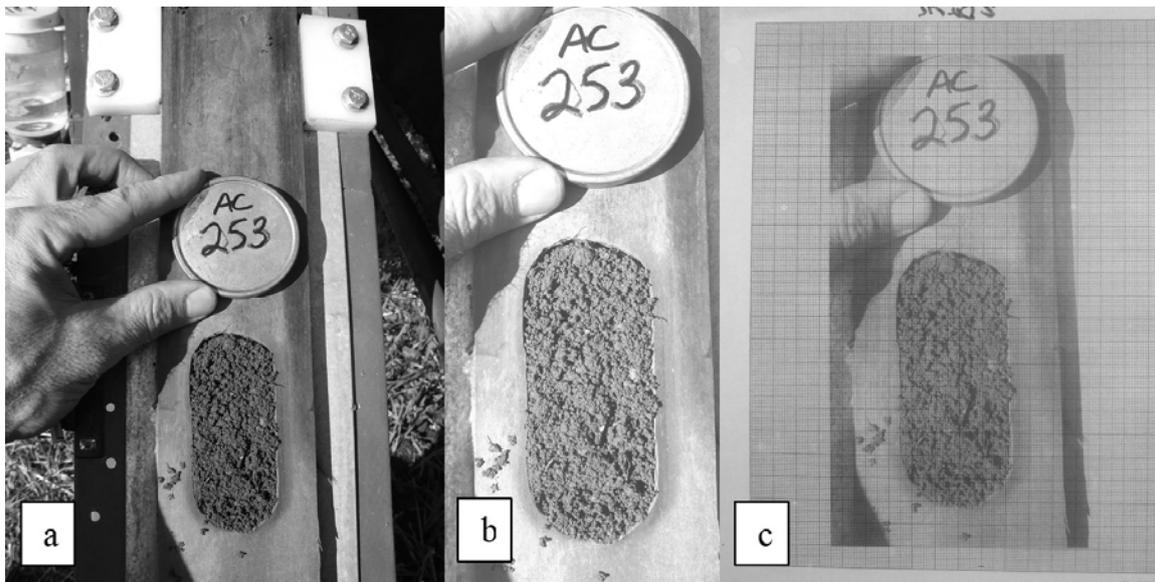


Fig. 3. Pocket fullness assessment procedure. (a) Raw photo of sample in pocket taken in field during sampling. (b) Cropped and enhanced photo of pocket area for analysis. (c) Cropped photo overlaid with grid-embossed transparent film.

It was assumed that the pocket was four unit-layers deep ($D_i = 4$), soil on the belt was one unit-layer deep ($D_i = 1$), and overfilled areas were one unit-layer deep ($D_i = 1$). Under-filled areas had estimates of 1, 2, 3 or 4 unit-layers of depth ($D_i = 1, 2, 3, \text{ or } 4$) as visually assessed.

Statistics and data analyses

Description and quantification of the levels and distribution of BD, DW, and PF was performed using exploratory data analysis (EDA) techniques, and Minitab (Minitab Inc., Pennsylvania, USA; Ver. 15.0) and Excel (Microsoft Corp., California, USA.; Ver. Prof. Ed. 2003) software.

Descriptive statistics of interest were computed: Mean, Standard Error of the Mean (SEM), Standard Deviation (SD), Coefficient of Uniformity (CU), Minimum (Min), and Maximum (Max). The coefficient of uniformity was used to assess the consistency of performance, since in this study uniformity was contextually of more interest than variation, as described by the coefficient of variation (CV).

The distribution characteristics of the data sets were computed and distribution goodness-of-fit was determined based on a combined analysis of data by probability plot and test statistic (D'Agostino et al., 1990) using the Anderson-Darling test in Minitab. Potential outliers identified from the histograms and probability plots were checked for data processing errors and possible sources of sampling error.

Correlation between variables was determined using Pearson's correlation analysis. Sensitivity analyses were performed using deviation frequency plots, regression plots, and error calculations. For each regression, the validity of normal distribution and constant variance of the error terms assumptions were verified by examining the residuals as described in Montgomery (2005).

All tests of significance were made at the 5% probability level unless otherwise noted.

Results and discussion

Exploratory data analyses

Histograms of the raw data sets (Fig. 4) and probability plots (not shown) revealed that BD, DW, and PF had normal distributions. Several extreme values (potential outliers) residing in tails of the normal distribution plots were identified and investigated for data processing errors and possible sources of sampling error. No errors were found.

Table 2. Descriptive statistics summary for bulk density, delivered weight, and pocket fullness.

Field	Statistic	Bulk density g cm ⁻³ wet basis	Delivered weight g	Pocket fullness %
Banting	Mean	0.833	15.9	100.8
	SEM [†]	0.008	0.4	2.2
	SD	0.045	2.3	12.0
	CU	94.7	85.4	88.1
	Min	0.759	9.3	67.3
	Max	0.944	19.3	117.3
F207S	Mean	0.726	12.4	80.9
	SEM	0.008	0.5	2.8
	SD	0.041	2.5	15.1
	CU	94.3	80.3	81.3
	Min	0.655	7.9	51.4
	Max	0.812	17.1	110.5
F207N	Mean	0.720	13.0	84.2
	SEM	0.008	0.4	2.2
	SD	0.036	1.7	10.0
	CU	94.9	86.6	88.1
	Min	0.614	9.3	62.1
	Max	0.776	16.3	98.9
F206	Mean	0.790	12.8	83.2
	SEM	0.005	0.4	2.3
	SD	0.025	2.1	12.7
	CU	96.9	83.4	84.7
	Min	0.733	6.3	42.6
	Max	0.833	17.7	111.9
F102	Mean	0.759	15.2	98.3
	SEM	0.005	0.3	1.8
	SD	0.030	1.6	9.8
	CU	96.1	89.3	90.1
	Min	0.692	11.9	77.7
	Max	0.828	18.7	119.0
All data combined	Mean	0.769	13.9	89.9
	SEM	0.005	0.2	1.2
	SD	0.055	2.5	14.7
	CU	92.9	82.0	83.6
	Min	0.614	6.3	42.6
	Max	0.944	19.3	119.0
All data combined @ 10% trim	Mean	0.768	14.0	90.3
	SEM	0.004	0.2	1.0
	SD	0.041	2.0	11.7
	CU	94.6	85.7	87.1
	Min	0.686	9.5	67.0
	Max	0.850	17.7	111.9

[†] SEM, standard error of the mean; SD, standard deviation; CU, coefficient of uniformity (100% – coefficient of variation); Min, minimum; Max, maximum.

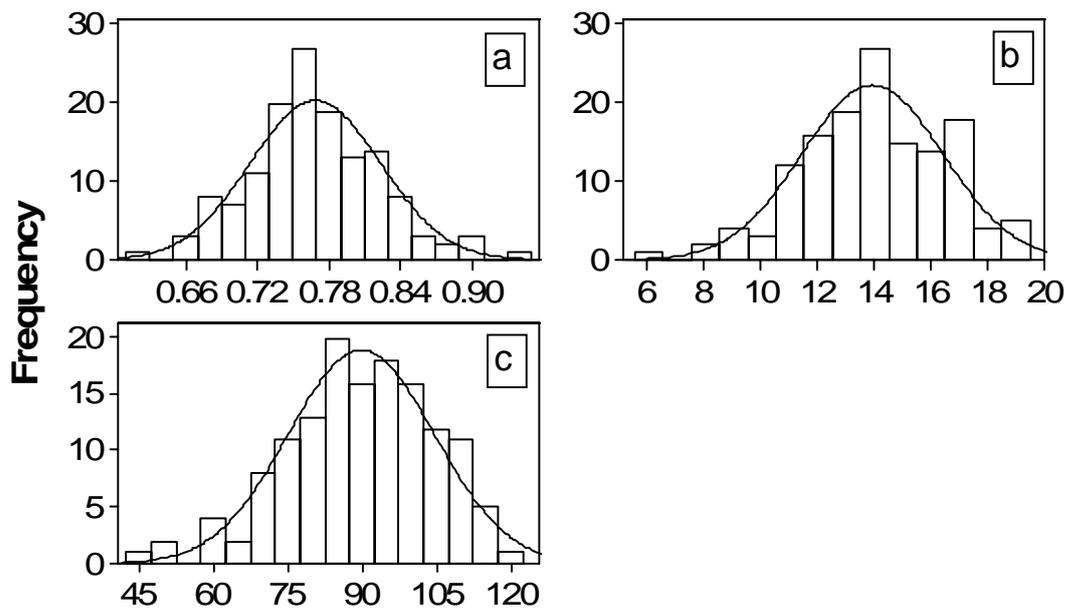


Fig. 4. Raw data histograms and normal distribution curve fits. (a) Bulk density (g cm^{-3}). (b) Delivered weight (g). (c) Pocket fullness (%).

Descriptive statistics were then computed as shown in Table 2. The potential of trimming the data sets (@ 10%) in order to reduce susceptibility of the results to the effects of the extreme values was investigated. Descriptive statistics computed from the trimmed data sets were not substantially different from the statistics computed from the raw data sets. The means were virtually identical, and the CUs were only between 1.7–3.7 percentage points higher. In the interest of being conservative in the assessment of sampler performance, it was decided to complete all final analyses using the raw data sets.

The degree of correlation between BD, DW, and PF is shown in Table 3. The potential influence of soil moisture content (MC) on the other variables was also investigated by including it as an additional variable in the correlation analysis.

Table 3. Pearson correlation values (r , $n = 140$) between bulk density, pocket fullness, delivered weight, and soil moisture content. All correlation values were significant at the 0.1% probability level.

Variable	Moisture content	Bulk density	Delivered weight
Bulk density	-0.666		
Delivered weight	-0.641	0.413	
Pocket fullness	-0.645	0.375	0.989

The correlation values indicate that a moderate influence ($r \approx 0.6$) of MC on BD, DW and PF was evident, while a weak influence ($r \approx 0.4$) of BD on DW and PF was evident. However, with the correlation values for MC and BD being virtually the same as the other factors, column-wise respectfully, and the fact that DW and PF fullness are very highly correlated ($r = 0.989$), as expected, it is likely that the influence was more from autocorrelation (interdependence) rather than from independent influence. To investigate this possibility, a stepwise regression analysis was performed sequentially fitting linear additive models of PF, BD, and MC to DW. It was found that PF explained 97.9% of the variation in DW, while BD and MC explained only an additional 0.21 and 0.08%, respectively. Therefore, it was concluded that BD and MC independently had very little influence on DW.

Bulk density uniformity

As shown in Table 2, the CUs among fields for soil sample BD ranged between 94.3–96.9%. Overall, the CU was 92.9% for all data combined. To determine whether this amount of variation had any practical effect on DW, a sensitivity analysis was conducted. First, the relationship between BD and DW was determined through regression analysis to be linear: $DW = -0.591 + 18.868 \times BD$; $R^2 = 0.171$, $n = 140$. This low R^2 value indicates that only a very weak relationship between BD and DW existed.

Second, based on this regression, the potential effect of 5, 10 and 20% deviations in BD on DW was calculated. The resulting DW deviations were 0.9, 5.5, and 14.8%, respectively.

Finally, to determine how often these deviations occurred, a frequency plot of BD deviations from the overall mean BD was prepared (Fig. 5). It was found that in the majority of the cases (55.7%) the BD deviation was less than 5%, resulting in less than a 1% deviation in DW (5% deviation data not shown in frequency plot to reduce clutter), while in most of the cases the DW deviation was less than 5.5% (10% deviation in BD occurred in 83.6% of the cases). Deviations in DW larger than 5.5% occurred in only 16.4% of the cases.

These results indicate that the uniformity in BD was excellent for all field conditions tested, and in practical terms the variation that did occur had less than a 5.5% deviation effect on DW most of the time. It was concluded that the sampler's main design principle of 'uniform bulk density' was validated for all intents and purposes of field use.

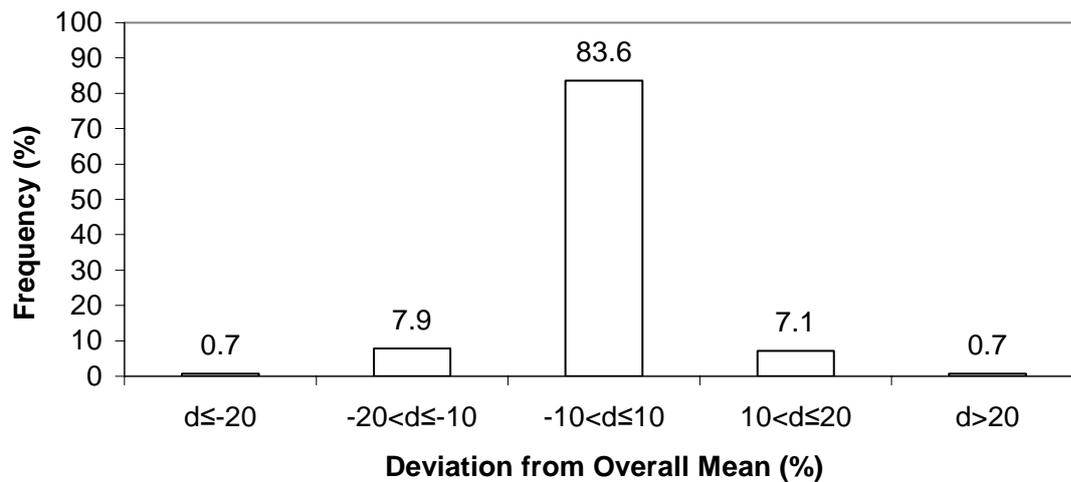


Fig. 5. Frequency of bulk density deviation from overall mean bulk density.

Pocket fullness uniformity

As shown in Table 2, among fields the PF means ranged between 80.9–100.8% and the CUs ranged between 81.3–90.1%. For all data combined, the mean PF was 89.9% and the CU was 83.6%. These results indicate good performance overall, however, the relatively large range in means and CUs among fields suggests that the level of performance was field-condition specific. As such, the results for the individual fields were examined more closely. Two of the fields, Banting and F102, had excellent performance with means of 100.8% and 98.3%, and CUs of 88.1% and 90.1%, respectively. The other three fields had only fair performance with means ranging between 80.9–83.2% and CUs ranging between 81.3–84.2%.

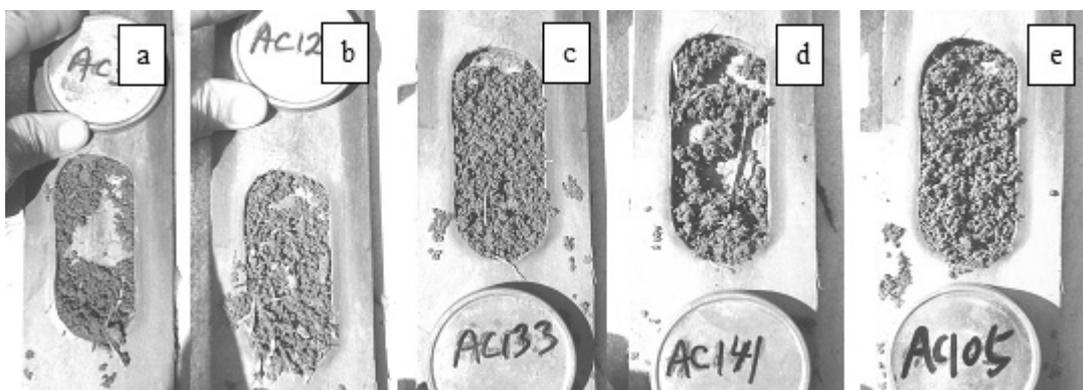


Fig. 6. Lowest pocket fullness (delivered weight) samples in Field 207N. (a) Location A: 52.1% (7.9 g). (b) Location B: 71.2% (10.6 g). (c) Location C: 71.9% (11.1 g). (d) Location D: 51.4% (8.0 g). (e) Location E: 75.2% (11.6 g).

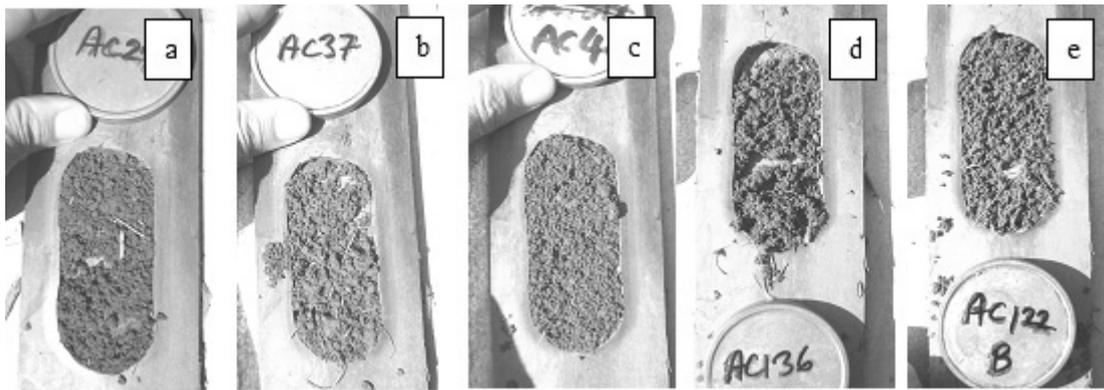


Fig. 7. Highest pocket fullness (delivered weight) samples in Field 207N. (a) Location A: 93.5% (14.8 g). (b) Location B: 87.1% (13.6 g). (c) Location C: 110.5% (17.1 g). (d) Location D: 77.8% (12.0 g). (e) Location E: 108.0% (16.9 g).

The lower level of performance in the other three fields was found to be because of two issues: (i) localized high clay content of soil, and (ii) straw chaff. Both issues caused ‘goughing out’ of soil collected in the pocket to occur in varying degrees, as seen in Figs. 6 and 7. These figures show the lowest and highest, respectively, PF (DW) samples of the six samples at each location in F207S, the field where PF performance was observed to be the worst. ‘Goughing out’ would occur when ‘blocky’ soil particles or straw, whichever the case, caught on the scraper as the pocket traveled beneath to level off the sample.

Localized high clay content (visual and feel-test assessed) was evident at several of the sampling locations in these three fields (particularly in F207S), despite them being reported as having a friable, coarse loamy solum (Webb and Langille 1996). This is not unusual, given the relatively large scale of soil classification maps (D. Langille 2007, personal communication). When high clay content was encountered while sampling, it was observed that soil being thrown onto the pocket area of the belt by the blade tended to have a ‘blocky’ versus ‘finely chopped’ granulation (Table 4). The varying degrees of blocky granulation are shown in Fig. 8.

Occasionally in fields F207S and F207N, a relatively long (3–5 cm) piece of straw chaff would get thrown into the pocket with the soil (Fig. 6(b), (d)), however most of the time any straw being thrown in was relatively finely chopped (Fig. 8). In contrast to the worst range of performance, as presented for F207S in Figs. 6 and 7, it should be noted that Figs. 3(b) and 7(a)(b) are typical of the better range of performance observed in the other four fields (additional sets of figures not shown in the interests of brevity).

Table 4. Field 207S location-specific sample conditions.

Location	Soil group [†]	Sample condition
Location A	DRT22	Blocky granulation from blade; clayey soil texture
Location B	DRT22	Blocky granulation from blade; clayey soil texture
Location C	DRT22	Powdery granulation from blade; loamy soil texture
Location D	DRT22	Blocky granulation from blade; clayey soil texture
Location E	PGW52	Semi-blocky powdery granulation; clayey-loamy texture

[†] DRT22, Debert 22; PGW52, Pugwash 52.



Fig. 8. Samples collected from Field 207S grouped by sampling location.

Pocket fullness and delivered weight relationship

The relationships between PF and DW for each field and all data combined were determined through regression analysis (Table 5).

All regression equations were linear, had very high R^2 values, and the predicted DWs at 100% pocket fullness were nearly the same for each field. The equation for Banting looked to be somewhat different from the rest ($I = -3.3$, $S = 19.0$), but in reality it was very close as the predicted DW at 100% PF was 15.7 g. A 0.1 g difference in DW from 15.6 g (all data combined predicted DW @ 100% PF) results in an error of 0.6%, while a 0.2 g maximum difference (15.6 g – 15.4 g) for F102 results in an error of 1.3%. These results indicate that DW was very highly correlated to PF and that the relationship was consistent over all field conditions tested.

Table 5. Relationships between pocket fullness and delivered weight for the test fields.

Field	Regression equation [†]	R ²	Delivered weight [‡] g
Banting	DW [§] = -3.3 + 19.0 × PF [¶]	0.975	15.7
F207S	DW = -0.6 + 16.1 × PF	0.987	15.5
F207N	DW = -1.2 + 16.9 × PF	0.955	15.6
F206	DW = -0.9 + 16.5 × PF	0.971	15.6
F102	DW = -0.9 + 16.3 × PF	0.969	15.4
All data combined	DW = -1.2 + 16.8 × PF	0.979	15.6

[†] Banting, $n = 30$; F207S, $n = 29$; F207N, $n = 21$; F206, $n = 30$; F102, $n = 30$; All data combined, $n = 140$.

[‡] Predicted delivered weight at 100% pocket fullness.

[§] DW, Delivered weight (g).

[¶] PF, Pocket fullness (%).

Delivered weight uniformity

As shown in Table 2, among fields the DW means ranged between 12.4–15.9 g and the CUs ranged between 80.3–89.3%. For all data combined, the mean DW was 13.9 g and the CU was 82.0%. These results indicate good performance overall, and because of the very high degree of correlation between DW and PF, it can be concluded that the DW and PF results were highly similar. Therefore, the performance issues as discussed above for PF were the same for DW, and they do not require any further discussion here.

To determine the practical effects this level of performance in DW would have on SNMS soil NO₃-N measurements, a sensitivity analysis was conducted. First, a mathematical calculation of potential error in NO₃-N measurement that could result from error in DW was made. It was determined that changes in NO₃-N measurement are directly proportional to changes in DW. Based on a full pocket having a DW of 15.6 g (from all data combined regression equation above), the mean DW of 13.9 g would result in a mean theoretical error in NO₃-N measurement of 10.9%.

Second, to determine how often it is likely that various degrees of error could occur, a frequency plot of the measured DW deviations from full pocket weight (15.6 g) was prepared, as shown in Fig. 9. It was found that the sampler delivered ±10% of full weight in 37.9% of the cases, ±20% of full weight in 70.8% of the cases, and deviations greater than 20% occurred in 29.3% of the cases.

A mean DW error of 10.9% is likely acceptable for most practical field use situations, however, a CU of 82.0% is not. These results clearly indicate that the DW

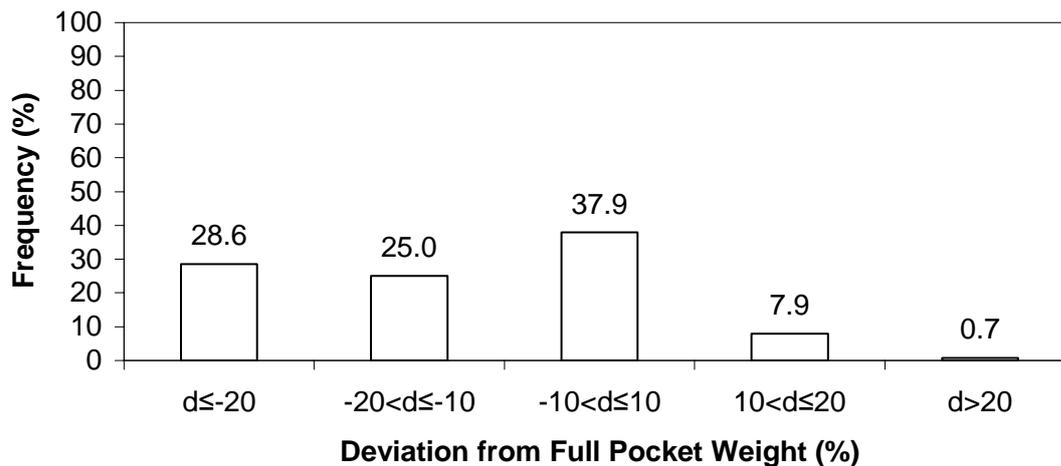


Fig. 9. Frequency of delivered weight deviation from full pocket weight.

uniformity of the sampler, particularly in clayey soil conditions, should be increased by improving the design.

The debate with the current design, then, would be whether design improvements should strive to obtain a consistently delivered known ‘weight’ (mass) of soil at some percentage of pocket fullness (i.e. a not quite full pocket), or a consistently full pocket of known weight. In either case it does not really matter what the relative magnitude of the weight is as long as it is known and consistent.

Therefore, it is important that the current design of the sampler be improved to either (i) ensure better consistency in DW if the ‘uniform bulk density’ design principle is continued to be used, or (ii) incorporate a method of ‘weighing’ individual samples as they are being delivered.

Summary and conclusions

An automated on-the-go soil sampler was developed as part of a soil nitrate mapping system that collects data for precisely analyzing small-scale variation in soil $\text{NO}_3\text{-N}$. An essential requirement of the sampler is the ability to reliably collect a soil sample of known ‘weight’ (mass). It was hypothesized that if a uniform bulk density sample could be collected in a device of fixed volume, then the mass of the sample would be known and constant. The sampler employs a woodsaw blade to cut a 15-cm deep slot in the soil at a sampling location as it travels forward and to throw a spray of finely chopped soil into a fixed-volume pocket milled into the surface of an automatically positioned flat-belt transfer conveyor. The field performance of the sampler was tested in five field conditions to determine the validity of the sampler’s ‘uniform bulk

density' design principle, the uniformity of pocket fullness, the relationship between pocket fullness and delivered 'weight' (mass), and the uniformity of delivered weight. Based on the results of this study, the following conclusions were made.

Bulk density uniformity

The overall uniformity in BD of 92.9% for all field conditions tested was excellent, and in practical terms the variation that did occur over all field conditions had less than a 5.5% deviation effect on DW in 83.6% of the cases. The sampler's main design principle of 'uniform bulk density' was validated for all intents and purposes of field use.

Pocket fullness uniformity

Among fields, PF means ranged between 80.9–100.8% and the CUs ranged between 81.3–90.1%. For all field conditions data combined, the mean PF was 89.9% and the CU was 83.6%. Pocket fullness uniformity was found to be field-condition specific, related mostly to localized high clay content at several sampling locations in three of the fields.

Pocket fullness and delivered weight relationship

Delivered weight was consistently very highly correlated to PF over all field conditions. The linear relationship between DW and PF for all field conditions data combined, $DW = -1.186 + 16.804 \times PF$, had an R^2 of 0.979 ($n = 140$).

Delivered weight uniformity

Overall, the sampler had a mean DW error of 10.9% and a CU of 82.0%. Delivered weight uniformity was found to be field-condition specific, related mostly to localized high clay content at several sampling locations in three of the fields. Delivered weight uniformity of the sampler, particularly when used in clayey soils, should be increased by improving the design.

CHAPTER 5

Field-scale validation of an automated soil nitrate measurement system¹

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Abstract

One gap which remains to be filled with *precision agriculture* technologies is the availability of an economical, automated, on-the-go mapping system that can be used to intensely and accurately collect 'real-time' data on the levels of NO₃-N in the soil. A soil nitrate mapping system (SNMS) has been developed to provide a way to collect these data. This study was conducted to provide extensive field-scale validation testing of the SNMS' nitrate extraction and measurement sub-assembly in two crop (wheat and carrot) production systems. Field conditions included conventional tillage vs. no tillage, inorganic vs. organic fertilization, four soil groups, and three time points throughout the season. Detailed data analysis revealed that: (i) the level of agreement, as measured by Root Mean Squared Error (RMSE), Mean Absolute Error (MAE) and Coefficient of Efficiency (CE), between SNMS soil NO₃-N and standard lab soil NO₃-N measurements was excellent; (ii) at the field-scale, there was little practical difference when using either integer math or whole math data processing; (iii) regression equations can be used to enable field measurements of soil NO₃-N using the SNMS to be obtained with lab-grade accuracy; (iv) future designs of the SNMS' control system can continue to use cheaper integer math chip technology for processing the NO₃⁻-ISE readings; and (v) future designs of the SNMS would not need a soil moisture sensor, ultimately saving on manufacturing cost and keeping the system simpler.

Keywords: Soil nitrate measuring, ion-selective electrode, precision agriculture.

¹ In review as: K.J. Sibley, T. Astatkie, G. Brewster, P.C. Struik, J.F. Adsett and K. Pruski. 2008. Field-scale validation of an automated soil nitrate measurement system. *Precision Agriculture*.

Introduction

The profitability and sustainability of modern agriculture are being challenged by economic globalization and environmental concerns. Fertility practices play a major role in both these challenges. The growth, yield and quality of farmer's crops, hence profit, can be negatively affected if over-fertilization occurs due to extra input costs and lower prices received. Over-fertilization, with either inorganic or manure fertilizers, can also result in water sources contamination and has been found to be the cause of many of the environmental issues with agricultural production practices (Spalding and Exner, 1993; Jemison and Fox, 1994; MacDonald, 2000; Dinnes et al., 2002).

Precision agriculture offers an exciting opportunity to use highly advanced technology to assist with the discovery of better production practices that not only mitigate associated environmental issues, but also increase the overall sustainability of modern agriculture. The ultimate goal of such technology is to enable farmers to more intensely and precisely analyze variations in field conditions throughout the growing season vis-à-vis environmental and crop response data to make the best possible site- and time-specific management decisions possible. This ability is offering new production efficiencies to farmers, while at the same time offering assurances to the public that agricultural production practices are being conducted with the lowest possible negative environmental impact.

One gap which remains to be filled with *precision agriculture* technologies is the availability of an economical, automated, on-the-go mapping system that can be used to intensely and accurately collect 'real-time' data on the levels of $\text{NO}_3\text{-N}$ in the soil. The inability to assess soil characteristics rapidly and inexpensively remains one of the biggest limitations of *precision agriculture* (Adamchuk et al., 2004b). If these limitations could be overcome, a positive contribution towards achieving the ultimate goal of *precision agriculture* would be made. The soil nitrate mapping system (SNMS) (Fig. 1) will be one such technology as it provides a way to collect the data necessary to analyze soil nitrate variation both spatially and temporally.

The SNMS consists of six sub-assemblies: (1) soil sampler sub-assembly, (2) soil metering and conveying sub-assembly, (3) nitrate extraction and measurement sub-assembly, (4) auto-calibration sub-assembly, (5) control sub-assembly, (6) GPS sub-assembly. The system automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyzes it electrochemically for nitrate concentration in real-time (6 s) using a nitrate ion-selective electrode (NO_3^- -ISE) as the analysis instrument. Additionally, global positioning system (GPS) geo-referenced data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field. The system can be used to analyse soil samples automatically

while on-the-go, or manually while stationary by hand-placing samples into the nitrate extraction and measurement sub-assembly. It is envisioned that two configurations of the system will eventually be used in practice – a tractor-mounted version (as shown in Fig. 1) and a ‘suitcase’ version.

From its first prototype (Adsett, 1990; Adsett and Zoerb, 1991), the SNMS has undergone several developmental iterations. The use of a NO_3^- -ISE in this type of application has been extensively lab tested (Thottan et al., 1994; Thottan, 1995; Brothers et al., 1997). Development and preliminary field testing of the five initial sub-assemblies and their integration into one complete system followed (Thottan, 1995; Adsett et al., 1999). In 2001, a completely new electronics and control system that incorporated the GPS sub-assembly was added.

A next step in the development of the SNMS was extensive field-scale validation of the nitrate extraction and measurement sub-assembly against standard lab measurements. As well, the use of cheaper integer math (IM) chip technology, as opposed to whole math (WM), in the new control system for processing the NO_3^- -ISE readings needed to be validated. It was also of interest to explore whether a soil moisture content sensor was necessary for achieving accurate results in the field.

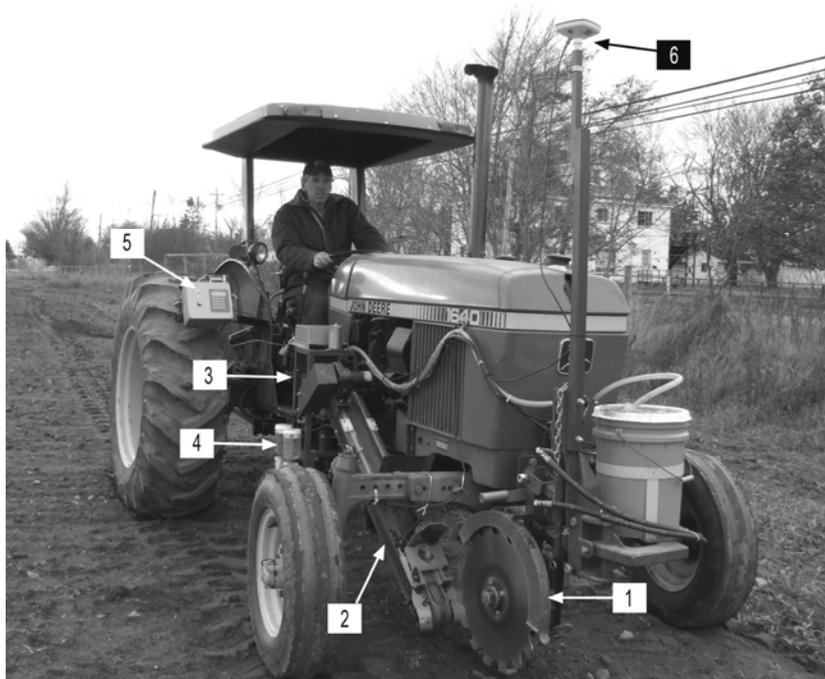


Fig. 1. Soil nitrate mapping system with six sub-assemblies.

Objectives and scope

In this study, extensive field-scale validation testing of the SNMS' nitrate extraction and measurement sub-assembly was conducted with the objectives of determining (i) the level of agreement between SNMS soil NO₃-N measurements and standard lab soil NO₃-N measurements for a variety of field conditions, (ii) whether IM or WM data processing of NO₃⁻-ISE readings gave closer agreement to standard lab NO₃-N measurements, (iii) regression equations to enable field measurements using the SNMS to be obtained with lab-grade accuracy, (vi) whether a soil moisture content sensor was necessary for achieving accurate results with the SNMS compared to standard lab measurements. The scope of this study was limited to testing in two locally available fields during the simultaneous execution of related multifaceted experiments in two crop production systems (wheat and carrot) having high economic importance to the Atlantic region of Canada in particular, and internationally in general. The field conditions included two crops, two tillage methods, two fertilization methods, and four soil groups, as described below.

Materials and methods

Field sites and experimental designs

During the 2006 season, field experiments were established in two adjacent fields (#203 and #207) on the Nova Scotia Agricultural College (NSAC) farm, Truro, Nova Scotia, Canada (45°22'N 63°16'W) concurrent with experiments being conducted by the Nova Scotia Water Quality Research Group (NSWQRG). These fields have been used by the NSWQRG since 1995 for many bio-environmental, cropping management, and water quality studies, and their soils characteristics and cropping histories have been well documented (Webb and Langille, 1996; Elmi et al., 2005; Gordon et al., 2005).

Four soil groups present in the fields were (i) Pugwash 52 (PGW52), (ii) Pugwash 82 (PGW82), (iii) Debert 22 (DRT22), and (iv) Debert 52 (DRT52). The PGW52 and PGW82 soils had a friable, fine sandy-loam textured Ap horizon 15- to 20-cm thick, underlain by a fine sandy-loam textured Bm horizon. Below the Bm horizon was a friable to firm, fine sandy-loam textured, platy structured, fragic BCxj horizon. They were moderately well-drained and well-drained, respectively. The DRT22 and DRT52 soils had a friable, sandy-loam textured Ap horizon 25- to 30-cm thick, underlain by a friable to firm sandy-loam textured Bmgj horizon. Below the Bmgj horizon were firm, poorly structured sandy-loam to loam textured subsoil horizons that included fragipan (BCxj, BCxjgi) and compact basil till (Cgj). They were both imperfectly drained. All descriptions of the soils are according to Webb and

Langille (1996). Both fields had systematic tile drainage systems (100-mm diameter) installed at 0.8-m depth with 12-m spacing between drains.

Field #203 was conventionally tilled, contained soil groups PGW82, DRT22, and DRT52, and was seeded with carrot (*Daucus carota* L.) being grown using liquid dairy manure (LDM) and inorganic fertilizer (IF) fertility management treatments. Field #207 had LDM applied to the entire field, contained soil groups PWG52, DRT22, DRT52, and was seeded with spring wheat (*Triticum aestivum* L.) being grown under conventional tillage (CT) and no tillage (NT) management treatments. Randomized complete block experimental designs were used in both fields, with soil group blocks. Field #207 had 10 plots (2 treatments \times 5 blocks) and Field #203 had 8 plots (2 treatments \times 4 blocks). This configuration allowed for simultaneous investigation of plant and soil nitrate responses under a variety of field management conditions using the SNMS in another sub-experiment, not being reported here.

Soil sampling and analyses

Within each field, soil samples were collected using a 6.5- by 7.0-m grid layout in the plots to provide soil NO₃-N data for the 0–15-cm soil depth. Each wheat plot grid had 13 sampling locations, whilst each carrot plot grid had eight. The grids in each plot were laid out manually directly above the tile drains which provided for spatially-located sampling at points along each drain tile, and at mid-drain tile spacing. Each sampling location was staked to enable repeat sampling and its Easting and Northing coordinates were recorded with the GPS unit. This configuration enabled data collection for this study simultaneously with two other related studies investigating the relationships between soil NO₃-N and drain water quality, and the spatial and temporal variation of soil NO₃-N respectively, not being reported here.

Soil samples were collected (i) just prior to planting and fertilizing (3 May for wheat, 4 May for carrot), (ii) approximately three weeks after fertilizing (30 May for wheat, 20 June for carrot), and (iii) after crop harvest (7 Nov. for both wheat and carrot). Samples were collected manually by coring with a standard 19-mm diameter soil sampling tool to a depth of 15 cm. Four cores were taken at each location and bulk-mixed into a small plastic bag. All samples were collected within a 0.3-m radius of the sampling location. All samples were kept in Styrofoam coolers while in the field, and were immediately transported to the lab where they were kept under refrigerated storage (4°C) until processing could be completed (6 to 38 days). A total of 582 soil samples were collected and analyzed for this study.

Standard lab analysis for NO₃-N content of the samples was performed in the NSAC's Soils Analysis Lab using inorganic N extraction procedures, according to the methods of Voroney et al. (1993). Moist sub-samples of ± 20 g each were combined

with 100 mL (1:5 soil/extractant ratio) of 2 M KCl and shaken for 60 min at 170 cps. After shaking, all samples were allowed to settle for 15 min, and then filtered through Whatman #42 filter paper into 20-mL HDPE scintillation vials. The vials were immediately placed into a freezer (-16°C) until $\text{NO}_3\text{-N}$ quantification could be completed (12–36 days). Samples were subsequently thawed, and $\text{NO}_3\text{-N}$ was quantified colorimetrically using a Lachat flow injection autoanalyzer (FIA) (Lachat Quickchem, Milwaukee, WI), according to the method of Keeney and Nelson (1982). Moist sub-samples of 10–15 g each were also weighed out at the time of extraction, and the moisture content of each sample was quantified gravimetrically using the standard oven dry method.

Soil nitrate mapping system analysis of the samples for $\text{NO}_3\text{-N}$ content was performed using only its nitrate measurement and extraction sub-assembly in order to isolate the performance of this sub-assembly from the performance of the soil sampling sub-assembly. Calibration of the ISE was performed using standards manually-prepared from reagent-grade KNO_3 powder and distilled water. Moist sub-samples of 15.1 g each were manually weighed out and placed in the nitrate extraction and measurement chamber. Extraction and quantification of $\text{NO}_3\text{-N}$ was completed automatically in 58.0 mL of vigorously stirred distilled water in 6.0 s per sample. The ISE used was a new Orion 9707 ionplus electrode (Thermo Electron Corp., USA). Details of the SNMS' calibration procedures and its functional operation are well documented elsewhere (Thottan et al., 1994; Thottan, 1995; Brothers et al., 1997; Adsett et al., 1999). Strict quality control measures (Table 1) were implemented during the analysis to minimize experimental error.

Data processing and statistical analyses

Four data processing methods (DPM) were used for calculating the $\text{NO}_3\text{-N}$ content of the soil samples analyzed using the SNMS: (i) Integer math (IM); (ii) Whole math (WM); (iii) Integer math plus moisture content correction (IM+MCC); and (iv) Whole math plus moisture content correction (WM+MCC). The level of agreement between SNMS measurements and standard lab measurements for each DPM was determined using two absolute measures, Root Mean Squared Error (RMSE) and Mean Absolute Error (MAE), and one relative measure, Coefficient of Efficiency (CE). While smaller values of RMSE and MAE indicate better performance, one needs a reference value to judge whether these models provide acceptably small values. Perfect agreement gives RMSE and MAE values of zero. On the other hand, for the unit-less relative measure CE, a negative value indicates the agreement is worse than estimating all lab measurements by the average, a value of zero indicates that the agreement is as good as estimating all values by the average, and a value of one indicates the agreement is

perfect. The DPM model that gives a CE closer to one performs better. Detailed description of these measures and their applications are available in Astatkie (2006).

For each DPM, simple linear regression models of Y (lab value) on X (DPM value) were fitted for the different sampling dates, treatments, soil groups, and crops. After verifying the validity of all model assumptions (normality, constant variance and independence), nested linear regression models (Bates and Watts, 1988) were fitted to determine if the different groups of data shared common intercept and slope at the 0.05 level of significance. After confirming that the different groups shared the same intercept and slope, one final linear regression model, for each DPM, was fitted using all data combined across sampling dates, treatments, soil groups and crops. These final regression models were fitted to enable field measurements using the SNMS to be obtained with lab-grade accuracy.

For determining whether a soil moisture content sensor was necessary for achieving accurate results with the SNMS compared to standard lab measurements, a comparison of the IM and WM regression equations' fitted values with the Lab values was made using the agreement measures RSME, MAE and CE discussed above.

All measures of agreement, and regression analyses were computed using macros written for and executed by Minitab (Minitab Inc., Pennsylvania, USA; Ver. 15.0). All data calculations were made using Excel (Microsoft Corp., California, USA.; Ver. Prof. Ed. 2003).

Table 1. Soil nitrate mapping system analyses quality control measures.

Control measure	Action
Sample placement timing	Sample placed into chamber as belt pocket rounded conveyor tail-end roller.
Sample consistency	Hand-granulated in plastic bag prior to weighing. Weighing ± 0.1 g.
Electrode calibration	Electrode calibrations were 59 ± 2 mV/decade.
Calibration standards	Manually prepared standards were checked against Orion ionplus certified NaNO_3 standard.
Temperature	Room temperature 20–22°C. Soil vs. calibration standards $\pm 1^\circ\text{C}$.
Electrode accuracy and repeatability	Electrode accuracy and repeatability checked against set of manually prepared decaded standards.
Electrode drift	At least one blank and repeat sample measurements were randomly made for each plot. When drift exceeded $\pm 2\%$ electrode sensing module was replaced.
Electrode response time	Electrode response time in standards compared to stirred soil sample solution.

Results and discussion

Soil nitrate mapping system data from the first sampling dates for each crop (3 May for carrot and 4 May for wheat) were excluded from the analyses because of intermittent issues with the control system programming routine that caused inconsistent operation of the SNMS during sample processing. The problem was identified and rectified prior to processing the later date's samples. Exclusion of these data did not limit the range of applicability of the SNMS results obtained because the full range of soil NO₃-N values covered by the data from the later dates included the range from the first dates. The soil NO₃-N Lab data from the first dates had a combined mean of 3.71 mg kg⁻¹, a standard error of 0.11 mg kg⁻¹, and a standard deviation of 1.55 mg kg⁻¹.

Representative graphs comparing SNMS and Lab measurements over all field conditions tested are shown in Fig. 2. These graphs illustrate admirable performance of the SNMS on an individual sample basis, regardless of the field condition from which the sample originated. As well, they also indicate the responsiveness of the ISE, as the values are displayed by sampling location (x-axis) in the order of measurement. It was found that the electrode responded equally well regardless of whether the NO₃-N level was changing from lower to higher, or higher to lower during measurement.

Soil nitrate mapping system vs. lab agreement

No significant differences in agreement measures (Table 2) were found for sampling date, treatment, crop, or soil group data sets. Therefore, all data sets were combined and overall agreement measures were calculated. The all data combined (first column in Table 2) RSME values ranged between 2.23 mg kg⁻¹ and 3.73 mg kg⁻¹, the MAE values ranged between 1.67 mg kg⁻¹ and 2.68 mg kg⁻¹, and the CE values ranged between 0.836 and 0.941. Although both RSME and MAE have the same unit, RSME values are larger than MAE values because RSME values are based on squared deviations, and hence more sensitive to the inflating effect of larger deviations (Astatkie, 2006). The order of closest to farthest agreement with the Lab values for all three agreement measures was also consistent between the four DPMs, with the WM+MCC DPM being the closest, followed by IM+MCC, IM, and WM. However, from a practical perspective all DPMs were in fact very close to each other as the maximum difference in MAE values between WM and WM+MCC was only 1.01 mg kg⁻¹ (2.68 mg kg⁻¹ - 1.67 mg kg⁻¹) which is equivalent to 2.32 kg ha⁻¹. And on an absolute basis, the maximum difference between the SNMS and the Lab values was 2.68 mg kg⁻¹ for the WM DPM, which is equivalent to 6.05 kg ha⁻¹. It is highly unlikely that either of these levels of difference would have much consequence on field-scale usage of the SNMS.

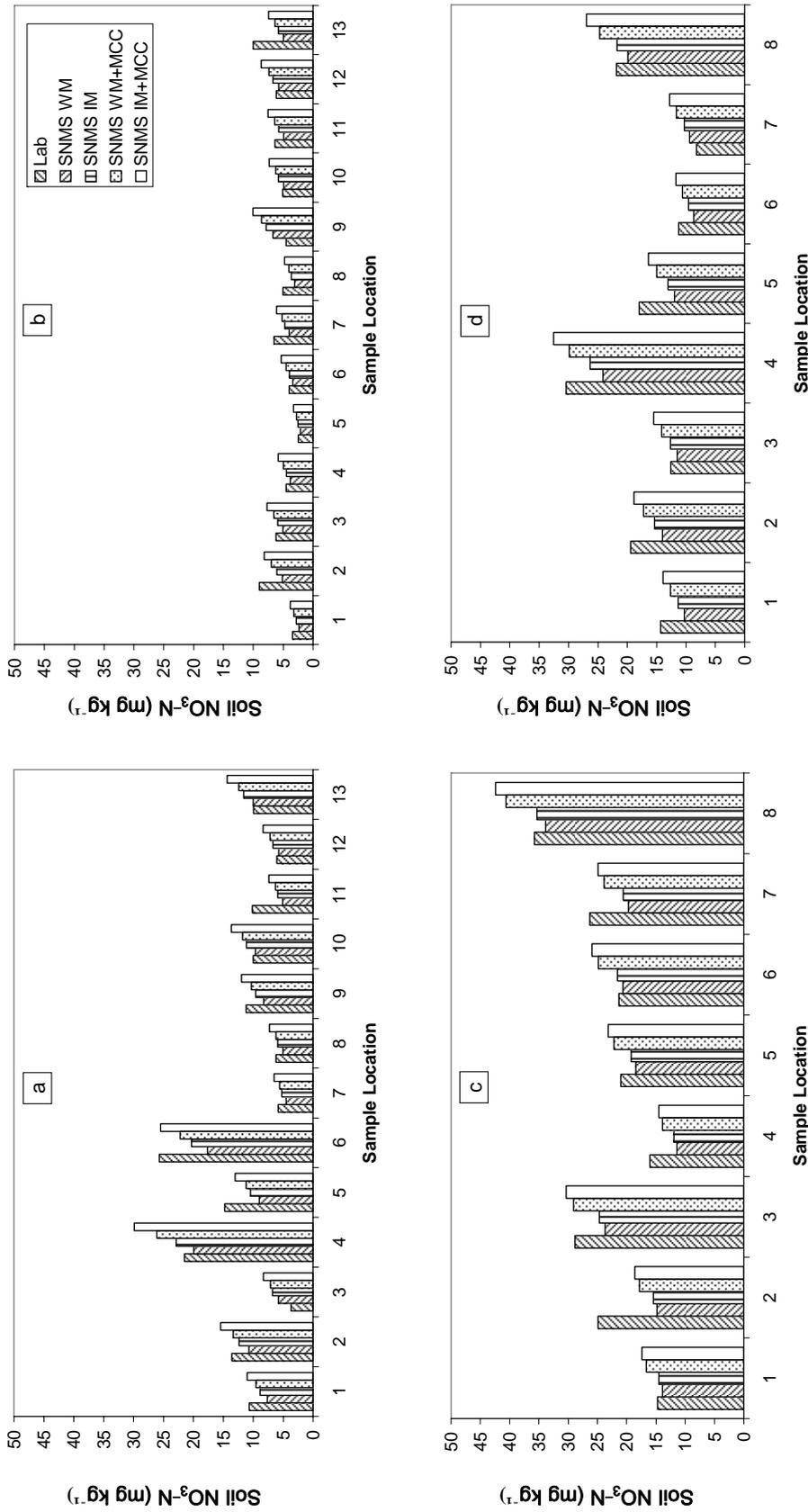


Fig. 2. Comparison of soil nitrate mapping system soil NO₃-N measurements for each data processing method vs. Lab soil NO₃-N measurements by sample location. Data processing method: IM, integer math; WM, whole math; IM+MCC, integer math with moisture content correction; WM+MCC, whole math with moisture content correction. (a) Wheat plot 6 (no tillage, Debert 52) on 30 May. (b) Carrot plot 2 (inorganic fertilizer, Pugwash 82) on 20 June. (c) Carrot plot 3 (liquid dairy manure, Debert 22) on 7 Nov. (d) Wheat plot 8 (conventional tillage, Pugwash 52) on 7 Nov.

Table 2. Soil nitrate mapping system vs. lab agreement measures for the sampling dates (excluding the first date as discussed above), treatments, crops, soil groups, and all field conditions data combined.

DPM [§] /RMSE	All data		Sampling Date				Treatment [†]				Crop				Soil Group [‡]			
			30	20	7	May	June	Nov.	NT	CT	LDM	IF	Carrot	Wheat	DRT22	DRT52	PGW52	PGW82
	combined		May	June	Nov.	May	June	Nov.	NT	CT	LDM	IF	Carrot	Wheat	DRT22	DRT52	PGW52	PGW82
											mg kg ⁻¹							
IM	3.18	3.80	3.38	2.60	2.80	3.47	2.59	3.70	3.20	3.15	3.70	3.20	3.20	2.80	3.81	3.27	3.20	3.20
WM	3.73	4.13	4.57	3.08	2.96	5.07	2.99	3.96	3.50	4.15	3.96	3.50	3.50	3.60	4.19	3.67	3.73	3.73
IM+MCC	2.89	2.66	3.62	2.77	2.04	4.59	2.46	2.55	2.50	3.55	2.55	2.50	2.50	3.30	2.72	2.58	2.72	2.72
WM+MCC	2.23	2.40	2.71	1.92	1.66	2.96	1.95	2.32	2.40	2.40	2.32	2.40	2.14	2.24	2.21	2.28	2.11	2.11
IMFits [¶]	2.63	2.91	2.91	2.31	1.97	3.40	2.17	2.87	2.78	2.78	2.87	2.78	2.55	2.66	2.85	2.61	2.40	2.40
WMFits [¶]	2.28	2.43	2.84	1.94	1.69	3.06	1.97	2.36	2.47	2.47	2.36	2.47	2.18	2.29	2.19	2.35	2.17	2.17
DPM/MAE											mg kg ⁻¹							
IM	2.30	2.74	2.45	1.97	2.17	2.65	1.89	2.61	2.41	2.41	2.61	2.41	2.25	2.10	2.68	2.33	2.39	2.39
WM	2.68	2.92	3.25	2.32	2.47	3.80	2.13	2.77	3.14	3.14	2.77	3.14	2.45	2.55	2.92	2.58	2.96	2.96
IM+MCC	2.11	2.06	2.57	1.98	1.59	3.52	1.77	2.01	2.55	2.55	2.01	2.55	1.89	2.39	2.00	1.91	2.00	2.00
WM+MCC	1.67	1.88	1.91	1.45	1.32	2.16	1.50	1.78	1.74	1.74	1.78	1.74	1.64	1.75	1.71	1.64	1.53	1.53
IMFits	1.97	2.18	2.19	1.75	1.47	2.67	1.64	2.20	2.07	2.07	2.20	2.07	1.92	2.07	2.11	1.91	1.77	1.77
WMFits	1.70	1.89	1.97	1.47	1.32	2.20	1.53	1.80	1.76	1.76	1.80	1.76	1.66	1.79	1.68	1.67	1.57	1.57
DPM/CE											decimal							
IM	0.881	0.840	0.920	0.847	0.764	0.892	0.815	0.859	0.892	0.892	0.859	0.892	0.854	0.889	0.887	0.876	0.836	0.836
WM	0.836	0.811	0.855	0.786	0.735	0.770	0.755	0.839	0.813	0.813	0.839	0.813	0.824	0.817	0.862	0.844	0.778	0.778
IM+MCC	0.902	0.922	0.909	0.828	0.874	0.811	0.834	0.933	0.863	0.863	0.933	0.863	0.910	0.846	0.942	0.923	0.882	0.882
WM+MCC	0.941	0.936	0.949	0.918	0.917	0.922	0.895	0.945	0.938	0.938	0.945	0.938	0.934	0.929	0.962	0.940	0.929	0.929
IMFits	0.919	0.906	0.941	0.880	0.883	0.896	0.870	0.915	0.916	0.916	0.915	0.916	0.907	0.900	0.936	0.921	0.908	0.908
WMFits	0.939	0.934	0.944	0.916	0.914	0.916	0.893	0.943	0.934	0.934	0.943	0.934	0.932	0.926	0.962	0.936	0.925	0.925

[†] Treatments: NT, no tillage; CT, conventional tillage; LDM, liquid dairy manure; IF, inorganic fertilizer.

[‡] Soil Group: DRT22, Debert 22; DRT52, Debert 52; PGW52, Pugwash 52; PGW82, Pugwash 82.

[§] DPM, data processing method: IM, integer math; WM, whole math; IM+MCC, integer math with moisture content correction; WM+MCC, whole math with moisture content correction.

[¶] IMFits, Integer math regression fit values; WMFits, whole math regression fit values.

The same can be said for the difference between SNMS measurements with and without moisture content correction. Statistically, moisture content correction of the SNMS measurements yielded better agreement with Lab values than without moisture content correction (CE values: WM+MCC = 0.941 and IM+MCC = 0.902 vs. WM = 0.836 and IM = 0.881). However, the difference from a practical field perspective was minimal. Again, in the worst case of MAE values between WM and WM+MCC, the difference of 1.01 mg kg⁻¹ (2.32 kg ha⁻¹) would be of little consequence in the field.

Based on these results, it was concluded that the level of agreement between SNMS NO₃-N measurements and standard lab NO₃-N measurements for the variety of field conditions tested was excellent. These results also strongly suggest that the SNMS is so robust that it can be used for both carrot and wheat crops, as well as in different soil groups, fertility levels, tillage conditions, and at any time throughout the season.

Integer math vs. whole math data processing

With respect to whether IM or WM data processing of NO₃⁻-ISE readings gave closer agreement to standard lab NO₃-N measurements, it was found that the difference was minimal. All three agreement measures were very close when comparing results between the IM and WM DPMs, either alone or with moisture content correction. Without moisture content correction, the RMSE, MAE, and CE values for IM vs. WM were 3.18 mg kg⁻¹ vs. 3.73 mg kg⁻¹, 2.30 mg kg⁻¹ vs. 2.68 mg kg⁻¹, and 0.881 vs. 0.836, respectively. With moisture content correction, the RMSE, MAE, and CE values for IM vs. WM were 2.89 mg kg⁻¹ vs. 2.23 mg kg⁻¹, 2.11 mg kg⁻¹ vs. 1.67 mg kg⁻¹, and 0.902 vs. 0.941, respectively. On an absolute basis, the maximum difference between IM and WM was 0.44 mg kg⁻¹ (0.98 kg ha⁻¹). It is highly unlikely that this level of difference would have much consequence on field-scale usage of the SNMS.

Based on these results, it was concluded that at the field-scale there was little practical difference in results when using either the IM or WM data processing method. The implication of this result is that future designs of the SNMS' control system can continue to use cheaper IM chip technology for processing the NO₃⁻-ISE readings.

Regression analyses

The nested linear regression models shared common intercepts and slopes for the different sampling dates (excluding the first dates as discussed above), treatments, soil groups, and crops (regressions not shown in the interests of brevity). These results indicate that the SNMS had the same level of performance over all field conditions tested. Therefore, linear regression models for each DPM were fitted for all data

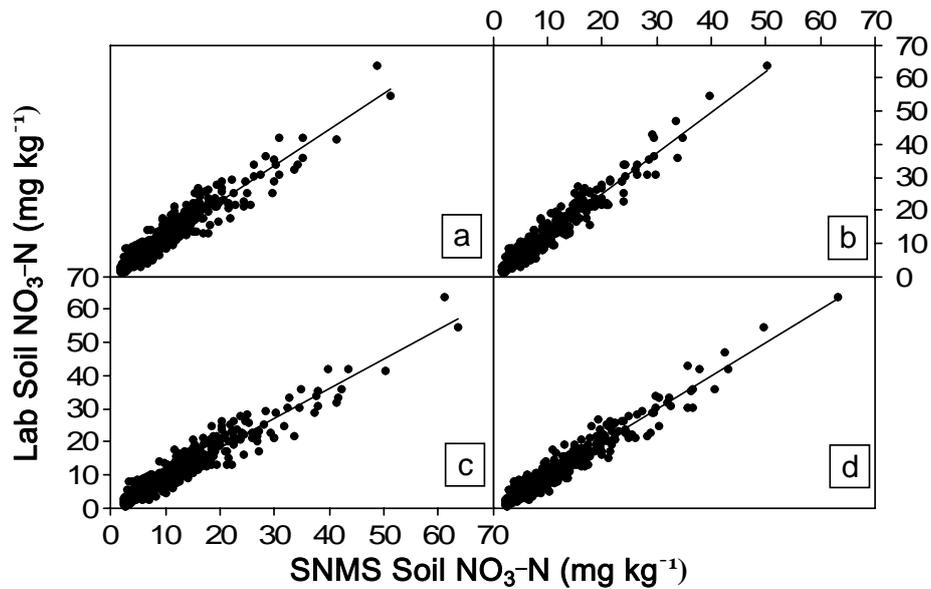


Fig. 3. Relationship between SNMS soil NO₃-N and Lab soil NO₃-N measurements for each data processing method; all field conditions data combined. (a) Integer math data processing. (b) Whole math data processing. (c) Integer math with moisture content correction processing. (d) Whole math with moisture content correction processing.

combined (Fig. 3). During regression fitting, either seven or eight outliers, depending on the data set being modeled, with standardized residuals greater than 3.0 were excluded. The final fitted regression equations below, then, were based on 380 or 381 data points:

For the IM DPM,

$$\text{Lab NO}_3\text{-N} = 0.727 + 1.09 \text{ SNMS IM NO}_3\text{-N} \quad (R^2 = 0.905, n = 381) \quad [1]$$

For the WM DPM,

$$\text{Lab NO}_3\text{-N} = 0.131 + 1.24 \text{ SNMS WM NO}_3\text{-N} \quad (R^2 = 0.933, n = 381) \quad [2]$$

For the IM+MCC DPM,

$$\text{Lab NO}_3\text{-N} = 0.490 + 0.89 \text{ SNMS IM+MCC NO}_3\text{-N} \quad (R^2 = 0.910, n = 380) \quad [3]$$

For the WM+MCC DPM,

$$\text{Lab NO}_3\text{-N} = -0.040 + 1.00 \text{ SNMS WM+MCC NO}_3\text{-N} \quad (R^2 = 0.936, n = 381) \quad [4]$$

As was found for the agreement measures discussed above, the WM+MCC DPM resulted in the best match to the Lab measurements ($R^2 = 0.936$, slope = 1.00).

However, from a practical perspective all models described the relationship between SNMS measurements and Lab measurements very well since their R^2 values were all above 90%.

It was concluded that any of the regression equations developed for describing the relationship between SNMS measurements and Lab measurements for the four data processing methods tested can be used to enable field measurements of soil $\text{NO}_3\text{-N}$ using the SNMS to be obtained with lab-grade accuracy.

Soil moisture content sensor

To determine whether a soil moisture content sensor was necessary for achieving accurate results with the SNMS compared to standard lab measurements, an agreement measures comparison of the IM and WM regression equations' fitted values (IMFits, WMFits) with the Lab values was made (Table 2). It was found that for all data combined the WMFits (CE = 0.939) gave closer agreement with Lab values than IMFits (CE = 0.919). However, from a practical field perspective either result was just as good (2.1% difference). Also from a practical perspective, the maximum difference in all data combined MAE values between WM+MCC, IMFits, and WMFits, (1.67 mg kg^{-1} , 1.97 mg kg^{-1} , and 1.70 mg kg^{-1} , respectively) of 0.30 mg kg^{-1} (0.67 kg ha^{-1}) would have no substantial consequence in the field. Therefore, it was concluded that future designs of the SNMS would not need a soil moisture sensor, ultimately saving on manufacturing cost and keeping the system simpler.

These results also confirm, as concluded above, that the IM and WM regression equations can be used as solid predictors of Lab measurements using SNMS measurements. Accurate predictions of Lab values can be obtained by simply using either regression equation during data processing calculations.

Summary and conclusions

Precision agriculture offers an exciting opportunity to use highly advanced technology to assist with the discovery of better production practices that not only mitigate associated environmental issues, but also increase the overall sustainability of modern agriculture. One gap which remains to be filled with *precision agriculture* technologies is the availability of an economical, automated, on-the-go mapping system that can be used to intensely and accurately collect 'real-time' data on the levels of $\text{NO}_3\text{-N}$ in the soil. A soil nitrate mapping system (SNMS) has been developed to provide a way to collect these data. This study was conducted to provide extensive field-scale validation testing of the SNMS in two crop production systems (wheat and carrot) having high economic importance to the Atlantic region of Canada in particular, and internationally

in general. Field conditions included conventional tillage vs. no tillage, inorganic vs. organic fertilization, four soil groups, and three time points throughout the season. Based on the results of this study, the following conclusions were made.

Soil nitrate mapping system vs. lab agreement

The level of agreement between SNMS soil NO₃-N measurements and standard lab soil NO₃-N measurements for the variety of field conditions tested was excellent. The results also strongly suggest that the SNMS is so robust that it can be used for both carrot and wheat crops, as well as in different soil groups, fertility levels, tillage conditions, and at any time throughout the season.

Integer math vs. whole math data processing

At the field-scale there was little practical difference in results when using either the IM or WM data processing method. The implication of this result is that future designs of the SNMS' control system can continue to use cheaper IM chip technology for processing the NO₃⁻-ISE readings.

Regression analyses

Any of the regression equations developed for describing the relationship between SNMS measurements and Lab measurements for the four data processing methods tested can be used to enable field measurements of soil NO₃-N using the SNMS to be obtained with lab-grade accuracy.

Soil moisture content sensor

Future designs of the SNMS would not need a soil moisture sensor, ultimately saving on manufacturing cost and keeping the system simpler. Accurate predictions of Lab values can be obtained by simply using either of the IM or WM regression equations during data processing calculations.

CHAPTER 6

Using an automated on-the-go mapping system to assess the spatial and temporal aspects of soil nitrate¹

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Abstract

An on-the-go soil nitrate mapping system (SNMS) has been developed that provides a quick, accurate and cost effective way to collect soil samples on a fine scale and analyze them for NO₃-N content. The SNMS can be used as an effective tool to assist soil scientists with experimental investigations of the spatial and temporal aspects of soil NO₃-N. Using data collected by the SNMS and a combination of classical and geostatistical analytical techniques and tools, the spatial and temporal aspects of NO₃-N variation in a wheat (*Triticum aestivum* L.) production system at several time points covering pre-seeding, growing season, and post-harvest soil conditions, as well as the intrinsic spatial structure of NO₃-N present in the field, were assessed. Posted values (contour) maps were generated that gave excellent visual pictures of the spatial variation. The means for each sampling date varied between 4.38–28.80 mg kg⁻¹, and coefficients of variation ranged between 24.1–71.2%. A very strong ‘proportional effect’, and significant positive autocorrelation at separation distances ≤20 m were found. Variograms of spatial structure for each sampling date were highly similar with nuggets between 0.291–0.510, ranges between 27–68 m, and nugget-to-sill ratios between 0.280–0.439. Spatial dependency was found overall to be moderate. The intrinsic spatial structure of NO₃-N variation was determined to be temporally stable over the study period. A scaled averaged variogram model representing the intrinsic spatial structure had a sill of 1.005, a nugget of 0.331, and a range of 44 m.

Keywords: Geostatistics, liquid dairy manure, NO₃-N variation, precision agriculture, soil nitrate mapping, spatial structure, variogram, semivariance, wheat.

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Introduction

Soil nitrate ($\text{NO}_3\text{-N}$) level in agricultural fields exhibits high variation spatially and temporally. Much research has been dedicated to assessing and characterizing this variation to improve our understanding of the effects of $\text{NO}_3\text{-N}$ on crop growth and the environment. *Precision agriculture* seeks to use this understanding to develop site-specific crop management (SSCM) practices for better agriculture.

The anion nitrate (NO_3^-) is highly soluble in water. Thus, it is contained in interstitial water within the soil matrix. There it is readily available for plant uptake. But, it can also move freely with water flow, eventually leaching into surface-water and groundwater bodies. As a result, nitrate has been found to cause many of the environmental issues in water sources associated with inorganic fertilizer and manure use (Spalding and Exner, 1993; Jemison and Fox, 1994; MacDonald, 2000; Dinnes et al., 2002).

Crop performance is affected by the ability of the plants to take up and utilize available inorganic soil nitrogen. Nitrate is the pre-eminent inorganic form of soil nitrogen which is taken up and utilized by plants. The presence or absence of it in the topsoil is often an indicator of how thoroughly they have been able to do this. Growing plants utilize varying amounts of $\text{NO}_3\text{-N}$ during different growth stages and its availability should ideally be in response to the need.

The availability of $\text{NO}_3\text{-N}$ in the soil depends on many soil forming, chemical, microbial, plant growth, environmental, and management factors that influence soil nitrogen dynamics. These factors include soil erosion, soil weathering, soil texture, soil organic matter content and soil pH, relative rates of N-uptake by plants, several N-transforming processes (e.g., mineralization, immobilization, and (de-)nitrification), precipitation, evaporation, tillage, drainage, and fertilizer inputs. These factors may be considered as either intrinsic or extrinsic depending on whether their main influence is internal to or external to the soil matrix, respectively (Rao and Wagenet, 1985; Trangmar et al., 1985). Obviously, intrinsic and extrinsic influences on $\text{NO}_3\text{-N}$ availability are not mutually exclusive as there are complex interdependencies between the two, but extrinsic affects intrinsic, and not vice-versa. Because the effects of these factors are distributed and highly variable, they also lead to the characteristic behavior of $\text{NO}_3\text{-N}$ being distributed and highly variable within the soil matrix. As well, there may be some variation² in measured levels of $\text{NO}_3\text{-N}$ introduced by experimental techniques.

Assessing and quantifying the variation and distribution of soil $\text{NO}_3\text{-N}$ levels,

² The word 'variation' is used in accordance with the recommendation of Webster (2001) to describe the actuality of change in levels of $\text{NO}_3\text{-N}$ rather than 'variability' which is used to mean the potential to vary. This convention accords the distinction between a 'variate' and 'variable'.

particularly in relation to crop responses, is helping to improve our understanding of the effects of soil nitrogen dynamics on crop growth through development and implementation of innovative SSCM practices (Larson and Robert, 1991; Cahn et al., 1994; Lund et al., 1999; Drummond et al., 2003; Eghball et al., 2003; Kitchen et al., 2003; Chang et al., 2004).

The variation and distribution of $\text{NO}_3\text{-N}$ levels in the soil have two main aspects from a working definition perspective: (i) spatial and temporal variation, and (ii) intrinsic spatial structure. Variation refers to the changing level of $\text{NO}_3\text{-N}$ within the soil matrix with respect to the continuums of space (spatial) and time (temporal). Intrinsic spatial structure refers to the dependency of $\text{NO}_3\text{-N}$ level on characteristic behavior of its variability in space (spatial dependency) within (intrinsic to) the soil matrix. We are aware that these working definitions of variation and spatial structure give rise to the paradoxical notion of 'ordered randomness' and subsequently fundamental questions such as: "Does soil $\text{NO}_3\text{-N}$ really have a spatial structure?" or "Is soil variation random?".

The answer to these two questions, we submit, is still debatable, and readers are referred to the recent papers by Heuvelink and Webster (2001), Webster (2000), and Baveye (2002) for eloquent discussion in that debate. What we do know is that the term 'spatial structure' is used as an attempt to describe spatial variability by hypothesizing that variation measured in the field has a structure. This hypothesis thus enables certain assumptions to be made in order to formulate mathematical descriptors that take account of the "double aspect of randomness and structure in such a way as to provide a simple representation of the spatial variability and lead to a consistent and operational approach to the solution of problems. One such formulation is the probabilistic interpretation as provided by random functions (Journel and Huijbregts, 1978, p29)". It is this formulation, based on the theory of regionalized variables (Matheron, 1965) which has led to the development of geostatistics as an addition to the capabilities offered by classical parametric statistics for assessing the variation and distribution of spatially dependent variables, such as soil $\text{NO}_3\text{-N}$.

Classical parametric statistics, although useful to a certain degree, are not fully adequate for assessing and quantifying spatially dependent variables because of their underlying assumptions of strict stationarity and ergodicity (Journel and Huijbregts, 1978; Isaaks and Srivastava, 1989; Cressie, 1991; Vieira et al., 1981; Trangmar et al., 1985; Hamlett et al., 1986; Cambardella et al., 1994; Jung et al., 2006; Webster and Oliver, 2001; Ruffo et al., 2005; and others). Geostatistical techniques, however, provide robust, resistant, and practically useful mathematical tools for assessing, modeling, and estimating the levels of spatially dependent variables in soils in-between sample locations, including $\text{NO}_3\text{-N}$ (Journel and Huijbregts, 1978; Burgess and

Webster, 1980; Webster and Burgess, 1984; Isaaks and Srivastava, 1989; Webster and McBratney, 1989; Cressie, 1991; Van Noordwijk and Wadman, 1992; McBratney and Pringle, 1997, 1999). This provision arises from the more general nature of the hypotheses of quasi-stationarity and intrinsity underlying the mathematical development of geostatistics (Journel and Huijbregts, 1978). Geostatistical tools include autocorrelograms, isarithmic maps, kriging, variograms (including semivariograms), average variograms, and proportional variograms among others. In this chapter, we will not delve into their derivation and formal mathematical description. Readers are referred to the cited authors for these details.

Research applying these tools on a field-scale, such as through SSCM-experimentation (Pringle et al., 2004) for example, has led to the development of a multitude of methods for determining minimum sample spacing, grid layouts and cell sizes (Vieira et al., 1981; Russo, 1984; Webster and Burgess, 1984; Han et al., 1994; Van Meirvenne, 2003; Lauzon et al., 2005), optimum number of samples (Webster and Burgess, 1984), sampling schemes and protocols for pre-planning experimental designs (Trangmar et al., 1985; Chang et al., 1999; Ruffo et al., 2005) and sample bulking (Webster and Burgess, 1984). However, when using these methods for implementing *precision agriculture* practices related to soil nitrogen management, the “most serious obstacles” are still the need to know the spatial structure in advance and the cost of obtaining this information even though the sampling effort required is much less than for full-scale sampling (Webster and Burgess, 1984; Lark, 1997; McBratney and Pringle, 1999; Jung et al., 2006).

A soil nitrate mapping system (SNMS) (Fig. 1) is a technology that can overcome these obstacles as it provides a quick, accurate and cost effective way to collect soil samples on a fine scale and analyze them for $\text{NO}_3\text{-N}$ content. The data it generates can be used for assessing the variation and spatial structure of soil $\text{NO}_3\text{-N}$ levels.

The SNMS consists of six sub-assemblies: 1) soil sampler sub-assembly, 2) soil metering and conveying sub-assembly, 3) nitrate extraction and measurement sub-assembly, 4) auto-calibration sub-assembly, 5) control sub-assembly, 6) GPS sub-assembly. The system automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyzes it electrochemically for nitrate concentration in real-time (6 s) using a nitrate ion-selective electrode (NO_3^- -ISE) as the analysis instrument. Additionally, global positioning system (GPS) geo-referenced data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field. The system can be used to analyze soil samples automatically while on-the-go, or manually while stationary by hand-placing samples into the nitrate extraction and measurement sub-assembly. It is envisioned that two configurations of the system will

eventually be used in practice – a tractor-mounted version (Fig. 1) and a ‘suitcase’ version (not shown). The SNMS currently has the ability to sample with (i) with lab-grade accuracy, (ii) at any desired spacing down to approximately one meter (very fine scale) when operated in manual mode, (iii) at the rate of approximately two samples per minute, and (iv) at approximately 1/10th the cost of conventional lab analysis.

From its beginnings as a first prototype (Adsett, 1990; Adsett and Zoerb, 1991), the SNMS has undergone several developmental iterations. The use of a NO₃⁻-ISE in this type of application has been extensively lab tested (Thottan et al., 1994; Thottan, 1995; Brothers et al., 1997). Development and preliminary field testing of the five initial sub-assemblies and their integration into one complete system followed (Thottan, 1995; Adsett et al., 1999). In 2001, a completely new electronics and control system that incorporated the GPS sub-assembly was added. A next step in the SNMS’ development was extensive field testing to confirm its usefulness for investigating the spatial and temporal aspects of soil NO₃-N, which is the work being reported in this chapter.

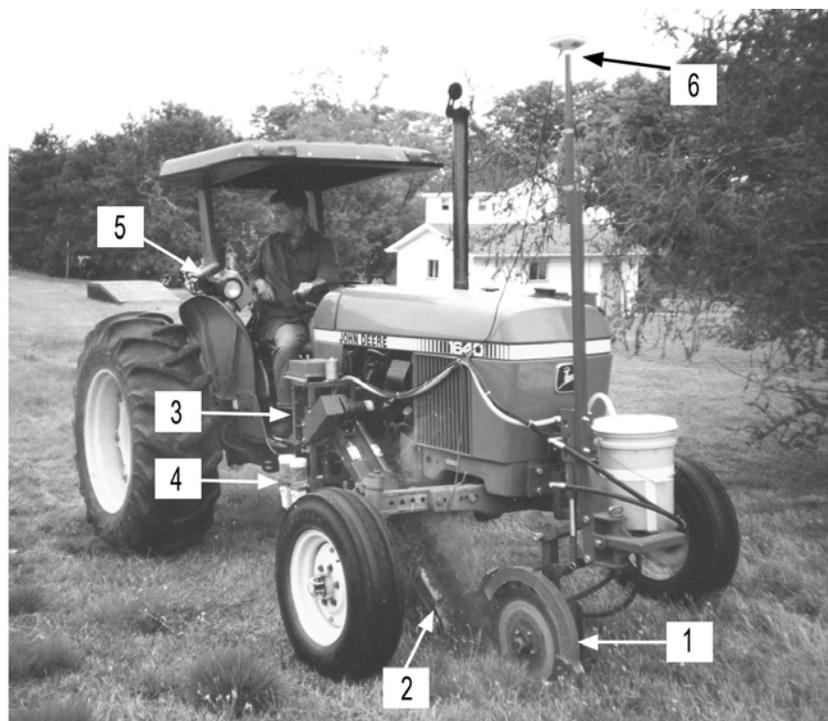


Fig. 1. Tractor-mounted soil nitrate mapping system with six sub-assemblies.

Objectives and scope

The primary objective of this study was to demonstrate that the SNMS could be used as an effective tool to assist soil scientists with experimental investigations of the spatial and temporal aspects of soil NO₃-N. Within that context, a multifaceted sub-experiment in a wheat production system having high economic importance to the Atlantic region of Canada in particular, and internationally in general was conducted with the objectives of using data collected with the SNMS (i) to assess the spatial and temporal variation of soil NO₃-N in the field at several time points covering pre-seeding, growing season, and post-harvest soil conditions and (ii) to assess the intrinsic spatial structure of soil NO₃-N present in the field.

Materials and methods

Field site

During the 2006 study period, a field experiment was established in a 0.32-ha section of field #207 on the Nova Scotia Agricultural College (NSAC) farm, Truro, Nova Scotia, Canada (45°22'N 63°16'W) concurrent with experiments being conducted by the Nova Scotia Water Quality Research Group (NSWQRG). These fields have been used by the NSWQRG since 1995 for many bio-environmental, cropping management, and water quality studies, and their soils characteristics and cropping histories are well documented (Webb and Langille, 1996; Elmi et al., 2005; Gordon et al., 2005).

Two soils groups were present in the field: Pugwash 52 (PGW52) and Debert 52 (DRT52). The PGW52 soil had a friable, fine sandy-loam textured Ap horizon 15- to 20-cm thick, underlain by a fine sandy-loam textured Bm horizon. Below the Bm horizon was a friable to firm, fine sandy-loam textured, platy structured, fragic BCxj horizon. It was classed as moderately well-drained. The DRT52 soil had a friable, sandy-loam textured Ap horizon 25- to 30-cm thick, underlain by a friable to firm sandy-loam textured Bmgj horizon. Below the Bmgj horizon were firm, poorly structured sandy-loam to loam textured subsoil horizons that included fragipan (BCxj, BCxjgi) and compact basil till (Cgj). It was classified as imperfectly drained. All descriptions of the soils are according to Webb and Langille (1996). The field had a systematic tile drainage system (100-mm diameter) installed at 0.8-m soil depth with 12 m between drains.

The field was conventionally tilled on 28 May, had liquid dairy manure (LDM) applied on 10 May at the rate of 80 kg ha⁻¹ available N and immediately disced to incorporate the manure, and seeded on 12 May with spring wheat (*Triticum aestivum* L.) at the rate of 140 kg ha⁻¹. Meteorological conditions at the site, including rainfall, air temperature (2-m height), and soil temperature (10-cm depth), were recorded

hourly using an automated weather station and a Campbell Scientific (Edmonton, Canada) CR10 datalogger at the edge of the field (data not shown). Rainfall over the study period created field moisture conditions that were described seasonally as a very wet Spring, a relatively dry Summer, followed by a wet Fall. The temperature trend resulted in creating environmental temperature conditions that were described seasonally as a cool Spring, relatively warm Summer, followed by a cool early Fall and a late-Fall warm period (typical of geographic location).

Survey-grade surface elevation data for the field was provided by the NSWQRG. These data were mapped as shown in Fig. 2. The field was generally flat, with some slight sloping evident in its N-E and S-W quadrants. There was a collection of slightly depressed spots in the North-middle area of the field (locations 11113, 11112, 11107, and 10302) that formed a visually noticeable shallow ‘bowl’, and in the middle-South area of the field (locations 10301, 11106, 10304, 11109, 11105, and 33) that formed a visually noticeable shallow ‘swale’ in the field.

The LDM was applied to the field with a liquid manure tanker-spreader using the switch-back spreading pattern method at approximately 6 m center-to-center intervals. The direction of the pattern was diagonal to the field as shown in Fig. 2.

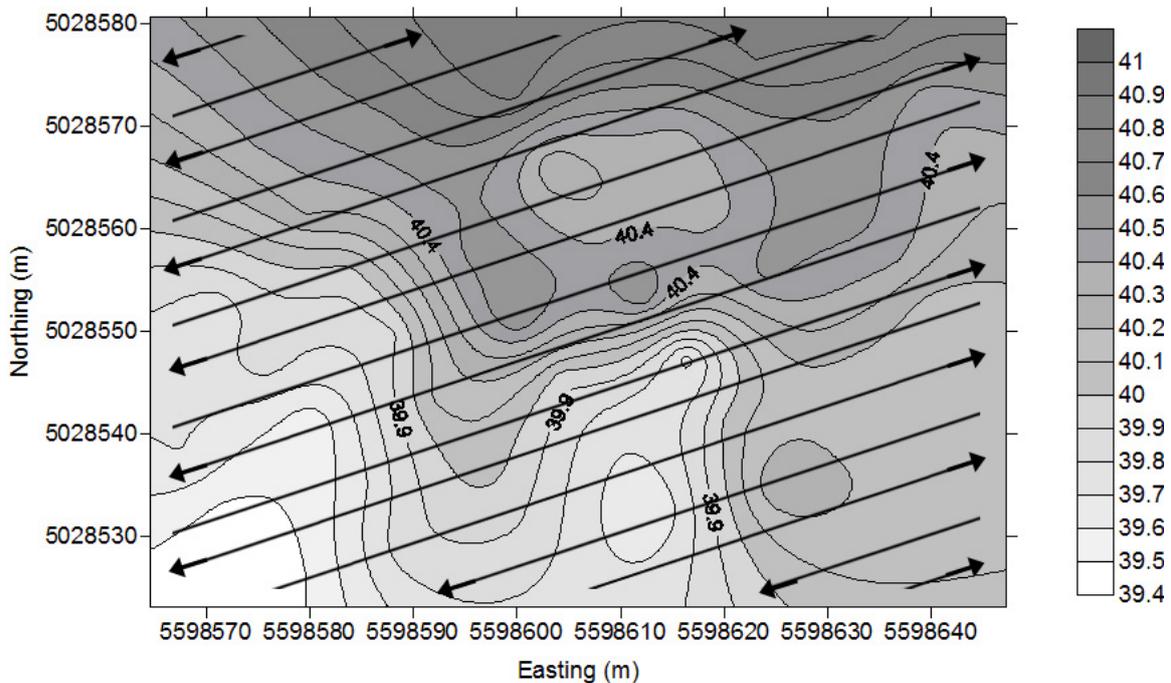


Fig. 2. Surface elevation contour map of the field, with liquid dairy manure spreading pattern overlay.

Soil sampling and analyses

Soil samples were collected using a 6.5- by 7.0-m grid layout to provide soil NO₃-N data for the 0–15-cm soil depth at 46 locations. The grid was laid out manually directly above the tile drains which provided for spatially-located sampling at points along each drain tile, and at mid-drain tile spacing. The Easting and Northing coordinates for each sampling location were recorded with the GPS unit, and staked to enable repeated sampling. This configuration enabled data collection for this study simultaneously with two other related studies investigating the relationships between soil NO₃-N and drain water quality, and investigating plant and soil nitrate responses in wheat and carrot production system, respectively, not being reported here.

Soil samples were collected: (i) pre-seeding just prior to planting/fertilizing (3 May), (ii) approximately three weeks after fertilizing (30 May), (iii) during crop growth (18 July, 1 Aug., 15 Aug.), (iv) at crop harvest (24 Aug.), and (iv) post-harvest (7 Nov.). To prevent damage to the crops, samples during the growing season were collected manually by coring with a standard 19-mm diameter soil-sampling tool to a depth of 15 cm (4 cores at each location bulked). All samples were collected within a 0.3 m radius of the sampling location. All manually collected samples were kept in Styrofoam coolers while in the field, and were immediately transported to the lab where they were kept under refrigerated storage (4°C) or frozen (-16°C) until processing could be completed.

Moist sub-samples were manually weighed out (15.1 g) and placed in the SNMS' nitrate extraction and measurement sub-assembly for analysis. An Orion 9707 ionplus ISE (Thermo Electron Corp., USA) was used to measure NO₃⁻ concentration. A total of 322 soil samples were analyzed by the SNMS during this study. Details of calibration procedures and functional operation of the SNMS are well documented elsewhere (Thottan et al., 1994; Thottan, 1995; Brothers et al., 1997; Adsett et al., 1999).

Spatial and temporal variation analyses

The spatial and temporal variation of the soil NO₃-N in the field was determined using a combination of classical descriptive statistics and isarithmic (contour) mapping analyses that quantified and graphically described the changing NO₃-N levels and distributions throughout the study period. These analyses were performed using Minitab (Minitab Inc., Pennsylvania, USA; Ver. 15.0), Excel (Microsoft Corp., California, USA.; Ver. Prof. Ed. 2003), and Surfer (Golden Software Inc., Colorado, USA; Ver. 8.03) software.

Classical descriptive statistics analyses

The following classical descriptive statistics relevant to spatial and temporal variation assessment (Isaaks and Srivastava, 1989) were computed and analyzed: Mean, Median, Variance, Standard Deviation, Skewness, Kurtosis, Minimum, Maximum, Interquartile Range, and Coefficient of Variation (CV). The distribution characteristics of the data sets were computed (Parkin and Robinson, 1992) and tested for goodness-of-fit based on a combined analysis of the data by probability plot and test statistic (D'Agostino et al., 1990) using the Anderson-Darling test in Minitab at the 0.05 level of significance. Potential outliers were identified on the probability plots, checked for data processing errors, and investigated for possible sources of sampling error. All potential outliers were determined to be good quality data (i.e. no errors) so they were left in the data sets for later evaluation as extreme values points during geostatistical analyses (described below).

Use of classical descriptive statistics for initially assessing the data and their presentation in this chapter was also made in accordance with the recommendations of Webster (2001). An initial assessment of degree of correlation between soil NO₃-N levels on each date and with field surface elevation was determined using Pearson's correlation analysis.

Isarithmic mapping analysis

Posted values isarithmic (contour) maps of the data sets (Rossi et al., 1992) were created using the default linear variogram model (Slope = 1, Aniso = 1, 0) in Surfer. Because of the fine-scale grid sampling scheme used in the study, these default settings were selected to create high resolution 'as found' maps of soil NO₃-N levels in the field.

Spatial structure analyses

The spatial structure of soil NO₃-N variation present in the field was assessed using a combination of geostatistical analysis techniques and tools. These analyses were performed using GS+ (Gamma Design Software Inc., Plainwell, MI; Ver. 5.1.1) software in addition to Minitab and Surfer software (as cited above).

Proportional effect analysis

The potential presence of a 'proportional effect' was investigated by conducting regression analyses between the data sets mean and standard deviation values (Isaaks and Srivastava, 1989; Rossi et al., 1992) and the squared mean and variance values (McBratney and Pringle, 1999).

Exploratory variograms analysis

All data sets determined during the classical descriptive statistics analysis to be log-normal distributed were \log_n -transformed to stabilize variance and minimize the effects of extreme values (Cambardella et al., 1994) and to create conditions of normality (Tabor et al., 1985). Back-transformed values of mean, standard deviation and variance were computed in GS+ using the Uniformly Minimum Variance Unbiased Estimators (UMVUE) weighted method of Krige (1981).

Exploratory variograms were created and the variance cloud plots for each lag distance were analyzed to identify extreme-value outliers. After careful investigation as to their possible cause and potential effect on data integrity for modeling the intrinsic spatial structure present, extreme values were removed, if justified, to clean the data sets (Rossi et al., 1992). Directional dependency (anisotropy) or directional independency (isotropy) was determined by analyzing directional anisotropic variogram plots ($0^\circ, 45^\circ, 90^\circ, 135^\circ @ 22.5^\circ$ tolerance) and 3D anisotropic surface plots.

Spatial autocorrelation analysis

Initial assessment of spatial structure was conducted using a spatial autocorrelation analysis based on Moran's I statistic. Autocorrelograms were computed using the cleaned data sets. Moran's I varied between +1 and -1 depending on whether the correlation between data values was positive or negative, respectively. Significant spatial autocorrelation was determined to be evident when the absolute value of Moran's I was >0.3 (Snedecor and Cochran, 1989; Lauzon et al., 2005; Jung et al., 2006).

Final variograms analysis and modeling

Final variograms and spatial structure models were created adhering to the following constraints for achieving a valid model: Maximum lag class distance equal to one-half the maximum separation distance to remove edge effects of lags comparing only edge points in the sampling region (Rossi et al., 1992); Minimum of 30 pairs per lag to ensure adequate statistical reliability in each lag class, with a greater number of pairs equaling greater statistical reliability (Journel and Huijbregts, 1978).

Spatial structure models of the spherical, exponential, linear, linear-to-sill, and Gaussian types were evaluated. The best-fit model was selected as the cross-validated model having the highest R^2 in combination with the lowest RSS (Isaaks and Srivastava, 1989; Webster and McBratney, 1989; Cambardella et al., 1994). Because the final variograms were created from both raw and \log_n -transformed data sets, they were scaled by dividing their semivariance by their sample variance to enable direct comparison of the selected models (Rossi et al., 1992).

Spatial dependency ratings were made on the basis of the nugget to sill ratio (N:S) after the work of Cambardella et al. (1994): Strong (S) for $N:S \leq 0.25$, Moderate (M) for $0.25 < N:S \leq 0.75$, and Weak (W) for $N:S > 0.75$.

Average variogram analysis

Averaging variogram models has been done by others using various techniques from simple arithmetic averaging of the models' semivariance values present at each lag-class (McBratney and Pringle, 1997) to fourth-root transformation prior to averaging (Cressie, 1991; McBratney and Pringle, 1999), depending on whether the data sets were normal or non-normal, respectively. Since we had created scaled spherical models from normalized data sets that were directly comparable, we took advantage of the additive properties related to the linearity of the geostatistical operators underlying the mathematical derivation of variogram models as representations of nested structures to simply arithmetically average the selected models' parameters to determine the parameters for an average model. For details of these underlying concepts and mathematics, readers are referred to Journel and Huijbregts (1978), Section III, Structural Analysis.

Results and discussion

Spatial and temporal variation

Classical descriptive statistics

The classical descriptive statistics computed for the soil $\text{NO}_3\text{-N}$ raw data sets for each sampling date are shown in Table 1. The means for each sampling date varied between 4.38 mg kg^{-1} just prior to field activity (3 May) and 28.80 mg kg^{-1} (30 May) one day before peak $\text{NO}_3\text{-N}$ availability (data not shown).

The general trend of mean $\text{NO}_3\text{-N}$ change over the study period was 'residual' level at pre-seeding time (3 May), which rose to a peak approximately three weeks after manure application (30 May), and then dropped over the active growth of the wheat until grain harvest (24 Aug.), followed by a modest post-harvest increase (7 Nov.). Lockman and Storer (1990) reported a similar trend during a study of soil nitrate and ammonium changes with area and date sampled for 134 field sites in the mid-West USA and Central Canada. Villar-Mir et al. (2002) reported the same trend for soil $\text{NO}_3\text{-N}$ in irrigated cornfields in Northeast Spain.

The CVs (Table 1) ranged between a low of 24.1% (24 Aug.) and a high of 71.2% (7 Nov.), indicating large variation in $\text{NO}_3\text{-N}$ level throughout the study period both spatially and temporally. Similar levels of variation have been reported by Bundy

Table 1. Descriptive statistics of soil NO₃-N raw data sets for each sampling date in 2006.

Statistic/Date	3 May	30 May	18 July	1 Aug.	15 Aug.	24 Aug.	7 Nov.
Mean (mg kg ⁻¹)	4.38	28.80	8.77	5.93	5.37	4.90	7.99
Median	4.49	23.20	7.64	5.02	4.89	5.07	5.51
Variance	1.64	277.86	21.58	14.46	6.80	1.39	32.32
Standard deviation	1.28	16.67	4.64	3.80	2.61	1.18	5.69
Skewness	0.22	1.77	2.69	2.88	0.96	0.05	1.72
Kurtosis	1.65	3.59	9.84	9.96	0.17	-0.88	2.41
Minimum	1.49	8.09	3.58	2.52	1.88	2.84	3.02
Maximum	8.56	90.77	30.07	23.13	12.27	7.22	27.60
Interquartile range	1.51	17.65	3.93	2.18	3.59	1.82	4.63
Coefficient of variation (%)	29.2	57.9	53.0	64.2	48.6	24.1	71.2
Distribution [†]	Normal	Log-Normal	Log-Normal	Log-Normal	Log-Normal	Normal	Log-Normal
<i>n</i>	46	46	45	46	45	46	46

[†]Based on Anderson-Darling test statistic ($\alpha = 0.05$) in Minitab.

and Meisinger (1994) who found a range of the CVs in winter wheat between 30–85%, with an average of 45%. These variations will be discussed in more detail in the isarithmic mapping section of the chapter below, where the spatial relatedness in levels is shown in the maps presented.

The distributions of the data sets were found to be normal for 3 May and 24 Aug., while all other dates were log-normal (Fig. 3). A few potential outliers on several of the dates were identified in the histogram plots and probability plots (probability plots not shown in the interests of brevity). These were checked for data processing errors and investigated for possible sources of sampling error. All points were found to be of good quality (i.e. no errors) so they were left in the data sets for evaluation as extreme values during geostatistical variance cloud plots analysis as discussed below.

Overall, correlation of NO₃-N level with surface elevation (Table 2) was not found except for the 18 July and 24 Aug. sampling dates. This result indicates that globally over the field NO₃-N level was not generally influenced by surface elevation except on those two dates. This result is not surprising since the field is generally flat, with only slight sloping and depressed areas as described above. Detailed assessments of the correlation on these dates, along with other location aspects of the variation of the NO₃-N level spatially and temporally over the field, and are discussed below in the

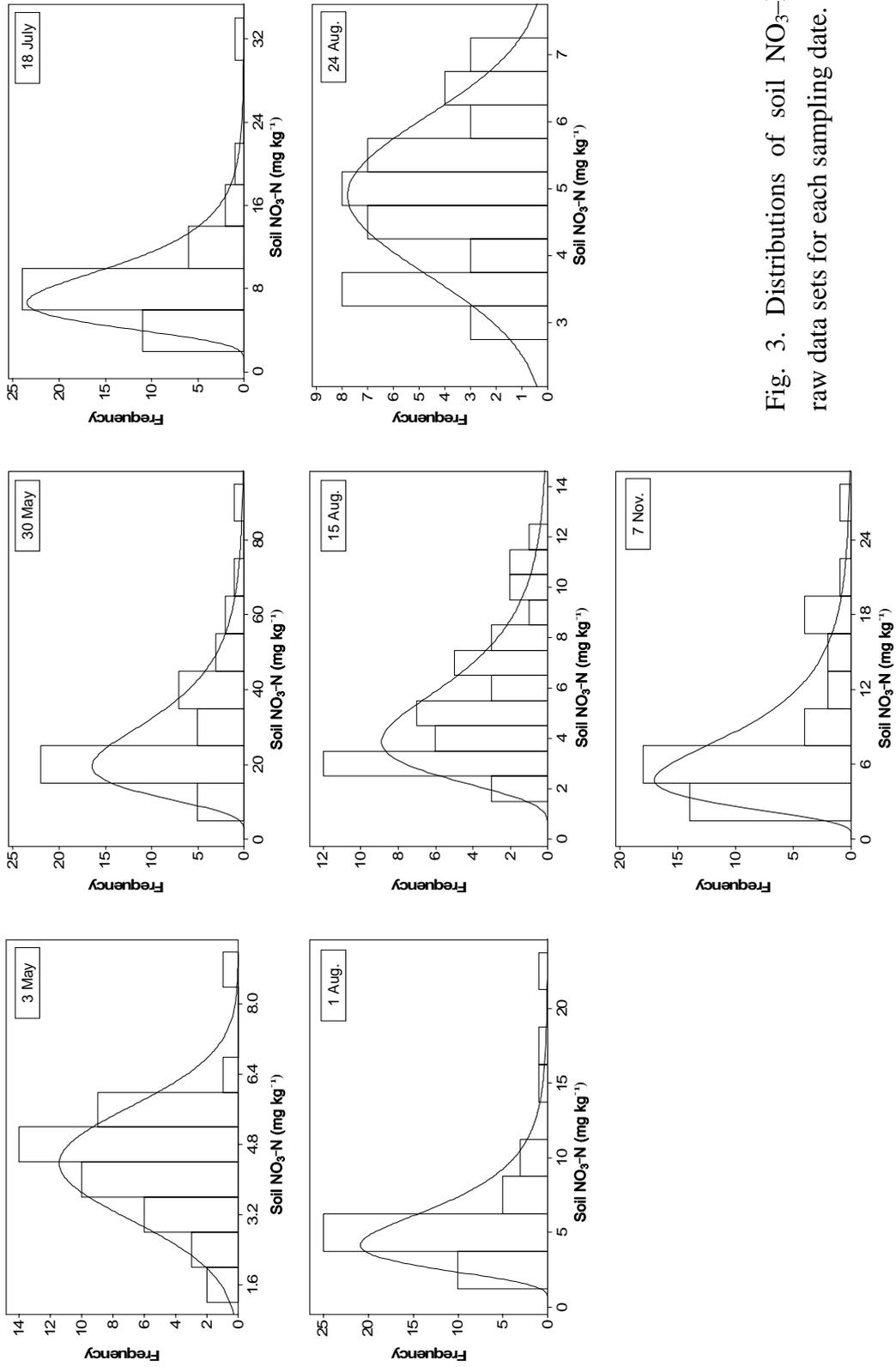


Fig. 3. Distributions of soil NO₃-N raw data sets for each sampling date.

Table 2. Pearson correlation[†] levels (r) between field surface elevation and soil NO₃-N values for each sampling date in 2006.

	Elevation	3 May	30 May [‡]	18 July [‡]	1 Aug. [‡]	15 Aug. [‡]	24 Aug.	7 Nov [‡]
Elevation		0.010	0.009	0.565**	0.223	0.286	0.499**	-0.122
3 May	0.079		0.282	-0.13	-0.111	-0.106	0.033	0.402**
30 May [‡]	0.039	0.233		-0.163	-0.027	0.065	0.098	0.120
18 Jul. [‡]	0.548**	-0.054	-0.111		0.281	0.421**	0.623**	-0.038
1 Aug. [‡]	0.187	0.271	0.009	0.309*		0.436**	0.466**	0.136
15 Aug. [‡]	0.257	-0.094	0.053	0.421**	0.290		0.642**	0.195
24 Aug.	0.488**	0.130	0.064	0.564**	0.442**	0.544**		0.218
7 Nov [‡]	-0.148	0.313*	0.291*	-0.087	0.124	0.178	0.316*	

[†] Values in lower-left half are for the raw data sets ($n = 45$ or 46), while values in upper-right half are for the cleaned data sets ($42 \leq n \leq 45$).

[‡] Data set \log_n -transformed.

* Significant at the 0.05 level. ** Significant at the 0.01 level.

isarithmic mapping section where details of the dispersion of NO₃-N levels can be visually seen.

The correlation results between NO₃-N values on the various sampling dates (Table 2) were inconsistent. Although several moderate positive and significant correlations were evident, these were not consistent between any one date and any one subsequent date or consecutive subsequent dates. This result indicates a lack of ability to use the mean value on any one date to predict the mean value on any other date consistently or reliably.

Isarithmic mapping

Posted values isarithmic (contour) maps of the data sets are shown in Figs. 4 through 10, and are discussed in detail below. The discussion will proceed with a general observation of what levels were found on each sampling date, relative to any pertinent field condition, management activity, or time in the study period. Then a detailed analysis of the spatial variation throughout the field, including a discussion of 'hot' and 'cold' spots evident will be given. In the context of the discussion, we have defined a 'hot spot' as a NO₃-N value that was greater than one standard deviation higher than the mean, appearing as a darker colored spot (usually encircled by a contour line) on the map. A 'cold spot' was defined as a NO₃-N value that was lesser than one standard deviation lower than the mean, appearing as a lighter colored spot (also usually encircled by a contour line) on the map.

Readers should also note that because of the fine-scale sampling grid used in the study, the maps have high resolution. Thus, very small variations in NO₃-N level are shown, akin to microscopically zooming in on the area, and some spots may appear as ‘hot spots’ or ‘cold spots’ visually, but are not called either because they are within \pm one standard deviation of the mean. The scales used to generate the maps for display purposes in this chapter were chosen to show maximum detail, without overcrowding the map with contour lines. All maps except for 30 May have a scale ranging from 0 to 32 mg kg⁻¹ in 1 mg kg⁻¹ increments to enable a reader’s direct comparison visually by color changes. The scale for 30 May ranges from 0 to 100 mg kg⁻¹ in 5 mg kg⁻¹ increments because of the high values compared to the other sampling dates. If this larger scale was used for the other dates too, their maps would have appeared as mostly white without much variation detail showing.

The contour map for 3 May (Fig. 4) corresponds to pre-seeding conditions. An even distribution of low residual levels of NO₃-N having relatively low variation was found (mean = 4.39 mg kg⁻¹, CV = 29.2%). This overall low level of NO₃-N is good from an environmental perspective as it indicates a low potential for leaching contamination of groundwater during winter and early spring when considered in comparison to similar low levels found in random samples taken as a base-line check the prior December (data not shown).

Two ‘hot spots’ were evident at locations 10305 (6.05 mg kg⁻¹) and 10307 (8.56 mg kg⁻¹). The 8.56 mg kg⁻¹ value also showed up as an outlier on the histogram and probability plots, so it was considered an unusual value. Four ‘cold spots’ were evident at locations 10206 (2.91 mg kg⁻¹), 10310 (1.49 mg kg⁻¹), 10308 (1.74 mg kg⁻¹), and 10313 (2.56 mg kg⁻¹). Some of these ‘hot’ and ‘cold’ spots corresponded to ‘low’ and ‘high’ spots in the field as seen in Fig. 2, but not consistently ‘hot’ with ‘low’ or ‘cold’ with ‘high’, or vice-versa.

The contour map for 30 May (Fig. 5) corresponds to 23 days after the LDM was applied to the field. May 30 was also one day before peak levels of NO₃-N were reached in the field (data not shown). High levels of NO₃-N overall, along with high variation, were evident on this date (mean = 28.80 mg kg⁻¹, CV = 57.9%). The increase in NO₃-N level was most likely due to mineralization of organic matter from the application of the LDM fertilizer to the field. It is highly likely there was high soil microbial activity during this time resulting from a combination of increasing Spring-time soil temperatures, and soil aeration and structure changes from tillage of the field.

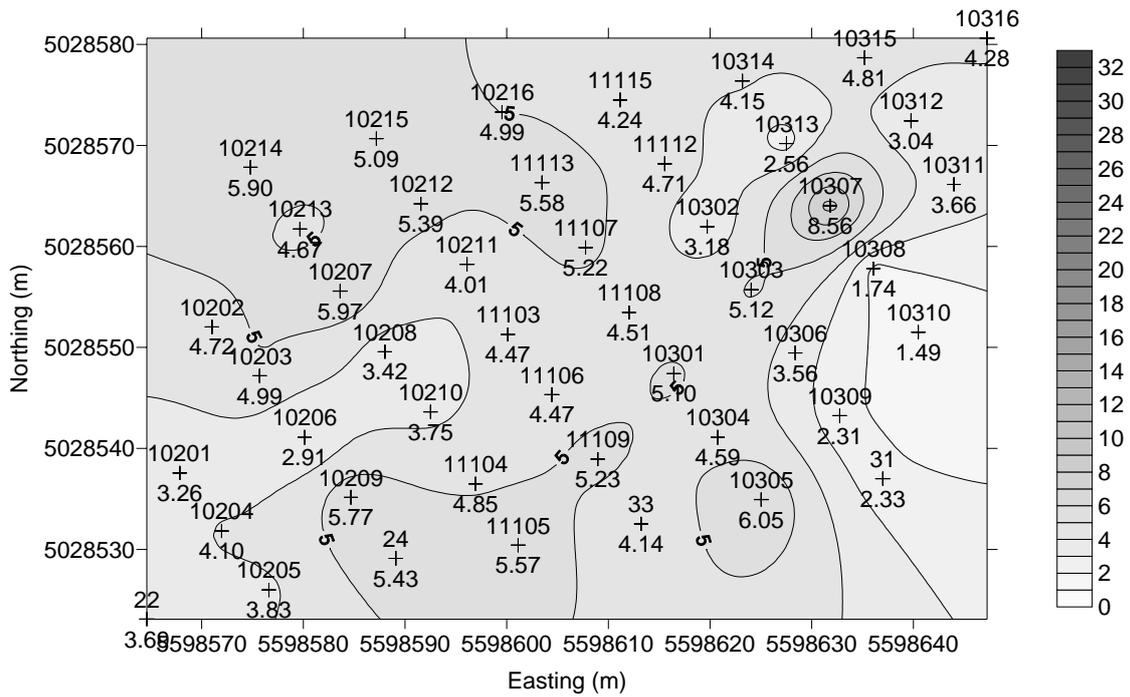


Fig. 4. Soil NO₃-N levels on 3 May 2006. Numbers above the posts are sample location codes. Numbers below the posts are NO₃-N level (mg kg⁻¹).

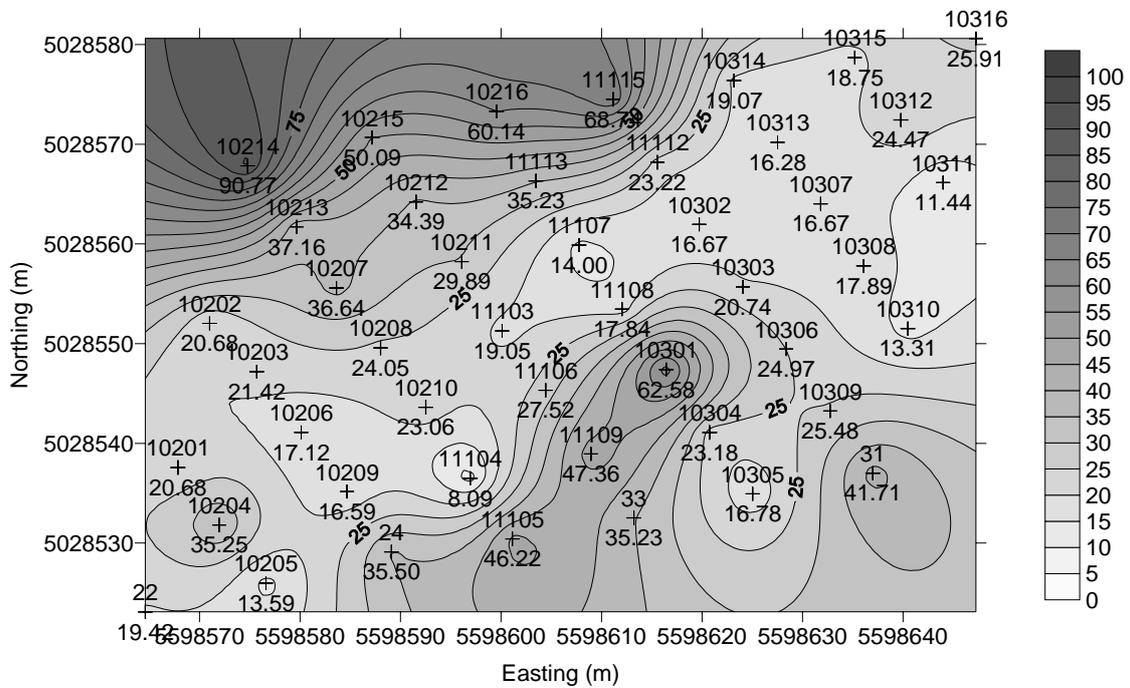


Fig. 5. Soil NO₃-N levels on 30 May 2006. Numbers above the posts are sample location codes. Numbers below the posts are NO₃-N level (mg kg⁻¹).

The high variation in levels of $\text{NO}_3\text{-N}$ spatially throughout the field was likely due to a combination of LDM spreading pattern irregularities and $\text{NO}_3\text{-N}$ transport with water movement, either laterally or vertically in the soil profile, from several rainfall events occurring prior to 30 May. Some evidence of lateral transport was apparent given the fact that ‘hot spots’ and ‘cold spots’ on this date (and subsequent dates), as discussed below, corresponded with low elevation and high elevation areas in the field, respectively. An investigation into the hydrology of the soil profile to confirm lateral transport, however, was beyond the scope of this study.

The N-W quadrant of the field had an area of very high $\text{NO}_3\text{-N}$ levels running more or less diagonally across the field, with values ranging between 50.09–90.77 mg kg^{-1} . It is suspected that these high levels were caused by excessive manure application in this area, as the spreader operator was observed making sweeping turns there during application to the adjoining field area. An overlay view of the spreading pattern onto the field as shown in Fig. 2 confirms the directional aspects of this high levels area.

There was also a ‘ridge’ of high spots evident in the South-middle area of the field formed by locations 10301 (62.58 mg kg^{-1}), 11109 (47.36 mg kg^{-1}), and 11105 (46.22 mg kg^{-1}). These spots ran along the bottom of a shallow swale in the field, as seen in the surface elevation contour map for the field (Fig. 2). Several of these ‘hot spots’ also showed up as outliers on the histogram and probability plot. ‘Cold’ spots were found at locations 10311 (11.44 mg kg^{-1}), and 11104 (8.09 mg kg^{-1}). These spots corresponded to high elevation areas in the field, although location 10311 was in an area of a slight down-slope.

The contour map for 18 July (Fig. 6) shows relatively low $\text{NO}_3\text{-N}$ levels overall that had high variation (mean = 8.77 mg kg^{-1} , CV = 53.0%). The significant decline in $\text{NO}_3\text{-N}$ levels between 30 May and 18 July was likely due to a combination of early growth crop uptake of $\text{NO}_3\text{-N}$ and leaching from several heavy rainfall events that occurred during that period.

Three ‘hot spots’ were evident at locations 11115 (15.48 mg kg^{-1}), 10302 (30.07 mg kg^{-1}), and 10311 (20.69 mg kg^{-1}) in the N-E quadrant of the field. These ‘hot spots’ also showed up as outliers on the histogram and probability plot and strikingly corresponded to lower elevation spots in the field. One ‘cold spot’ was evident at location 10201 (3.58 mg kg^{-1}) which corresponded to a high elevation spot in the field. The ‘M’ at location 11113 signifies a missing value due to a lost sample at that location.

The contour map for 1 Aug. (Fig. 7) shows low $\text{NO}_3\text{-N}$ levels overall that had high variation (mean = 5.92 mg kg^{-1} , CV = 64.2%). The continued decline in $\text{NO}_3\text{-N}$ levels between 18 July and 1 Aug was likely due only to crop utilization, as rainfall during that period was substantially lower.

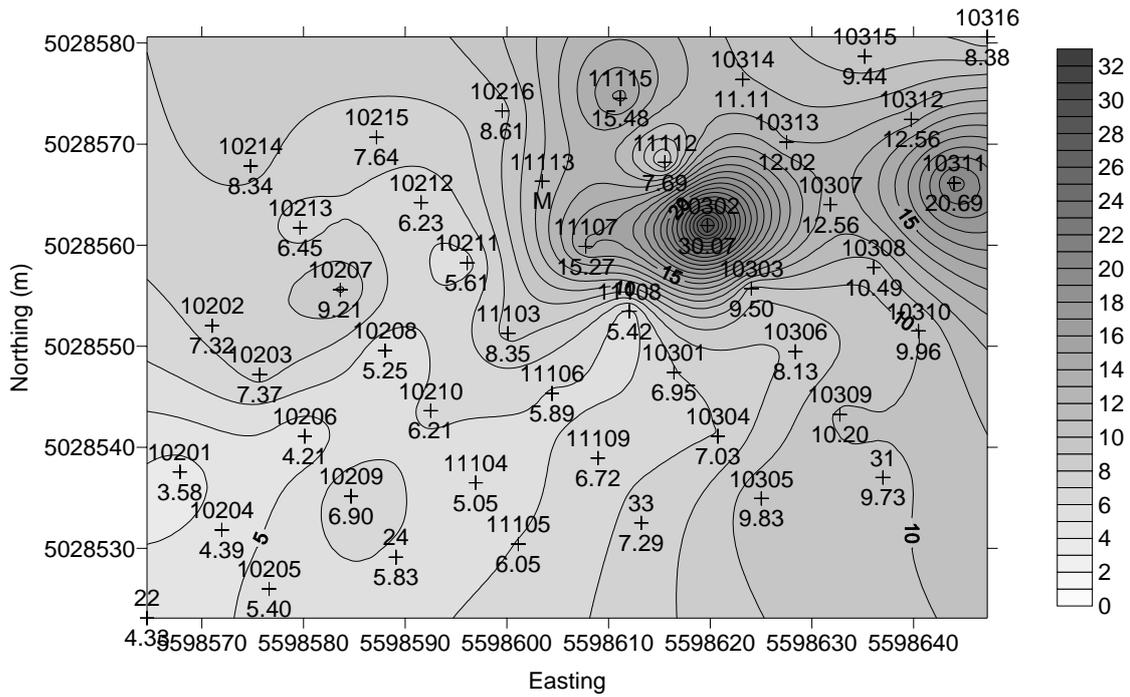


Fig. 6. Soil NO₃-N levels on 18 July 2006. Numbers above the posts are sample location codes. Numbers below the posts are NO₃-N level (mg kg⁻¹).

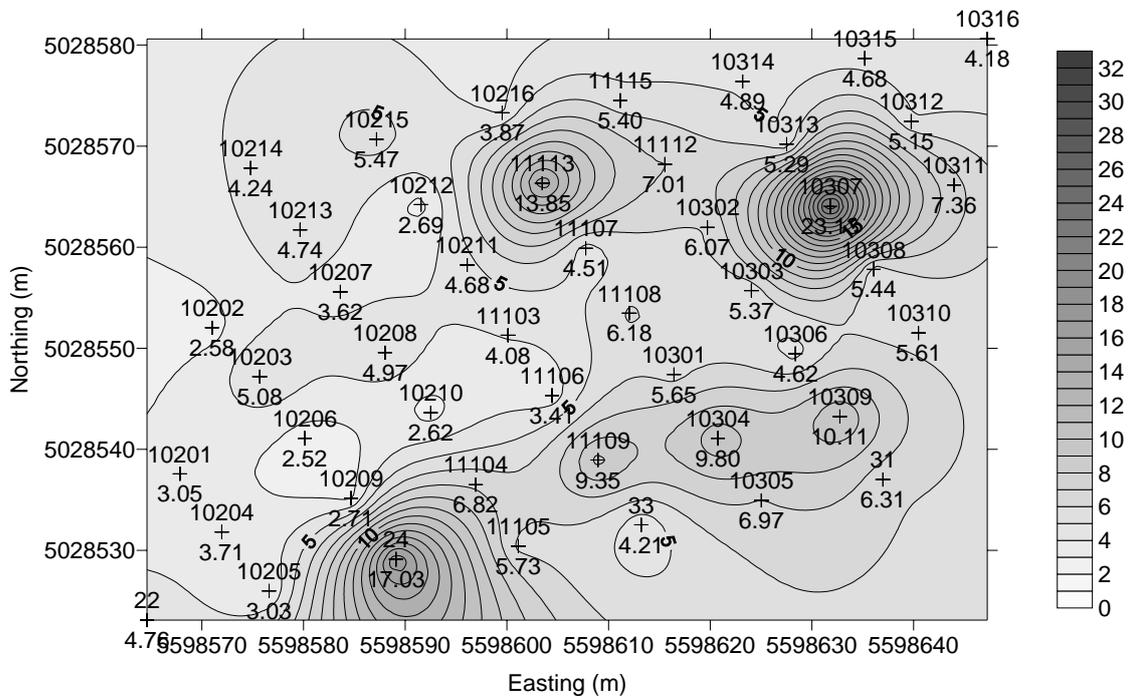


Fig. 7. Soil NO₃-N levels on 1 Aug. 2006. Numbers above the posts are sample location codes. Numbers below the posts are NO₃-N level (mg kg⁻¹).

Three ‘hot spots’ were evident at locations 11113 (13.85 mg kg⁻¹) and 10307 (23.13 mg kg⁻¹) in the upper-right quadrant, and another one at location 24 (17.03 mg kg⁻¹) in the lower-left quadrant. These ‘hot spots’ also showed up as outliers on the histogram and probability plot. Locations 11113 and 24 again matched a lower spots; however location 10307 was at a higher elevation spot.

There was also a ‘three-peak ridge’ of slightly elevated NO₃-N levels running diagonally across the S-E quadrant through locations 10309 (10.11 mg kg⁻¹), 10304 (9.80 mg kg⁻¹), and 11109 (9.35 mg kg⁻¹) that corresponded with a slight ‘valley’ (run of lower elevations) in the same vicinity. However, these values were not larger than one standard deviation higher than the mean, so were not considered ‘hot spots’. There were some low NO₃-N values at locations 10206 (2.52 mg kg⁻¹), 10210 (2.62 mg kg⁻¹), 10212 (2.69 mg kg⁻¹), and 10202 (2.58 mg kg⁻¹) that corresponded to higher elevation areas, but they were not lesser than one standard deviation lower than the mean, so were not considered ‘cold spots’.

The contour map for 15 Aug. (Fig. 8) had low NO₃-N levels overall that had quite a bit of variation (mean = 5.37 mg kg⁻¹, CV = 48.6%). The NO₃-N levels between 1 Aug. and 15 Aug. declined slightly, again likely due only to crop utilization, as rainfall during that period was minimal, except for a total of 19.3 mm on 21 July and 22 July.

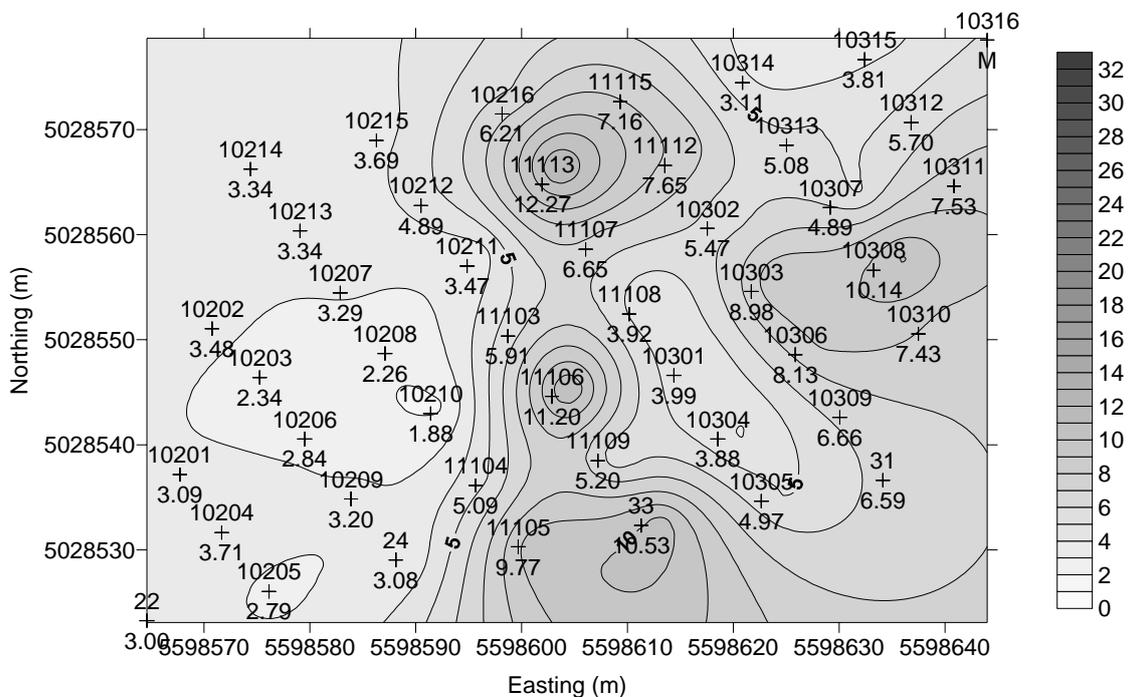


Fig. 8. Soil NO₃-N levels on 15 Aug. 2006. Numbers above the posts are sample location codes. Numbers below the posts are NO₃-N level (mg kg⁻¹).

Three 'hot spots' were evident at locations 11113 (12.27 mg kg⁻¹), 11106 (11.20 mg kg⁻¹), and 33 (10.53 mg kg⁻¹) that formed a three-peak ridge of elevated NO₃-N levels running North-South through the middle of the field. Location 11105 (9.77 mg kg⁻¹) adjacent to location 33 was also a hot spot. These 'hotspots' also strikingly corresponded to low elevation spots in the field. Additional 'hot spots' were evident at locations 10303 (8.98 mg kg⁻¹), 10306 (8.13 mg kg⁻¹) and 10308 (10.14 mg kg⁻¹) in the N-E quadrant of the field. These were located in the down-slope area at that edge of the study area. Several of the 'hot spots' also showed up as outliers on the histogram and probability plot. The 'M' at location 10316 signifies a missing value due to a lost sample at that location.

The contour map for 24 Aug. (Fig. 9) corresponds to the day the wheat was harvested. An even distribution of low levels of NO₃-N having relatively low variation was evident on that date that was strikingly similar to pre-seeding levels as shown in the 3 May contour map. These two dates have normal distributions with nearly equal means and CVs (3 May: 4.38 mg kg⁻¹, 29.2%; 24 Aug.: 4.90 mg kg⁻¹, 24.1%). The NO₃-N levels between 15 Aug. and 24 Aug. declined slightly, again likely due only to crop utilization, as rainfall during that period was virtually nil except for one event on 21 Aug. (13.2 mm).

'Hot spots' at locations 10215 (6.74 mg kg⁻¹), 10314 (6.48 mg kg⁻¹), 10312 (6.25 mg kg⁻¹), 10316 (6.89 mg kg⁻¹), and 10305 (7.22 mg kg⁻¹) corresponded to higher elevation spots in the field. 'Hot spots' at locations 11113 (6.52 mg kg⁻¹), 11107 (6.86 mg kg⁻¹), 11112 (6.29 mg kg⁻¹) corresponded to a low elevation area in the field. A large 'cold spot area' was evident in the generally down-sloping area in the S-W portion of the field with levels ranging between 2.84–3.54 mg kg⁻¹.

The contour map for 7 Nov. (Fig. 10) corresponds to post-harvest conditions. The mean NO₃-N level for this date increased from the 24 Aug. date (from 4.90 to 8.00 mg kg⁻¹), as did the variation (from 24.1 to 71.2%). It is highly suspected that these increases were due to mineralization of remaining organic material from the initial LDM application, and fibrous root material and straw residue which have a relatively low C:N ratio. The field likely had a high mineralization capacity as suggested by the work of Havlin et al. (1990) who found higher mineralization capacity from applied organic fertilizer and increased organic-N level with increasing residue level under both tilled and no-tilled conditions in their study of several crops, crop rotations, and tillage effects on soil organic carbon and nitrogen. Post-harvest increases in soil NO₃-N between Sept.–Oct. were also found by Lockman and Storer (1990) in their study of soil nitrate and ammonium with area and date sampled. Heavy rains during the wet Fall may have leached out some of the newly available NO₃-N, otherwise the increase may have been larger.

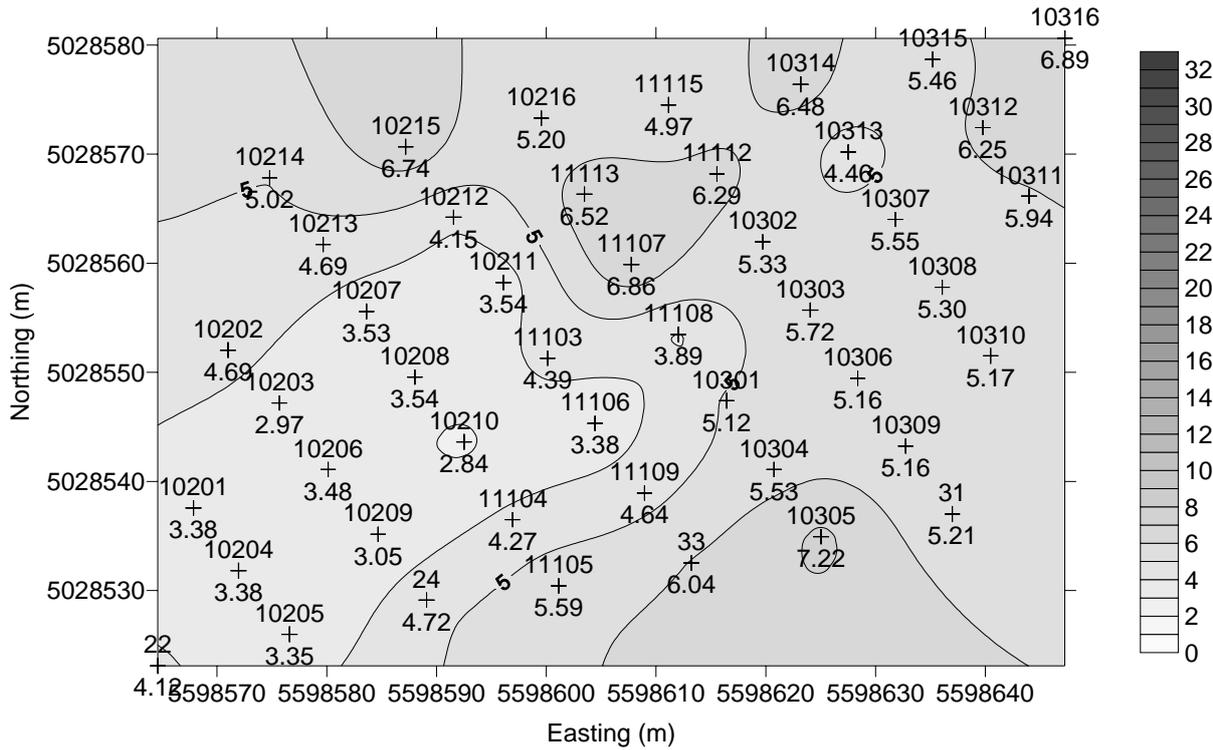


Fig. 9. Soil NO₃-N levels on 24 Aug. 2006. Numbers above the posts are sample location codes. Numbers below the posts are NO₃-N level (mg kg⁻¹).

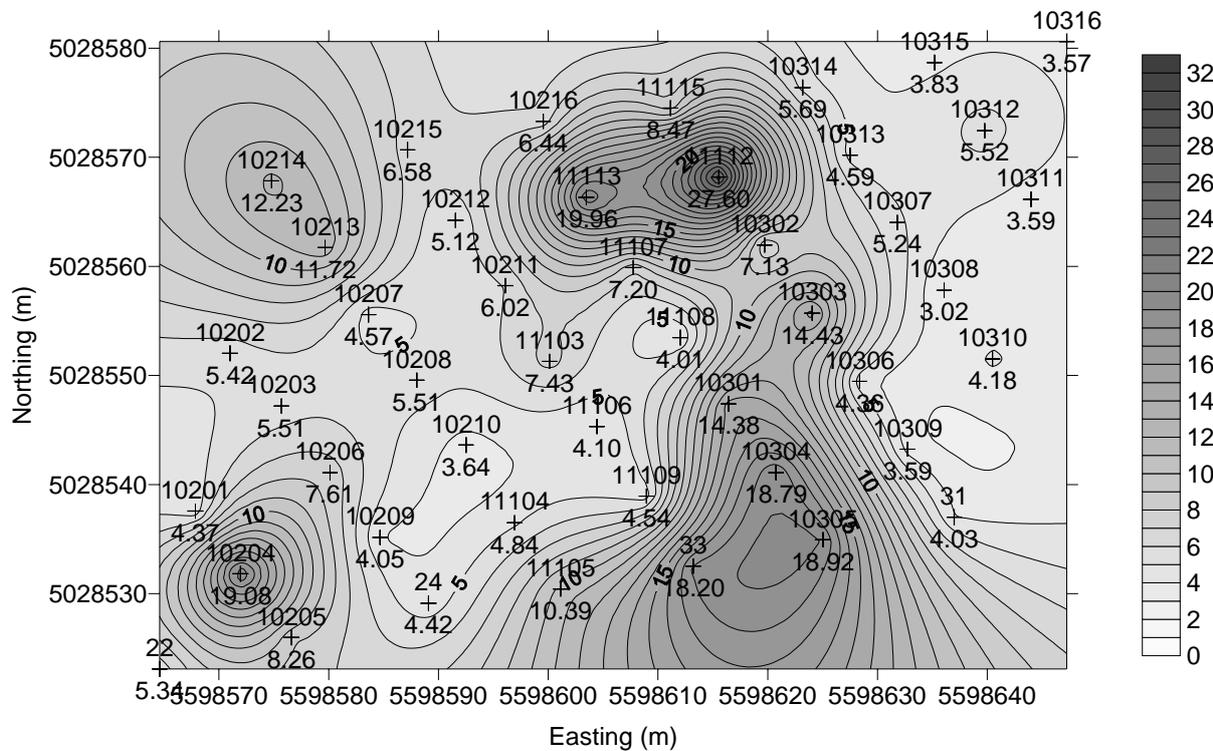


Fig. 10. Soil NO₃-N levels on 7 Nov. 2006. Numbers above the posts are sample location codes. Numbers below the posts are NO₃-N level (mg kg⁻¹).

A high degree of ‘patchiness’ (many spatially distributed ‘hot spots’) was evident over the entire field likely from straw residue. It was noted during a walk-about of the field at the time that there was quite a bit of straw residue present. There were ‘hot spots’ at three locations: 11113 (29.96 mg kg⁻¹), and 11112 (27.60 mg kg⁻¹), and 10204 (19.08 mg kg⁻¹). As well, a ‘swale’ was evident being formed by five adjacent hot spots at locations 10303 (14.43 mg kg⁻¹), 10301 (14.38 mg kg⁻¹), 10304 (18.79 mg kg⁻¹), 10305 (18.92 mg kg⁻¹), and 33 (18.20 mg kg⁻¹) running through the S-E quadrant. Five of these ‘hot spots’ also showed up as outliers on the histogram and probability plot.

There were not any ‘cold spots’ evident, although there were several low NO₃-N levels at locations 10210 (3.64 mg kg⁻¹), 10209 (4.05 mg kg⁻¹), 10308 (3.02 mg kg⁻¹), and 11108 (4.01 mg kg⁻¹). These locations generally corresponded to higher elevation spots in the field.

Overall, the posted values contour maps give excellent visual pictures of the NO₃-N spatial variation that was evident just prior to, at peak nitrogen release, during, and just after the growing season. Clearly there were some extrinsic management factors effects present as indicated by the presence of ‘ridging’, ‘hot spots’ and the ‘swale’ as described above. As well, several locations of the ‘hot spots’ and the ‘swale’ were relatively consistent and strikingly corresponded to low areas in the field even though NO₃-N level, generally, did not correlate with elevation as discussed above.

Spatial structure

Proportional effect

A very strong linear proportional effect (Fig. 11) was found between the NO₃-N raw data sets mean and standard deviation values ($R^2 = 0.972$, $n = 7$), and the squared mean and variance values ($R^2 = 0.996$, $n = 7$). The potential leverage effect of the single large values on the regression fits, resulting from the high levels of NO₃-N on 30 May, was checked by performing an additional regression analysis using only the smaller values for the other dates. It was found that these values alone also had a high degree of linear proportional effect (means regression $R^2 = 0.818$, $n = 6$, squared means regression $R^2 = 0.767$, $n = 6$; regression plots not shown).

Isaaks and Srivastava (1989) have reported that a proportional effect is common and linear for log-normal data sets. The very high R^2 values found for the regression fits indicate the relationships are highly predictable. Therefore, they can be used for predicting high-quality average and proportional variograms, which in turn can be used for determining NO₃-N soil sampling schemes for the field to a desired level of accuracy following the methods of McBratney and Pringle (1999). But, average and

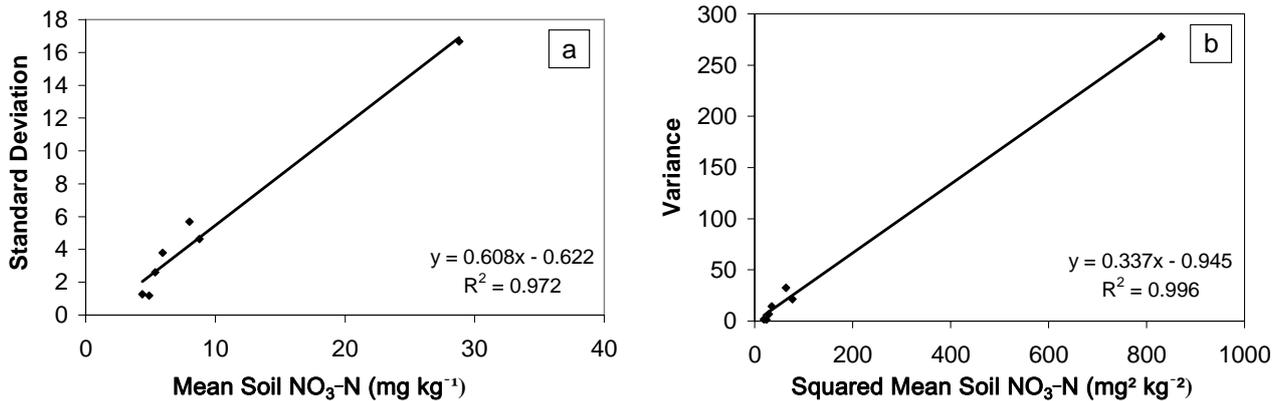


Fig. 11. Proportional effect in soil NO₃-N spatial variation. (a) Between raw data sets mean and standard deviation values. (b) Between raw data sets squared mean and variance values.

proportional variograms are not expected to be useful for kriging when creating isarithmic maps due to the 'fixed' nature of certain model parameters (McBratney and Pringle, 1999).

Exploratory variograms

Exploratory variograms created for each sampling date were analyzed for the presence and effects of extreme values. Unusually large (and even small) data points can greatly affect the intrinsic spatial structure modeled by a variogram. It is critical, therefore, to be aware of methods for their identification and to have an understanding of the circumstances in which their removal is valid (Rossi et al., 1992). Therefore, extrinsic factors (i.e. field management practices, excessive rainfall, etc.) which can mask the intrinsic spatial structure were considered to be valid circumstances for removing data points in order to clean the data sets.

Variance cloud plots for each lag distance were examined and several extreme values that were potentially problematic were identified. After careful consideration as to their possible cause and potential effect on data integrity, up to 3 of such data points, that were all large values, were removed to clean the data sets. A maximum of three data points were removed from any one data set in order to retain enough points to get the minimum 30 lag class pairs required for valid variogram modeling. This is a maximum of 6.5% (3 pts out of 46 = 6.5%) which is also very close to the accepted norm of up to 5% data point's removal for maintaining high statistical reliability. These extreme values were also the same outliers identified earlier when analyzing the histogram and probability plots for each data set and were the same 'hot spot' values showing up in the posted values contour maps, as discussed above. Results of the correlation analysis of the cleaned data sets (Table 2) did not substantially differ from

the results of the raw data sets correlation analysis and confirmed removal of these points did not negatively impact data set integrity.

From the analysis of directional dependency, it was found generally that there was some minor to moderate anisotropy present for all the dates. However, the anisotropic variogram models had relatively much larger range parameters, much lower R^2 values, and much higher RSS values (data not shown) compared to the isotropic variogram models. Therefore, it was concluded that isotropic variogram models described the data sets best.

Spatial autocorrelation

The results of the spatial autocorrelation analysis of the cleaned data sets (Fig. 12) revealed that $\text{NO}_3\text{-N}$ levels on all dates except 30 May exhibited significant positive autocorrelation at separation distances ≤ 20 m (encircled area A, Fig. 12). This result indicates that for accurately estimating values in un-sampled locations by kriging, sample spacing in this field should be limited to no more than 20 m. It is suspected that the lack of significant autocorrelation on 30 May was due to residual extrinsic management effects on $\text{NO}_3\text{-N}$ level that could not be completely removed during data set cleaning as discussed above.

Further, it was found that the separation distance at which no autocorrelation was evident varied between approximately 20–45 m (encircled area B, Fig. 12). This result indicates that the range of intrinsic spatial structure beyond which $\text{NO}_3\text{-N}$ values did not have spatial dependency was likely approximately 45 m. This distance, then, would be the minimum sample spacing for conducting soil $\text{NO}_3\text{-N}$ experiments in this field that require analysis by classical statistical methods. Otherwise, the independence assumption underlying the analysis will not be met and steps to mitigate this issue will need to be taken during analysis.

There was also significant negative autocorrelation evident for the 1 Aug. and 15 Aug. sampling dates at separation distances greater than approximately 45 m (encircled area C, Fig. 12). It is suspected that this result indicates the presence of large-scale variation having a spatial structure pattern with dimensions larger than the sampling area and or significant lag classes (Rossi et al., 1992). Such large-scale variation was likely masking the intrinsic spatial structure present within the sampling area in the field on these two dates.

Overall, the autocorrelograms exhibited a high degree of similarity in their shapes, indicating a high likelihood that the intrinsic spatial structure of $\text{NO}_3\text{-N}$ variation was temporally stable over the study period. At first blush, this finding seemed to be a paradox – how could stability and variation co-exist? However, upon closer reflection, it was concluded that temporal stability of spatial structure indicates

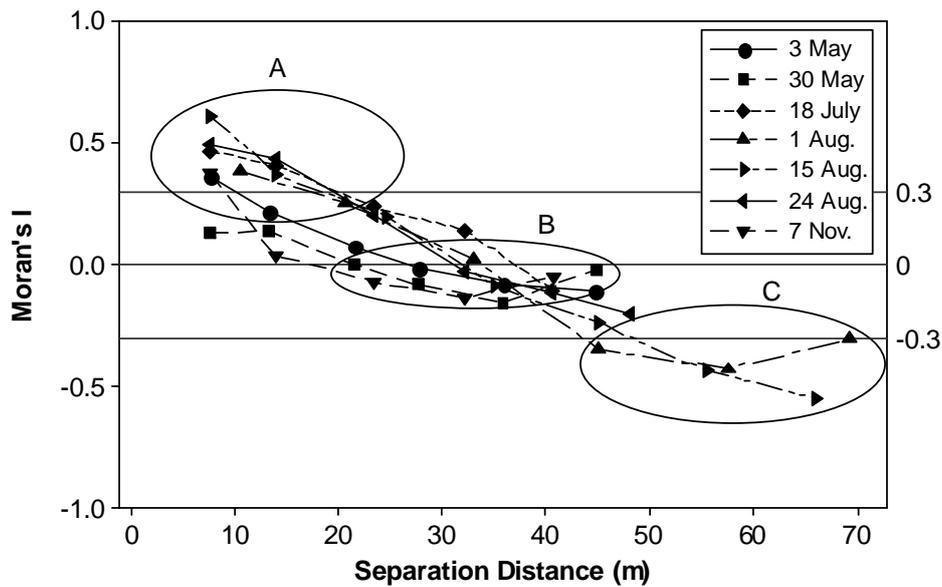


Fig. 12. Spatial autocorrelation of NO₃-N levels for each sampling date. Significant information conveyed by the autocorrelograms that is discussed below is indicated by the encircled areas A, B, and C.

that the variation of NO₃-N level followed a similar pattern of change over time, not that the level was the same everywhere and at all times.

Final variogram models and spatial structure analysis

Scaled variogram models of the spherical, exponential, linear, linear-to-sill, and Gaussian types were created for each sampling date using the cleaned data sets and examined for goodness-of-fit. In total there were 78 valid models considered for final selection, all having an R² value above 0.9 (models not shown in interest of brevity). A comparative summary of the models' parameters ranges is shown in Table 3. Although a variogram model is derived from highly mathematical and least squares statistical procedures which by design are intended to be objective, the creation of a model is actually somewhat subjective. The model that the mathematics and statistics produces is sampling scale dependent and related to the modeler's choice of the active lag and lag interval criteria which determine the separation distance classes and ultimately the lag semivariances to which the model is fitted. As a result, even well-fitted valid models created tend to have a range of parameter values within which they can be considered similar.

Final variogram models of the spherical type were selected from the 78 valid models on the basis of their best fit to the lag semivariances and to enable direct

Table 3. Comparative summary of parameter ranges for the scaled model variograms of soil NO₃-N for each sampling date.

Date	Nugget C _o	Sill (C _o +C)	Range [†] A _o	N:S C _o /(C _o +C)	Spatial Dependency [‡]
3 May	0.021–0.530	1.000–1.893	31–107	0.270–0.492	M
30 May	0.482–0.708	1.162–1.417	36–87	0.348–0.500	M
30 July	0.291–0.418	0.899–1.106	37–80	0.243–0.452	S–M
1 Aug.	0.367–0.549	1.311–1.343	58–62	0.280–0.409	M
15 Aug.	0.001–0.608	0.921–2.932	23–169	0.001–0.463	S–M
24 Aug.	0.172–0.451	1.063–2.253	46–217	0.089–0.395	S–M
7 Nov.	0.385–0.473	1.086–1.352	27–71	0.350–0.373	M

[†] Range values are in meters.

[‡] S, strong spatial dependency (N:S ≤ 0.25); M, moderate spatial dependency (0.25 < N:S ≤ 0.75); W, weak spatial dependency (N:S > 0.75) (Cambardella et al., 1994).

Table 4. Parameters of final selected scaled variogram models for each sampling date.

Parameter/Date	3 May	30 May	18 July	1 Aug.	15 Aug.	24 Aug.	7 Nov.
Nugget, C _o	0.397	0.510	0.291	0.367	0.457	0.304	0.396
Sill, C _o + C	1.031	1.162	0.899	1.311	1.296	1.084	1.110
Range [†] , A _o	41	43	39	62	68	51	27
N:S, C _o /(C _o + C)	0.385	0.439	0.324	0.280	0.353	0.280	0.357
R ²	0.999	0.954	0.955	0.904	0.979	0.987	0.929
RSS (×10 ⁻⁴)	1.10	8.67	6.40	4.36	6.95	3.70	6.52
Lag Pairs [‡]	33–185	35–192	30–59	47–232	44–263	35–190	30–167
Spatial Class [§]	M	M	M	M	M	M	M
Model	Spherical						

[†] Range values are in meters.

[‡] Range in number of pairs for each lag class interval.

[§] S, strong spatial dependency (N:S ≤ 0.25); M, moderate spatial dependency (0.25 < N:S ≤ 0.75); W, weak spatial dependency (N:S > 0.75) (Cambardella et al., 1994).

comparison. A combined plot of these models is shown in Fig. 13. The models' parameters and goodness-of-fit-measures are shown in Table 4. All models had lag class pairs ranging between 30–232. Ninety percent of the classes had more than 100 pairs. The high R² values ranging between 0.904–0.999 combined with very low RSS values indicate very high goodness-of-fit for all models and that they describe the spatial structure of NO₃-N variation very well.

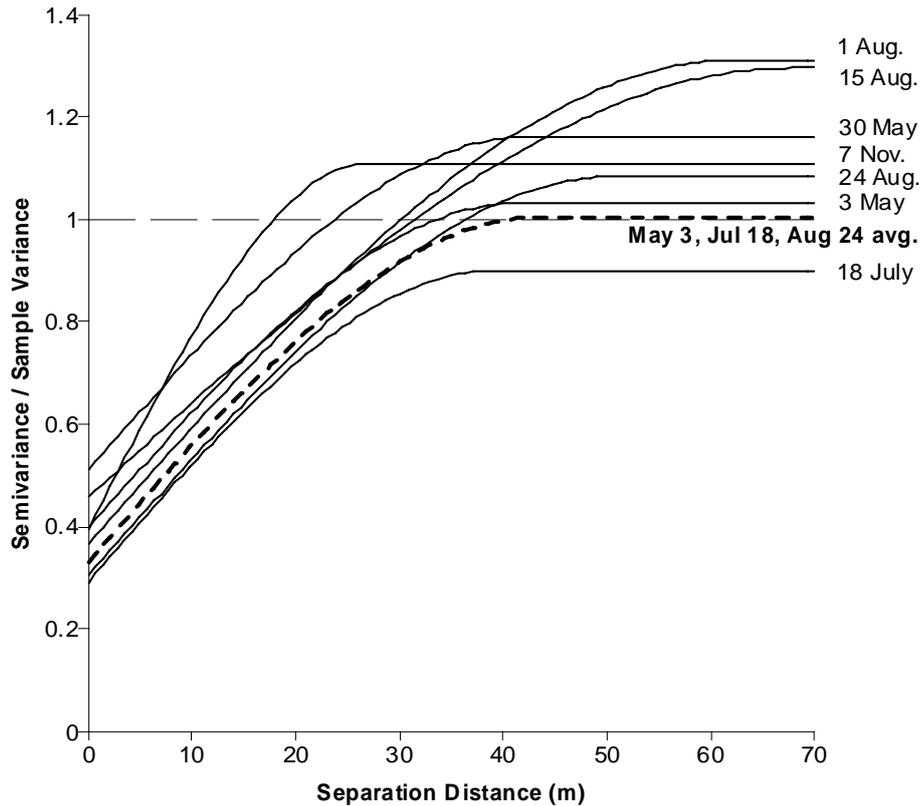


Fig. 13. Average and final selected model variograms for each sampling date.

Similarities in the spatial structure of soil $\text{NO}_3\text{-N}$ on the sampling dates were evident as the final selected variogram models had similar slopes, nuggets, ranges and nugget-to-sill ratios. The models' nuggets were between 0.291–0.510, the ranges were between 27–68 m, and the nugget-to-sill ratios were between 0.280–0.423. Spatial dependency was found overall to be moderate for all dates.

These results are in general agreement with those reported in the literature, although it is difficult to make direct comparisons due to the variety of reporting methods and models used to represent the spatial structure of the soil $\text{NO}_3\text{-N}$ data collected. McBratney and Pringle (1999) also noted this difficulty. The closest agreement found to our work was that of Simmelsgaard and Djurhuus (1997), who reported ranges of 31 to 63 m for exponential variograms of soil mineral-N at a depth of 0.25 m, and Baxter et al. (2003), who reported “similarity” in spherical variograms for soil mineral-N having ranges between 45–69 m.

Since the final selected models represent data from time-spaced sampling dates, their similarity, as does the similarity in the spatial autocorrelograms discussed above, indicates a high likelihood that the intrinsic spatial structure of soil $\text{NO}_3\text{-N}$ in this field exhibited temporal stability over the study period. What appears on the surface to be

differences in the models for the 30 May, 1 Aug. and 15 Aug., and 7 Nov. were determined to be fluctuations in model parameters resulting from large-scale trend effects and residual effects of extrinsic management factors that were somewhat masking the intrinsic spatial structure. Removal of these effects would lead to scaled model sills becoming 1.0 (if complete removal was accomplished), the ranges and nuggets becoming closer estimates of the intrinsic range and nugget values, and the slopes becoming more parallel (Journel and Huijbregts, 1978; Isaaks and Srivastava, 1988; Cressie, 1991; Rossi et al., 1992). Visually, this would lead to a convergence of the model curves shown in Fig. 13, resulting in curves that were more-or-less coincident. Due to the minimal size of our data sets ($n = 45$ or 46), however, attempting to de-trend the data or remove any more points to clean the data sets than has already been done undermines any further effort in this regard.

Average variogram and intrinsic spatial structure model

Average variograms are good for experimental sampling scheme planning and simulation modeling, but not for kriging due to the fixed nature of certain model parameters (McBratney and Pringle, 1999). Because of the similarity of all the final selected models (as discussed above), they all could have been combined to create an average model. However, we were interested in characterizing not only an average model, but one that represented the intrinsic spatial structure of $\text{NO}_3\text{-N}$ for this field. Having an intrinsic model available, by virtue of our working definition of intrinsic, means that future researchers could apply this model to this field as a “known in advance” variogram for experimental planning purposes. Thus, for averaging, we selected the models for 3 May, 18 July, and 24 Aug. because they were considered to be essentially ‘clean’ data sets by virtue of their sill values being within $\pm 10\%$ of the experimental variance. The resulting averaged scaled model had a sill of 1.005, a nugget of 0.331, and a range of 44 m. A plot of this model is shown in Fig. 13. The sill being equal to the variance (1.0 rounded) indicates that the average variogram estimates the experimental variance perfectly, and therefore very likely accurately represents the intrinsic spatial structure present in the field. The range, as well, matches closely with the approximately 45 m determined from the spatial autocorrelation analysis above.

Soil nitrate mapping system’s utility as a tool for experimental planning

The utility of the SNMS for assessing $\text{NO}_3\text{-N}$ variation and spatial structure has been successfully demonstrated with the results and discussion presented above. We will now discuss the utility of the SNMS for experimental planning. McBratney and Pringle (1999) have made an excellent analysis of the utility of variogram models for

planning soil NO₃-N sampling schemes and predicting mean-dependent sample size requirements. In their case example for soil NO₃-N presented, for which the mean was 16 mg kg⁻¹ and the desired site-specific management zone resolution was 20 × 20 m, they determined that a grid spacing of 27 m was required to adequately measure the spatial variation to within 10% of the mean at a 95% confidence level. And further, if desiring to use a management zone resolution of 10 × 10 m, a grid spacing of 20 m would be required. Based on Fig. 5e in McBratney and Pringle (1999) it was determined that the sampling density (6 × 7.5 m effective grid) used in our study had a kriging accuracy smaller than 0.5 mg kg⁻¹ (this is as low as the figure goes) with a 95% confidence level, for a mean level of 16 mg kg⁻¹. Since many of the sampling dates mean value in our study were found to be much smaller than 16 mg kg⁻¹, the kriging accuracy can be safely assumed to be even smaller than 0.5 mg kg⁻¹. This analysis indicates that the SNMS can be used to generate highly accurate, dense, contour maps with minimal interpolation error during kriging. The ability of the SNMS to sample down to densities of approximately 1 m (very fine-scale focus) when operated in manual sampling mode, which is very near continuous sampling, gives its user an unprecedented ability to zoom in at nearly any ‘magnification’ (sampling density) desired, and in real-time, right in the field, directly measure soil NO₃-N. Being able to analyze samples with the SNMS at these densities much quicker, as accurately as, and more affordably than conventional lab analysis means, in practical terms, that the SNMS can provide a long-awaited solution to the problem of conducting soil NO₃-N experiments at an affordable cost. In addition, it provides a way to collect data so that the spatial structure of the NO₃-N in a field of interest is “known in advance” of the experimental planning. With this knowledge, the experimental sampling scheme and optimal sample size required for statistical analysis reliability can be prior determined with confidence.

Summary and conclusions

Soil nitrate (NO₃-N) is highly variable spatially and temporally. Much research has been dedicated to assessing and characterizing this variability to improve our understanding of the effects of NO₃-N on crop growth and the environment. *Precision agriculture* seeks to use this understanding to develop site-specific crop management (SSCM) practices for better agriculture. An on-the-go soil nitrate mapping system (SNMS) has been developed that provides a quick, accurate and cost effective way to collect soil samples on a fine scale and analyze them for NO₃-N content.

This study was conducted to demonstrate that the SNMS could be used as an effective tool to assist soil scientists with experimental investigations of the spatial and

temporal aspects of soil NO₃-N. Within that context, a multifaceted sub-experiment in a wheat production system having high economic importance to the Atlantic region of Canada in particular and internationally in general was conducted. Using data collected by the SNMS and a combination of classical and geostatistical analyses techniques and tools, the spatial and temporal aspects of soil NO₃-N variation in the field at several time points covering pre-seeding, growing season, and post-harvest soil conditions, as well as the intrinsic spatial structure of NO₃-N present in the field, were assessed.

Soil nitrate mapping system use

The SNMS was successfully used to collect data for assessing the variation and spatial structure of soil NO₃-N at any time during the study period. Being able to analyze samples with the SNMS on a fine-scale sampling grid much quicker, as accurately as, and more affordably than conventional lab analysis means, in practical terms, that the SNMS can provide a long-awaited solution to the problem of conducting soil NO₃-N experiments at an affordable cost. In addition, it provides a way to collect data so that the spatial structure of the NO₃-N in a field of interest is “known in advance” of the experimental planning. With this knowledge, the experimental sampling scheme and optimal sample size required for statistical analysis reliability can be prior determined with confidence. The proof-of-concept use of the SNMS as an effective tool to assist soil scientists with experimental investigations of the spatial and temporal aspects of soil NO₃-N was successfully demonstrated.

Spatial and temporal variation

The mean soil NO₃-N level for each sampling date varied between 4.38 mg kg⁻¹ just prior to field activity (3 May) and 28.80 mg kg⁻¹ (30 May) one day before peak NO₃-N availability. The general trend of mean NO₃-N change over the study period found was ‘residual’ level at pre-seeding time (3 May), which rose to a peak approximately three weeks after manure application (30 May), and then dropped over the active growth of the wheat until grain harvest (24 Aug.), followed by a modest post-harvest increase (7 Nov.). The CVs ranged between a low of 24.1% (24 Aug.) and a high of 71.2% (7 Nov.), indicating large variation in NO₃-N level throughout the study period both spatially and temporally.

Accurate, high resolution posted values (contour) maps were generated that give excellent visual pictures of the NO₃-N spatial variation that was evident just prior to, at peak nitrogen release, during, and just after the growing season. The presence of some extrinsic management factors effects, as indicated by the presence of ‘ridging’, ‘hot spots’ and a ‘swale’ of NO₃-N levels was revealed in the maps. Several of these ‘hot spots’ and the ‘swale’ were relatively consistent and strikingly corresponded to

lower areas in the field even though $\text{NO}_3\text{-N}$ level, generally, did not correlate with surface elevation.

Spatial structure

A very strong proportional effect was found between the data sets mean and standard deviation values ($R^2 = 0.972$), and the squared mean and variance values ($R^2 = 0.996$). These relationships can be used for predicting high-quality average and proportional variograms, which in turn can be used for determining $\text{NO}_3\text{-N}$ soil sampling schemes for the field to a desired level of accuracy.

Soil $\text{NO}_3\text{-N}$ levels exhibited significant positive autocorrelation at separation distances ≤ 20 m. Consequently, for accurate estimation of values in un-sampled locations by kriging, the sample spacing in this field should be limited to no more than 20 m. Further, it was found that the separation distance at which no autocorrelation was evident varied between approximately 20–45 m. This result indicates that the range of intrinsic spatial structure beyond which $\text{NO}_3\text{-N}$ values did not have spatial dependency was likely approximately 45 m. This distance, then, would be the minimum sample spacing for conducting soil $\text{NO}_3\text{-N}$ experiments in this field that require analyses by classical statistical methods.

Spatial autocorrelograms of $\text{NO}_3\text{-N}$ levels exhibited a high degree of similarity in their shapes indicating a high likelihood that the intrinsic spatial structure of $\text{NO}_3\text{-N}$ variation was temporally stable over the study period. At first blush, this finding seemed to be a paradox – how could stability and variation co-exist? However, upon closer reflection, it was concluded that temporal stability of spatial structure indicates that the variation of $\text{NO}_3\text{-N}$ level followed a similar pattern of change over time, not that the level was the same everywhere and at all times.

Final selected variogram models of the isotropic spherical type had high R^2 values ranging between 0.904–0.999 combined with very low RSS values indicating very high goodness-of-fit for all models and that they describe the spatial structure of $\text{NO}_3\text{-N}$ variation very well. Similarities in the spatial structure of soil $\text{NO}_3\text{-N}$ on the sampling dates were evident as these variogram models had similar slopes, nuggets, ranges and nugget-to-sill ratios. The models' nuggets were between 0.291–0.510, the ranges were between 27–68 m, and the nugget-to-sill ratios were between 0.280–0.439. Spatial dependency was found overall to be moderate. Since the final selected models represent data from time-spaced sampling dates, their similarity, as does the similarity in the spatial autocorrelograms, indicates a high likelihood that the intrinsic spatial structure of soil $\text{NO}_3\text{-N}$ in this field exhibited temporal stability over the study period.

A scaled averaged variogram model that very likely accurately represents the

intrinsic spatial structure present in the field was created having a sill of 1.005, a nugget of 0.331, and a range of 44 m. By virtue of our working definition of intrinsic, future researchers could apply this model to this field as a “known in advance” variogram for experimental planning purposes.

CHAPTER 7

Using an automated on-the-go soil nitrate mapping system to investigate plant and soil nitrate responses in wheat and carrot production systems¹

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Abstract

An on-the-go soil nitrate mapping system (SNMS) has been developed that provides a way to quickly, accurately and cost effectively collect data necessary for analysing small-scale variation in soil NO₃-N while crops are being grown, thus enabling this variation to be linked to crop performance. The SNMS can be used as an effective tool for assisting with the conduct of agronomic experiments. Soil NO₃-N, plant nitrogen, and yield responses in (i) spring wheat (*Triticum aestivum* L.) under liquid dairy manure (LDM) management with conventional tillage (CT) and no tillage (NT) treatments, and (ii) carrot (*Daucus carota* L.) under CT management with inorganic fertilizer (IF) and LDM fertility treatments were determined at seven time-points over a growing season. In wheat, mean soil NO₃-N level varied with sampling date, but not between treatments except early in the season when it was nearly two times higher for CT. Mean plant tissue-sap NO₃-N, grain yield, and grain Total N showed no difference between treatments. In carrot, mean soil NO₃-N level varied with sampling date and between treatments. Early in the season, it was nearly three times higher for IF and then dropped to remain at two times higher during the remainder of the season. Mean plant tissue-sap NO₃-N and tissue Total N varied with sampling date but not between treatments, except for Total N at the end of the season. Fresh root yield and root Total N showed no difference between IF and LDM. The proof-of-concept use of the SNMS as a tool for assisting with the conduct of agronomic experiments was successfully demonstrated.

Keywords: Tissue-sap, conventional tillage, no tillage, inorganic fertilizer, liquid dairy manure.

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Introduction

As modern agriculture scrambles to feed the mushrooming world population, environmental issues associated with the use of nitrogen fertilizers will increasingly have to be dealt with. Water sources contamination and associated socio-economic costs indicate a great need for precise soil fertility management practices – using the right form of fertilizer, applied at the right time, in the right amount, and in the right way (Power and Schepers, 1989; Dinnes et al., 2002). Because nitrate (NO_3^-) is highly soluble in water, it is readily available for plant uptake but can also runoff or leach, and therefore it has been found to cause many of the environmental issues in water sources associated with inorganic fertilizer and manure use (Spalding and Exner, 1993; Jemison and Fox, 1994; MacDonald; 2000, Dinnes et al., 2002). For farmers, inaccurate application of nitrogen fertilizers, either in organic or in-organic form, is detrimental to the profitability of their crops due to the extra input costs involved and the negative effects on crop performance (growth, yield and quality) experienced.

Crop performance is affected by the ability of the plants to take up and utilize available inorganic soil nitrogen. Nitrate is the pre-eminent inorganic form of soil nitrogen which is taken up and utilized by plants, and the presence or absence of it in the topsoil is often an indicator of how thoroughly the plants have been able to do this. Growing plants utilize varying amounts of soil $\text{NO}_3\text{-N}$ during different phenological (growth) stages and its availability should ideally be in response to the need. Nitrate availability in the soil depends on soil texture, soil organic matter content and soil pH, relative rates of N-uptake by plants, several N-transforming processes (e.g., mineralization, immobilization, and (de-)nitrification), precipitation, evaporation, tillage, drainage, and fertilizer inputs.

In most cases where fertilizer inputs have been implicated for causing water pollution, it has been due to poor soil and plant management practices that resulted in leaching of soil $\text{NO}_3\text{-N}$ into groundwater (Follett, 1989; Dinnes et al., 2002). *Precision agriculture* offers an exciting opportunity to use highly advanced technology for better practices in agriculture. The ultimate goal of such technology is to enable farmers to more intensely and precisely analyze variations in field conditions throughout the growing season, in correlation with environmental and crop response data, in order to make the most sound management decisions possible. This ability will offer new production efficiencies to farmers, while at the same time offering assurances to the public that agricultural practices are being conducted in the most environmentally sustainable way.

A soil nitrate mapping system (SNMS) (Fig. 1) will be one such technology that can contribute to *precision agriculture* as it provides a way to quickly, accurately and

cost effectively collect the data necessary to analyze small-scale variation in soil nitrate while crops are being grown, thus enabling this variation to be linked to crop performance.

The SNMS consists of six sub-assemblies: 1) soil sampler sub-assembly, 2) soil metering and conveying sub-assembly, 3) nitrate extraction and measurement sub-assembly, 4) auto-calibration sub-assembly, 5) control sub-assembly, 6) GPS sub-assembly. The system automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyses it electrochemically for nitrate concentration in real-time (6 s) using a nitrate ion-selective electrode (NO_3^- -ISE) as the analysis instrument. Additionally, global positioning system (GPS) geo-referenced position data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field. The SNMS can be used to analyse soil samples automatically while on-the-go (fully automatic mode), or manually while stationary by hand-placing samples into the nitrate extraction and measurement sub-assembly (manual-sampling and auto-analysis mode). It is envisioned that two configurations of the system will eventually be used in practice – a tractor-mounted version (Fig. 1) and a ‘suitcase’ version (not shown). The SNMS currently has the ability to sample with (i) with lab-grade accuracy, (ii) at any desired spacing down to approximately one meter (very fine scale) when operated in manual mode, (iii) at the rate of approximately two samples per minute, and (iv) at approximately $1/10^{\text{th}}$ the cost of conventional lab analysis.

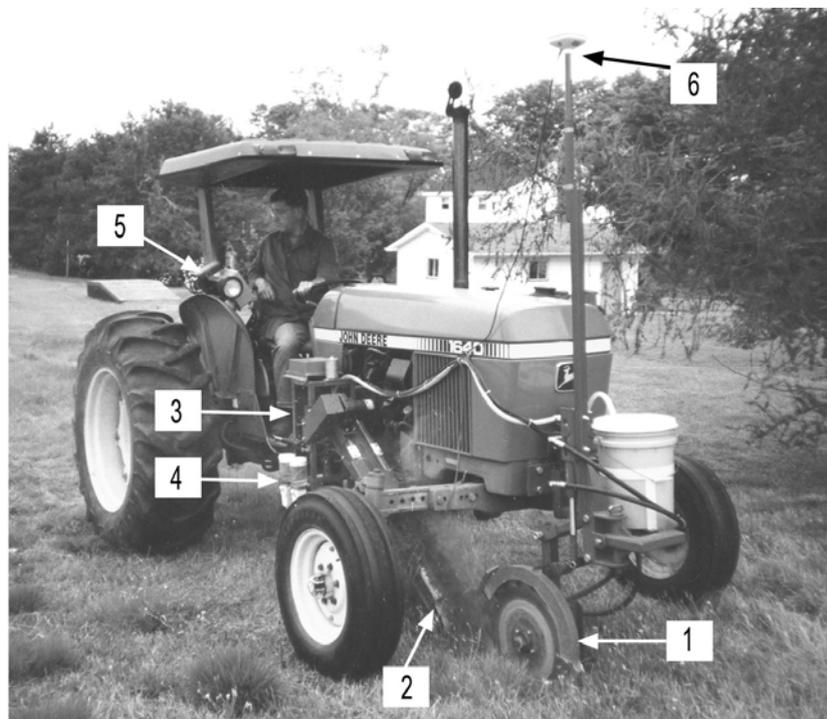


Fig. 1. Tractor-mounted soil nitrate mapping system with six sub-assemblies.

From its beginnings as a first prototype (Adsett, 1990; Adsett and Zoerb, 1991), the SNMS has undergone several developmental iterations. The use of a NO_3^- -ISE in this type of application has been extensively lab tested (Thottan et al., 1994; Thottan, 1995; Brothers et al., 1997). Development and preliminary field testing of the five initial sub-assemblies and their integration into one complete system followed (Thottan, 1995; Adsett et al., 1999). In 2001, a completely new electronics and control system that incorporated the GPS sub-assembly was added. A next step in the SNMS' development was extensive testing in crop production systems to confirm its usefulness in the field, which is the work being reported in this chapter.

Objectives and scope

The primary objective of the current study was to demonstrate that, as a proof of concept, the SNMS could be used as an effective tool to assist crop scientists with their experimental investigations of plant and soil nitrate responses under a variety of field management conditions. Within that context, multifaceted sub-experiments in two crop production systems (wheat and carrot) having high economic importance to the Atlantic region of Canada in particular, and internationally in general, were conducted with the agronomic objectives to (i) determine the effect of conventional tillage vs. no tillage on soil nitrate, plant nitrogen and yield responses in spring wheat under liquid dairy manure fertilization and (ii) determine the effect of inorganic fertilizer vs. organic fertilizer on soil nitrate, plant nitrogen and yield responses in carrot under conventional tillage. Plant nitrogen responses under investigation included tissue-sap nitrate and total N, and storage organ (grain or carrot) tissue nitrate and total N as described below.

Materials and methods

Field sites and experimental designs

During the 2006 growing season, field experiments were established in two adjacent fields (#203 and #207) on the Nova Scotia Agricultural College (NSAC) farm, Truro, Nova Scotia, Canada (45°22'N 63°16'W) concurrent with experiments being conducted by the Nova Scotia Water Quality Research Group (NSWQRG). These fields have been used by the NSWQRG since 1995 for many bio-environmental, cropping management, and water quality studies, and their soils characteristics and cropping histories are well documented (Webb and Langille, 1996; Elmi et al., 2005; Gordon et al., 2005).

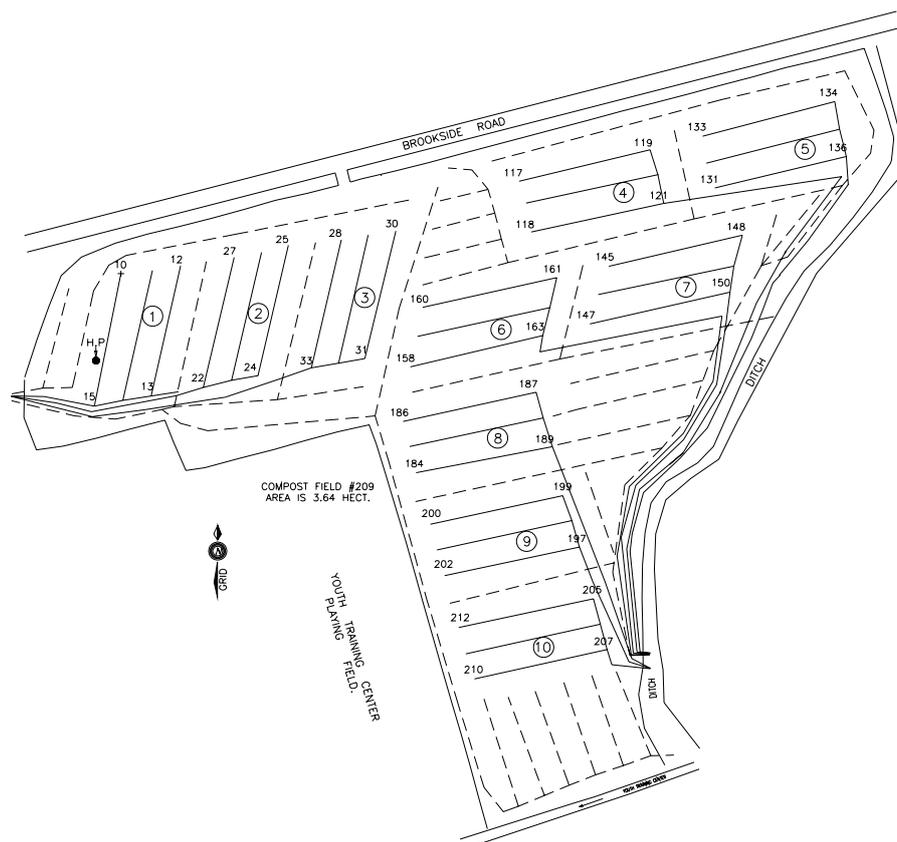


Fig. 2. Wheat field experimental plots layout. Solid lines are tile drains. Dashed lines are buffer drains and also represent plot boundaries (48 × 80 m). Circled numbers indicate plot numbers. Plots 2, 3, 5, 8, and 9 had conventional tillage treatment. Plots 1, 4, 6, 7, and 10 had no tillage treatment. Blocking was by soil group: Pugwash 52 (plots 1 and 2; plots 4 and 8), Debert 22 (plots 5 and 7; plots 9 and 10); Debert 52 (plots 6 and 3).

Four soil groups present in the fields were (i) Pugwash 52 (PGW52), (ii) Pugwash 82 (PGW82), (iii) Debert 22 (DRT22), and (iv) Debert 52 (DRT52). The PGW52 and PGW82 soils had a friable, fine sandy-loam textured Ap horizon 15- to 20-cm thick, underlain by a fine sandy-loam textured Bm horizon. Below the Bm horizon was a friable to firm, fine sandy-loam textured, platy structured, fragic BCxj horizon. They were moderately well-drained and well-drained, respectively. The DRT22 and DRT52 soils had a friable, sandy-loam textured Ap horizon 25- to 30-cm thick, underlain by a friable to firm sandy-loam textured Bmgj horizon. Below the Bmgj horizon were firm, poorly structured sandy-loam to loam textured subsoil horizons that included fragipan (BCxj, BCxjgi) and compact basil till (Cgj). They were both imperfectly drained. All descriptions of the soils are according to Webb and Langille (1996). Both fields had systematic tile drainage systems (100-mm diameter) installed at 0.8-m depth with 12-m spacing between drains.

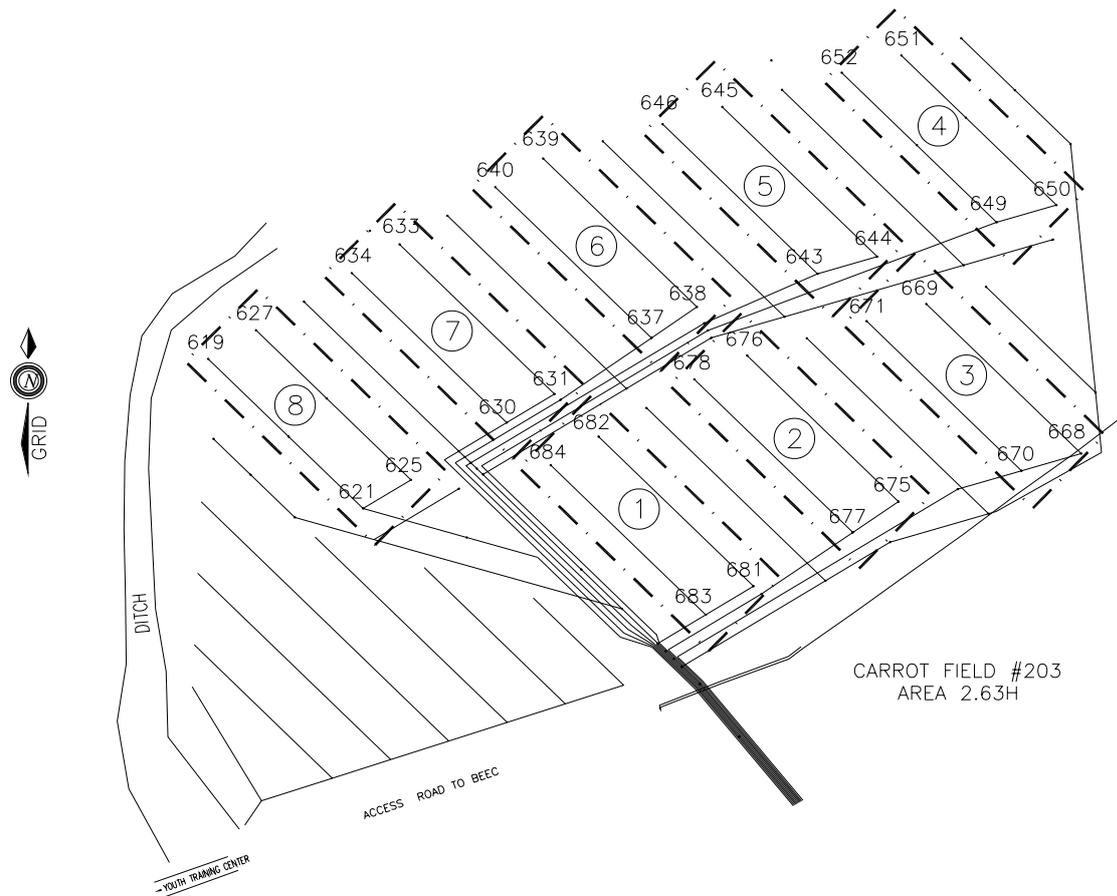


Fig. 3. Carrot field experimental plots layout. Solid lines are tile drains. Dashed lines are plot boundaries (24×60 m). Circled numbers indicate plot numbers. Plots 2, 4, 6, and 8 had inorganic fertilizer treatment. Plots 1, 3, 5, and 7 had liquid dairy manure treatment. Blocking was by soil group: Pugwash 52 (plots 4 and 5), Pugwash 82 (plots 1 and 2; plots 6 and 7), Debert 22 (plots 3 and 8).

Randomized complete block experimental design was used in both fields, with blocking by soil group. Field #207 (Fig. 2) was seeded with spring wheat and had two tillage treatments, conventional tillage (CT) and no tillage (NT), randomly assigned within each of five blocks; two of PWG52, two of DRT22, and one of DRT52. All plots in Field #207 were under liquid dairy manure (LDM) fertility management. Field #203 (Fig. 3) was seeded with carrot and had two fertility treatments, inorganic fertilizer (IF) and LDM, assigned randomly within each of four blocks; two of PGW82, one of DRT22, and one of DRT52. All plots in Field #203 were under CT management.

Details of the crop varieties and cultural management practices for the field experiments in 2006 are shown in Table 1.

Table 1. Crop varieties and cultural management practices for the wheat and carrot field experiments in 2006.

Activity/Crop(Field)	Wheat (F207)	Carrot (F203)
Variety or Hybrid Name	Hoffman	Red Cored Chantenay
Date [†] @ seeding rate	12/5/2006 (DOY132) @ 140 kg ha ⁻¹	31/5/2006 (DOY151) @ 52 seeds m ⁻¹ of row length
Row spacing	17.8 cm NT [‡] plots, 15.3 cm CT [‡] plots	63.5 cm
Plowed	CT plots - 28/4/2006 (DOY118)	15/5/2006 (DOY135)
Disced	CT plots - 28/4/2006 (DOY118)	16/5/2006 (DOY136)
Herbicide	Glyphosate (48.8%) {N-(phosphonomethyl)glycine}	Glyphosate (48.8%) {N-(phosphonomethyl)glycine}
Date @ rate	8/5/2006 (DOY220) @ 3.5 L ha ⁻¹	8/5/2006 (DOY220) @ 3.5 L ha ⁻¹
Liquid dairy manure	All plots	Plots 1, 3, 5 & 7
Date @ Available N rate	10/5/2006 (DOY130) @ 80 kg ha ⁻¹	16/5/2006 (DOY136) @ 70 kg ha ⁻¹
Available N supplied (kg ha ⁻¹)		
Fertilizer 14-7-20	n/a	Plots 2, 4, 6 & 8
Date @ Available N rate		31/5/2006 (DOY151) @ 70kg ha ⁻¹
Pre-emergent herbicide	n/a	Gesagard 480 SC
Date @ rate		3/6/2006 (DOY154) @ 4.5 L ha ⁻¹
Post-emergent herbicide 1	MCPA Dimethylamine (53–55%) {2-methyl-4-chlorophenoxyacetic acid} and Thifensulfuron methyl (50 %) {Methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl) amino] carbonyl] amino]-sulfonyl]-2-thiophenecarboxylate}	Linuron 50% {3-(3,4-dichlorophenyl)-1-methoxy-l-methylurea}
Date @ rate	23/6/2006 (DOY174) @ 1.0 L ha ⁻¹ and 20.0 g ha ⁻¹	26/7/2006 (DOY207) @ 1.5 L ha ⁻¹
Post-emergent herbicide 2	n/a	Fluazifop-P-Butyl (13%) {Butyl(R,S)-2-[4-[[5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoate}
Date @ rate		26/7/2006 (DOY207) @ 1.0 L ha ⁻¹
Top-dress fertilizer 12-0-24	n/a	All plots
Date @ available N rate (kg ha ⁻¹)		29/8/2006 (DOY242) @ 12 kg ha ⁻¹

[†] Date format is dd/mm/yyyy.

[‡] NT, no tillage; CT, conventional tillage.

Soil sampling and analyses

Within each field, soil samples were collected using a 6.5- by 7.0-m grid layout in the plots to provide soil NO₃-N data for the 0–15-cm depth. Each wheat plot grid had 13 sampling locations, whilst each carrot plot grid had eight. The grids in each plot were located in the lower-half of the plot (drain tile outlet end) and laid out manually directly above the tile drains which provided for spatially-located sampling at points along each drain tile, and at mid-drain tile spacing. Each sampling location was staked to enable repeat sampling and its Easting and Northing coordinates were recorded with the GPS unit. This configuration enabled data collection for this study simultaneously with two other related studies investigating the relationships between soil NO₃-N and drain water quality, and the spatial and temporal variation of soil NO₃-N respectively, not being reported here.

Soil samples were collected (i) just prior to planting and fertilizing (3 May, Daynumber of Year [DOY] 123) for wheat; 4 May, DOY124 for carrot), (ii) approximately three weeks after fertilizing (30 May, DOY150 for wheat; 20 June, DOY171 for carrot), (iii) approximately bi-weekly several times throughout the growing season simultaneously with plant tissue and yield samples (details of dates below in next section), and (iv) after crop harvest (7 Nov., DOY311 for both wheat and carrot). To prevent damage to the crops, samples during the growing season were collected manually by coring with a standard 19-mm diameter soil-sampling tool to a depth of 15 cm (4 cores at each location bulked). All samples were collected within a 0.3-m radius of the sampling location. All manually collected samples were kept in Styrofoam coolers while in the field, and were immediately transported to the lab where they were kept under refrigerated storage (4°C) or frozen (-16°C) until processing could be completed. Moist sub-samples were manually weighed out (15.1 g) and placed in the SNMS' nitrate extraction and measurement sub-assembly for analysis. An Orion 9707 ionplus ISE (Thermo Electron Corp., USA) was used to measure NO₃⁻ concentration. A total of 1,422 soil samples were analyzed by the SNMS during this study. Details of calibration procedures and functional operation of the SNMS are well documented elsewhere (Thottan et al., 1994; Thottan, 1995; Brothers et al., 1997; Adsett et al., 1999).

Plant tissue sampling and analysis

Plant tissue samples were collected by hand approximately bi-weekly during the critical phenological stages, including harvest. For wheat, the samples were collected on 18 July (DOY199, 67DAP [Days after Planting], grain set), 1 August (DOY213, 81DAP, grain filling), 15 August (DOY227, 95DAP, maturity), and 24 August (DOY236, 104DAP, harvest). For carrot, the samples were collected on 15 August

(DOY227, 76DAP, mid-growth), 13 September (DOY256, 105DAP, root bulking), 26 September (DOY269, 118DAP), 31 October (DOY284, 133DAP, homeostasis), and 24 October (DOY297, 156DAP, harvest).

For wheat, between 40 to 60 flag leaves were randomly collected from plants within a one-meter radius of the sample locations and bulked to form an aggregate sample. For carrot, leaves seven and nine (Pettipas et al., 2004) were collected from three carrot plants randomly selected within a one-meter radius of the sample locations and bulked to form an aggregate sample.

For analysis, the aggregate samples were split into paired sub-groups. One sub-group was oven dried and analyzed for Total N using a LECO model 1000 CNS analyzer (LECO Corp., Michigan, USA) following the protocols and procedures as described in the operators manual. The other sub-group was frozen (-16°C) and later thawed to release tissue-sap $\text{NO}_3\text{-N}$ for analysis.

Tissue-sap $\text{NO}_3\text{-N}$ analysis was performed using the SNMS' ISE (Orion 9707 ionplus electrode, Thermo Electron Corp., USA) and bench-top Orion Ion Analyzer (model EA 940) using a specially developed procedure. Prior to analysis, the ISE was calibrated according to its operating manual using standards manually prepared from reagent-grade KNO_3 powder and distilled water. During analysis the ISE was re-calibrated every plot-set of samples (8 samples for carrot, 13 samples for wheat). Plant tissue samples were removed from the freezer, allowed to thaw at room temperature (approximately 21°C), and then immediately squeezed using a clean garlic press to extract the tissue sap into a disposable small plastic cup. Depending on the volume of sap collected, up to 2.0 mL of sap was transferred into another plastic cup using a disposable-tipped micro-pipette (Nichipipet EX 1000-5000 μL , Nichiryo, Japan). The sap was diluted with distilled water to bring the volume up to 10.0 mL using a bottle-top dispenser. The diluted sap sample was then stirred using a small magnetic stir bar and magnetic stirrer machine (American Stirrer 20, American Dade Corp., USA) set at medium speed. While the sample was being stirred, the ISE was inserted into the sample solution for measurement of $\text{NO}_3\text{-N}$ concentration. In-between each sample, the ISE was rinsed with distilled water to read blank molarity. During analysis of each plot-set of samples, repeat measurements were randomly made of two samples to confirm measurements.

Yield sampling

Wheat yield data was manually collected on 24 August (DOY236, 104DAP). At each sampling location, a 1.0 m^2 metal quadrat was randomly placed in the crop at a one-meter radius from the location stake. The wheat within the quadrat boundary was then harvested using grass shears by cutting the stalks at approximately five centimeters

above ground. The harvested stalks were bagged and transported to a drying facility where forced-air drying occurred for 48 hours. The dried stalks were then manually fed through a plot combine (HEGE 125C, Wintersteiger AG, Germany) to thresh the grain from the heads on the stalks. The threshed grain was collected, cleaned using a seed cleaner (Clipper K, Blount/Ferrell-Ross Inc., USA), and weighed (± 0.1 g).

Carrot yield data was manually collected on 24 October (DOY297, 156DAP) using standard yield sampling methods of NSAC's Processing Carrot Research Program (PCRP) Group (Pettipas et al., 2006). Carrots were manually harvested from a randomly selected section of a row two meters in length, beginning at a one-meter radius of the location stake.

Statistical analyses

Yield and Total N responses measured at one time point were analyzed as Randomized Block Design whereas soil $\text{NO}_3\text{-N}$, tissue Total N (for carrot and wheat), and tissue-sap $\text{NO}_3\text{-N}$ (for carrot) that were measured repeatedly were analyzed as Repeated Measures in time. The analyses were completed using Proc Mixed (SAS Institute, 2003), which overcame several shortcomings of Proc GLM for analyzing repeatedly measured data (Littell et al., 1996, 1998). The most appropriate covariance structure for the repeated measures analysis was determined based on the AIC and SBC values. For each response, the validity of normal distribution and constant variance of the error terms assumptions were verified by examining the residuals as described in Montgomery (2005). When either the main or the interaction effects of the factors (Treatment, Time) were significant (p-values <0.05) or marginally significant ($0.05 < \text{p-value} < 0.10$), the least squares means of the treatment combinations were compared to generate letter groupings at the 5% level of significance.

It was planned to conduct a repeated measures analysis of wheat tissue-sap $\text{NO}_3\text{-N}$. However, of the four dates for which samples were collected, only the DOY199 samples could be analysed. The samples from DOY213 were decayed resulting from a fridge breakdown during initial storage while waiting to be frozen. The samples from DOY227 and DOY236 did not contain enough sap to be analysed due to senescence.

Meteorological data

Meteorological conditions at the site, including rainfall (Fig. 4), and air temperature (one-meter height) and soil temperature (10-cm depth) (Fig. 5), were recorded hourly using an automated weather station and a Campbell Scientific (Edmonton, AB) CR10 datalogger at the edge of F207 adjacent to plot eight.

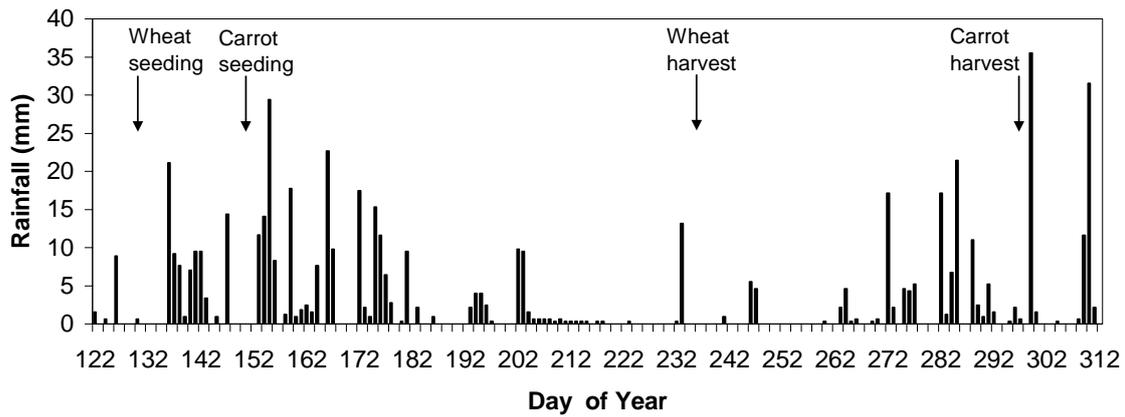


Fig. 4. Total daily rainfall during 2006 study period.

Mean rainfall for the May–Aug. growing period in wheat (F207) was 349 mm, compared to 275 and 339 mm in 2004 and 2005 (data not shown), respectively, for the same period. Mean rainfall for the May–Oct. growing period in carrot (F203) was 510 mm, compared to 507 and 764 mm in 2004 and 2005 (data not shown), respectively, for the same period. The rainfall trend resulted in creating field moisture conditions that were described seasonally as a very wet Spring, a relatively dry Summer, followed by a wet Fall.

The temperature trend resulted in creating environmental temperature conditions that were described seasonally as a cool Spring, relatively warm Summer, followed by a cool early Fall and a late-Fall warm period (typical of geographic location).

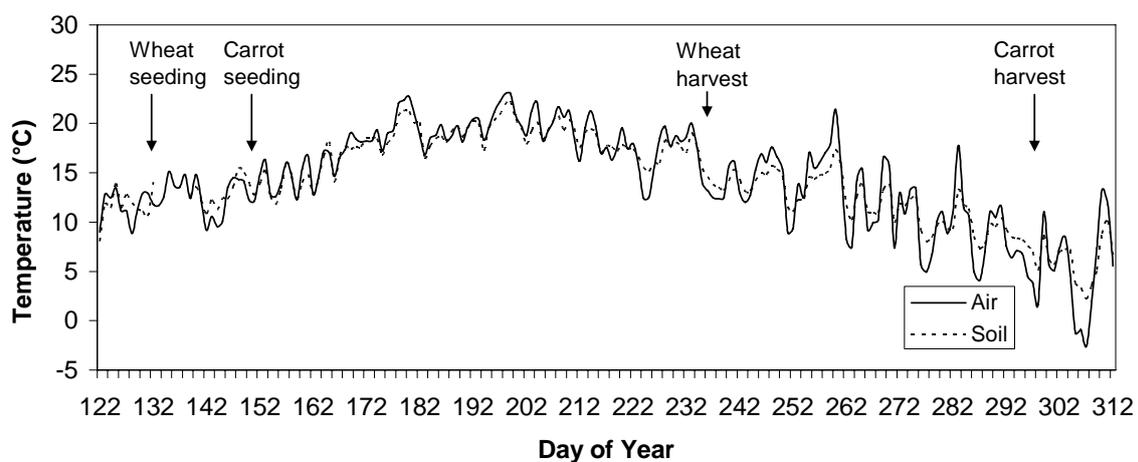


Fig. 5. Mean daily air (one-meter height) and soil temperature (10-cm depth) during 2006 study period. Temperature data missing for DOY132–DOY138 due to thermistor removal from ground to enable wheat seeding on DOY132.

Results and discussion

Analysis of variance (ANOVA) results testing for the effects of block (soil group) and treatment (tillage for wheat, fertilizer for carrot) on tissue-sap $\text{NO}_3\text{-N}$ (for wheat), yield and Total N (grain for wheat, root for carrot) are shown in Table 2.

Generally, it was found that there was no significant difference in yield-related response measures for the plants over all soil groups (blocks) and treatments, except for a significant block effect (soil group) on root Total N in carrot. This lack of difference is a good result from a yield perspective as it shows that at the end of the growing season the plants produced the same yields regardless of the treatments and regardless of the varying soil $\text{NO}_3\text{-N}$ and meteorological changes over the growing season, as will be discussed further in the crop production systems sections below.

The results of the repeated measures analysis testing for the effects of block (soil group), treatment (tillage for wheat, fertilizer for carrot), and Day on soil $\text{NO}_3\text{-N}$, tissue Total N, and tissue-sap $\text{NO}_3\text{-N}$ (for carrot) are shown in Table 3. Generally, it was found that there were significant time-related (Day) effects on soil $\text{NO}_3\text{-N}$ level and plant responses either alone or in interaction with the treatments. Further detailed discussions of these results, including multiple means comparisons when significant interactions were present (*italic p-values* in Table 3), are contained in the specific crop related sub-sections below.

Table 2. P-values testing the effects of block (soil group) and treatment (Trt: tillage for wheat, fertility amendment for carrot) on tissue-sap $\text{NO}_3\text{-N}$, grain yield, and grain Total N for wheat, and root yield and root Total N for carrot.

Source of variation	Wheat			Carrot	
	Tissue-sap $\text{NO}_3\text{-N}$	Yield	Grain Total N	Yield	Root Total N
Block	0.184	0.131	0.416	0.300	0.043
Trt	0.306	0.210	0.707	0.832	0.239

Table 3. P-values testing for the effects of block (soil group), treatment (Trt: tillage for wheat, fertilizer for carrot), and Day on soil $\text{NO}_3\text{-N}$ and tissue Total N for wheat, and soil $\text{NO}_3\text{-N}$, tissue-sap $\text{NO}_3\text{-N}$, and tissue Total N for carrot. Significant effects that needed further multiple means comparison are shown in *italics*.

Source of variation	Wheat		Carrot		
	Soil $\text{NO}_3\text{-N}$	Tissue Total N	Soil $\text{NO}_3\text{-N}$	Tissue-sap $\text{NO}_3\text{-N}$	Tissue Total N
Block	0.629	0.565	0.139	0.407	0.695
Day	0.001	<i>0.001</i>	0.001	<i>0.001</i>	0.001
Trt	0.539	0.970	0.002	0.815	0.334
Day×Trt	<i>0.002</i>	0.324	<i>0.001</i>	0.123	<i>0.001</i>

Wheat production system experiment*Soil nitrate*

The significant Day×Trt interaction (Table 3) suggests that the effect of tillage on soil NO₃-N level in wheat was not uniform throughout the study period. As the multiple means comparison results indicate (Fig. 6), the only significant difference in mean soil NO₃-N level between the two tillage treatments occurred on DOY150 early in the growing season shortly after fertilizing.

Over the study period, the general trend in soil NO₃-N level was the same for both NT and CT treatments: starting at pre-seeding level (DOY123), rising to near peak release (availability) on DOY150 (one day before peak availability, data not shown), then dropping over the active growth of the wheat until grain harvest on DOY236, followed by what appeared to be a modest post-harvest increase to DOY311, but this increase was not statistically significant. This same general trend has been reported by Lockman and Storer (1990) resulting from their study of soil nitrate and ammonium changes with area and date sampled during crop growth for 134 field sites in the mid-West USA and Central Canada. As well, Villar-Mir et al. (2002) reported the same trend resulting from their study of soil NO₃-N in irrigated cornfields in Northeast Spain.

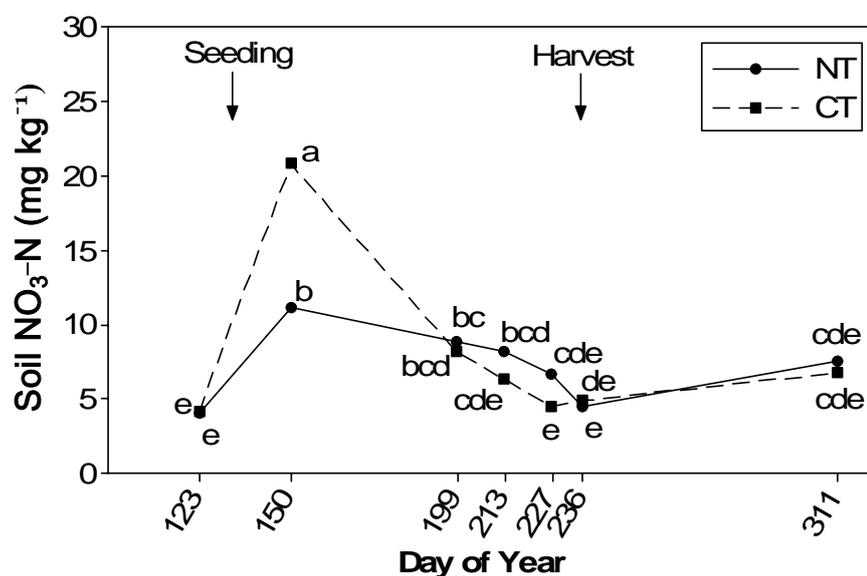


Fig. 6. Soil NO₃-N response at 0–15-cm depth to conventional tillage (CT) and no tillage (NT) treatments in the wheat field over the study period. Least squares means sharing the same letter are not significantly different at the 5% level of significance. Although there are some gaps in the time scale, a line graph is used rather than a bar chart to better illustrate trends evident.

The initial increase in soil $\text{NO}_3\text{-N}$ between DOY123 and DOY150 was most likely due to the application of the LDM to the plots, in combination with the increasing soil temperatures during that period which facilitated mineralization of organic matter. The general rate of increase was faster for the CT treatment, despite fluctuations coincident with rainfall events (data not shown), with the level rising to nearly two times higher than for the NT treatment on DOY150, which was at near peak availability (data not shown). This large difference in the DOY150 values was likely due to higher microbial activity resulting from soil aeration and soil structure changes of the CT treatment. Such effects on microbial activity in tilled soil have been reported by Doran (1987) and Randall et al. (1997).

The significant decline in soil $\text{NO}_3\text{-N}$ level beyond DOY150 to DOY199 for both treatments was likely due to a combination of early vegetative growth crop utilization and leaching from several heavy rainfall events that occurred during that period. The continued decline between DOY199 and DOY236 (harvest date) was likely due only to crop utilization, as rainfall during that period was substantially lower. The pre-seeding and harvest date soil $\text{NO}_3\text{-N}$ levels were not significantly different which indicates that the level at harvest had returned to equal the level at pre-seeding.

With respect to using the SNMS, soil $\text{NO}_3\text{-N}$ changes were measured over the study period, and response differences between the CT and NT treatments were able to be detected. This result clearly demonstrates the ability of the SNMS to measure soil $\text{NO}_3\text{-N}$ at any time in a wheat production system before or after the addition of LDM and when either CT or NT is used as a tillage management practice.

Plant tissue total nitrogen

ANOVA results showed no significant difference in the response of tissue Total N to the CT and NT treatments; however a significant Day effect was detected (Table 3). Further analysis of this effect (Fig. 7) indicates there were significant differences in mean tissue Total N level between grain set (DOY199, 67DAP), grain filling (DOY213, 81DAP), and maturity (DOY227, 95DAP), but no significant difference thereafter.

At the approximate time of grain set (DOY199, 67DAP) the plant tissue Total N level was at 3.0%. As grain setting progressed, tissue Total N decreased until the grain filling stage was reached (approx. DOY213, 81DAP) after which the rate of decrease quickened (between DOY213 and DOY227, 95DAP) during grain filling and flag leaf senescence. Between DOY227 and DOY236 (104DAP) tissue Total N changed insignificantly indicating maturity had been reached and senescence had been completed. These results are characteristic of Total N levels and re-translocation from

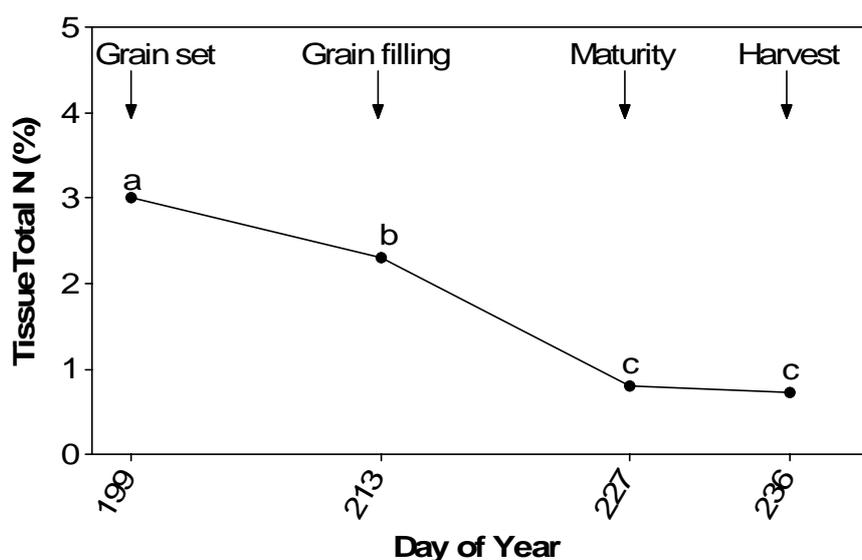


Fig. 7. Plant tissue Total N response in wheat flag leaves over the study period and at approximate phenological stage. Least squares means sharing the same letter are not significantly different at the 5% level of significance. Although there are some gaps in the time scale, a line graph is used rather than a bar chart to better illustrate trends evident.

leaf tissues to developing grains in wheat reported by other researchers (Crawford et al., 1961; Gardner and Jackson, 1976; Moll et al., 1982; Simpson et al., 1983; Abreu et al., 1993; Barbottin et al., 2005).

Plant tissue-sap nitrate, grain yield, and grain total nitrogen

Mean plant tissue-sap $\text{NO}_3\text{-N}$ (CT = $96.6 \mu\text{g g}^{-1}$, NT = $116.8 \mu\text{g g}^{-1}$), grain yield (CT = 1139 kg ha^{-1} , NT = 943 kg ha^{-1}), and grain Total N (CT = 1.85%, NT = 1.87%) all showed no significant difference in response to the CT and NT treatments (Table 2). These results suggest that the plants responded equally well at producing final grain yield under either the CT or NT tillage management practice and despite there being significant changes in soil $\text{NO}_3\text{-N}$ level over the growing season as discussed above.

Carrot production system experiment

Soil nitrate

The significant Day \times Trt interaction (Table 3) suggests that the effect of fertility amendment treatment on soil $\text{NO}_3\text{-N}$ level in carrot was not uniform throughout the study period and that soil $\text{NO}_3\text{-N}$ level may have been influenced differently by weather conditions, crop effects, or a combination of both at various times over the

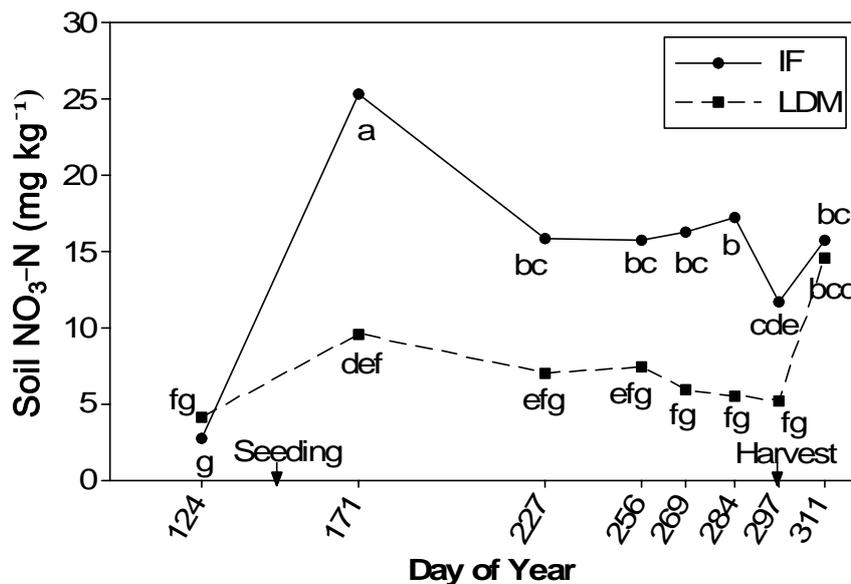


Fig. 8. Soil NO₃-N response at 0–15-cm depth to inorganic fertilizer (IF) and liquid dairy manure (LDM) treatments in the carrot field over the study period. Least squares means sharing the same letter are not significantly different at the 5% level of significance. Although there are some gaps in the time scale, a line graph is used rather than a bar chart to better illustrate trends evident.

study period. This effect was most pronounced early in the growing season, at the end of the growing season, and post-harvest (Fig. 8).

Over the study period, the general trend in soil NO₃-N level was the same for both IF and LDM: starting at pre-seeding level (DOY124), rising to near peak availability on DOY171 (peak data not shown), then dropping over the active growth of the carrot until root harvest on DOY297, followed by a significant post-harvest increase (DOY311). Again, this general trend follows that reported by Lockman and Storer (1990) and Villar-Mir et al. (2002).

The initial increase in soil NO₃-N between DOY124 and DOY171 was most likely due to the application of the fertilizer treatments to the plots and also soil tillage from row-forming and planting equipment in combination with the increasing soil temperatures during that period which facilitated mineralization of organic matter. The general rate of increase was faster for the IF treatment, despite fluctuations coincident with rainfall events (data not shown), with the level rising to nearly three times higher than for the LDM treatment on DOY171, which was at near peak availability (peak data not shown). This large difference in the DOY171 levels was likely due to higher availability of N for the IF treatment despite the same amount of N-equivalent being applied (Table 1) for both treatments. On the other dates during plant growth (up to

harvest on DOY297), the soil $\text{NO}_3\text{-N}$ level for the IF treatment remained in the order of two times higher than for the LDM treatment. The LDM treatment level returned to and remained at pre-seeding level (no significant difference) throughout the growing season.

The soil $\text{NO}_3\text{-N}$ level for the IF treatment between DOY284 and DOY297 dropped significantly, likely from leaching due to the rainfall during that time period (51.5 mm total). The soil $\text{NO}_3\text{-N}$ level for the LDM treatment, however, remained stable (no significant difference) for that same period. This could be reflective of the ability of the LDM treated soil to resist leaching, or just that the levels were so low that very little was available for leaching.

There was a significant increase in soil $\text{NO}_3\text{-N}$ for each treatment after harvest at the end of the growing season between DOY297 and DOY311 (Fig. 8). It is suspected that these increases were partially due to a 'tillage effect' during mechanical harvesting. The harvester's digger blade essentially chisel plowed the soil, mixing and reducing the size of soil structures, thereby increasing soil aeration. Increased aeration increased microbial activity, which in turn caused a rapid release of available $\text{NO}_3\text{-N}$ into the soil matrix through mineralization. Again as cited above, such effects on microbial activity in tilled soil have been reported by Doran (1987) and Randall et al. (1997). As well, there was a soil temperature increase during this period, typical of the geographic area, which likely would have further contributed to increased microbial activity. Evidence of these effects is indicated in our data as well. A similar increase in soil $\text{NO}_3\text{-N}$ can be seen in Fig. 6 between DOY123 and DOY150 for the tilled treatment in the wheat field, where, at the beginning of the growing season LDM had been applied and disced into the soil, and a soil temperature increase followed. Remaining organic material from the LDM application, carrot tops residue, un-harvested carrot roots, and fibrous root material, that generally have a relatively low C:N ratio, were the likely mineralization sources of the $\text{NO}_3\text{-N}$. For the LDM treatment, the increase was larger than that for the IF treatment likely because of the presence of a higher mineralization capacity of the LDM plots built up over the growing season. These conclusions are strongly supported by the work of Havlin et al. (1990) who found higher mineralization capacity from organic fertilizer and increased organic-N level with increasing residue level under both tilled and no-tilled conditions in their study of several crops, crop rotations, and tillage effects on soil organic carbon and nitrogen. Post-harvest increases in soil $\text{NO}_3\text{-N}$ between September and October were also found by Lockman and Storer (1990) in their study of soil nitrate and ammonium with area and date sampled.

With respect to the performance of the SNMS, these results clearly demonstrate that it can be successfully used to measure soil $\text{NO}_3\text{-N}$ level at any time in a carrot

production system before or after the addition of fertilizer and when either IF or LDM is used as a fertility management practice.

Plant tissue-sap nitrate

ANOVA results showed no significant difference in the response of plant tissue-sap $\text{NO}_3\text{-N}$ to the IF and LDM treatments, however a significant Day effect was detected (Table 3). Further analysis of this effect (Fig. 9) indicates that there were significant differences in mean tissue-sap $\text{NO}_3\text{-N}$ level between mid-growth (DOY227, 76DAP), root bulking (DOY256, 105DAP), and homeostasis (DOY284, 133DAP), but no significant difference thereafter.

The period between DOY227 (76DAP) and DOY256 (105DAP) corresponds approximately to the mid-growth stage for carrot. During this period, the plant tissue-sap $\text{NO}_3\text{-N}$ levels were sufficient for maximum top-biomass growth and root yield, with the average concentration of 218.8 mg L^{-1} (original concentration data [mg L^{-1}] not shown in figure as we are reporting in units of content [$\mu\text{g g}^{-1}$]) being higher than the 200 mg L^{-1} required according to Warncke (1996). Between DOY256 and DOY284 (133DAP) the tissue-sap $\text{NO}_3\text{-N}$ level dropped off dramatically indicating re-translocation took place from leaf tissue to roots during active root bulking. Between DOY284 (133DAP) and DOY297 (harvest date, 146DAP), the tissue-sap $\text{NO}_3\text{-N}$ level remained unchanged (no significant difference), indicating that no more re-translocation had occurred and that homeostasis had been reached on DOY284 (133DAP). These results are consistent with tissue-sap $\text{NO}_3\text{-N}$ changes during carrot growth reported by other researchers (Blanc et al., 1979; Venter, 1979).

Plant tissue total nitrogen

The significant Day \times Trt interaction (Table 3) suggests that the effect of fertility amendment treatment on plant tissue Total N level in carrot was not uniform throughout the study period and that tissue Total N level may have been influenced differently by weather conditions, crop effects, or a combination of both at various times over the study period. However, multiple means comparison results (Fig. 10) indicate that the only significant difference in tissue Total N response for the IF and LDM treatments was at harvest (DOY297, 156DAP).

Tissue Total N level at harvest (DOY297, 156DAP) for the LDM treatment was well below the sufficiency range for carrots of 3.0 to 3.5% as reported by Mills and Jones (1996). It was noted during sampling that the plants in the LDM treatment plots appeared weaker and slightly yellowed compared to plants in the IF treatment plots, especially the older bottom leaves from which the tissue samples were collected (leaves seven and nine).

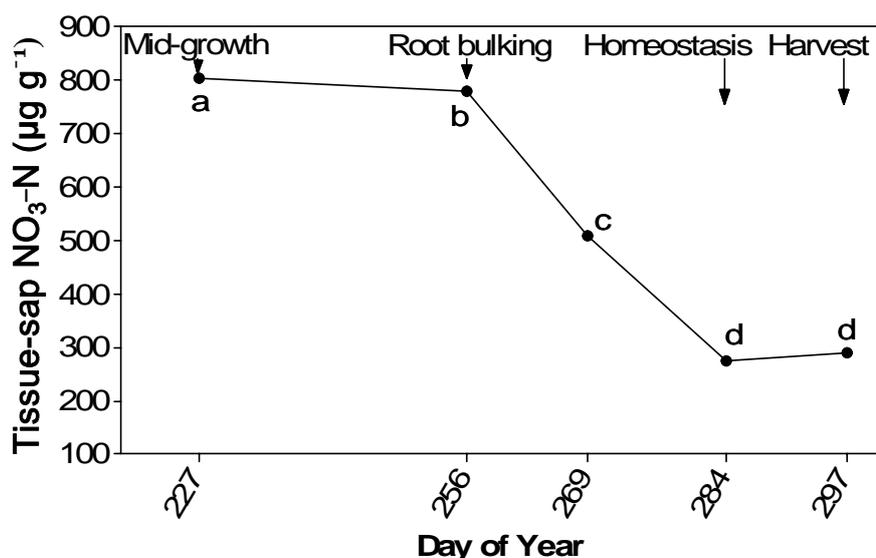


Fig. 9. Plant tissue-sap NO₃-N response in carrot leaves (seven and nine) over the study period and at approximate phenological stage. Least squares means sharing the same letter are not significantly different at the 5% level of significance. Although there are some gaps in the time scale, a line graph is used rather than a bar chart to better illustrate trends evident.

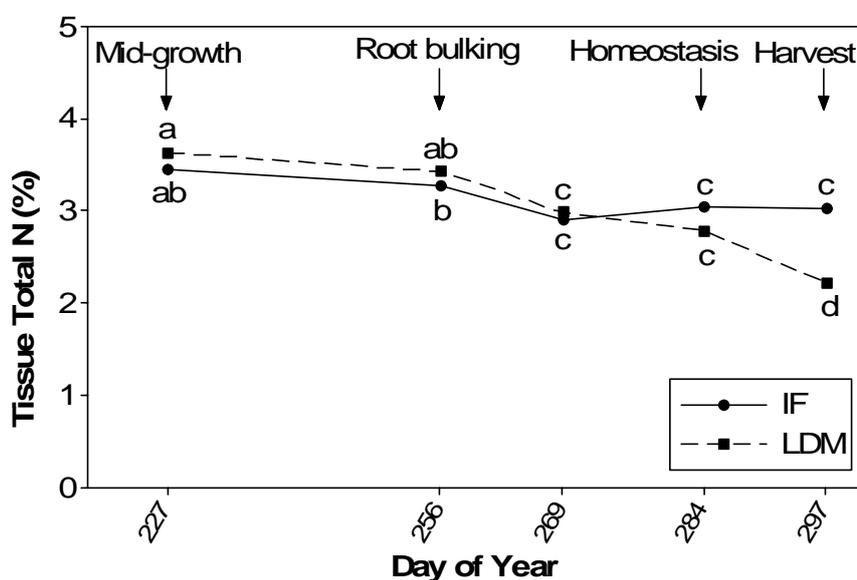


Fig. 10. Plant tissue Total N response in carrot leaves (seven and nine) to inorganic fertilizer (IF) and liquid dairy manure (LDM) treatments in the carrot field over the study period and at approximate phenological stage. Least squares means sharing the same letter are not significantly different at the 5% level of significance. Although there are some gaps in the time scale, a line graph is used rather than a bar chart to better illustrate trends evident.

As well, the field was waterlogged from the heavy rains, despite having tile drainage. The waterlogged soil may have been in a state of short-term, rain-fall-induced nitrification which was limiting N availability to the plants. The weakness of the LDM treated plants at that time likely resulted in a higher rate of leaf senescence that enabled sufficient N re-translocation to meet the needs of the bulking roots. As well, there was likely a leaching effect of the heavy rains on the senescing leaves.

Root yield and root total nitrogen

Despite the significant differences in soil NO₃-N levels between the treatments, significant changes over the growing season, and the persistently low levels for the LDM treatment, there was no significant difference in fresh root yield (IF = 40.5 t ha⁻¹, LDM = 39.8 t ha⁻¹) or root Total N (IF = 1.53%, LDM = 1.59%) between the treatments (Table 2). These results suggest that the plants took up enough N during shoot growth to sustain root bulking, thereby utilizing stored N for root bulking rather than relying on available N in the soil. These results are also further evidence that the drop in soil NO₃-N level for the IF treatment between DOY284 and DOY297 discussed above was due to leaching, since the plant-required nitrogen was obviously in excess for the IF treatment. As well, these results indicate the ability of the LDM treatment to reduce the potential of groundwater contamination from soil NO₃-N leaching without sacrificing yield. Gordon et al. (2005) reported a similar ability for liquid hog manure treatment during their study of nitrate and pesticide leaching from a processing carrot production system in Nova Scotia.

These results further suggest that although there were significant changes in soil NO₃-N level over the growing season, and between the IF and LDM treatments, they did not affect very much what was happening in the carrot plants. This finding stresses the environmental implications of managing soil NO₃-N in a carrot production system. Similarly, Villar-Mir et al. (2002) found that there was no relationship between soil-available nitrogen and above ground plant uptake in their two-year study in irrigated cornfields when required-N level was exceeded.

Summary and conclusions

An on-the-go soil nitrate mapping system (SNMS) has been developed that provides a way to quickly, accurately and cost effectively collect data necessary for analyzing small-scale variation in soil NO₃-N while crops are being grown, thus enabling this variation to be linked to crop performance. This study was conducted to demonstrate that the SNMS could be used as an effective tool to assist crop scientists with their experimental investigations of plant and soil nitrate responses under a variety of field

management conditions. Within that context, multifaceted sub-experiments in two crop production systems (wheat and carrot) having high economic importance to the Atlantic region of Canada in particular, and internationally in general, were conducted. In wheat under organic fertilizer management, the effect of conventional tillage vs. no tillage on soil nitrate, plant nitrogen and yield responses were determined. In carrot under conventional tillage management, the effect of inorganic fertilizer vs. organic fertilizer on soil nitrate, plant nitrogen and yield responses were determined.

Soil nitrate mapping system use

The SNMS was successfully used to measure soil NO₃-N level at any time during the study period in both wheat and carrot production systems when the plants were not growing using fully automatic mode, and when plants were growing using manual-sampling and auto-analysis mode. As well, it was successfully used under the management practices of (i) conventional tillage and no tillage, (ii) with and without the addition of fertilizer to the soil, and (iii) inorganic fertilizer and liquid dairy manure fertility treatments. The proof-of-concept use of the SNMS as a tool for assisting with the conduct of agronomic experiments was successfully demonstrated.

Wheat production system responses

The only significant difference in mean soil NO₃-N level between the two tillage treatments occurred early in the growing season shortly after fertilizing, when the level for the CT treatment was nearly two times higher than for the NT treatment.

There was no significant difference in the response of plant tissue Total N to the CT and NT treatments; however a significant Day effect was detected. Significant differences were found in mean tissue Total N level between grain set, grain filling, and maturity, but no significant difference thereafter. Mean plant tissue-sap NO₃-N (CT = 96.6 µg g⁻¹, NT = 116.8 µg g⁻¹), grain yield (CT = 1139 kg ha⁻¹, NT = 943 kg ha⁻¹), and grain Total N (CT = 1.85%, NT = 1.87%) all showed no significant difference in response to the CT and NT treatments. These results suggest that the plants responded equally well at producing final grain yield under either the CT or NT tillage management practice and despite there being significant changes in soil NO₃-N level over the growing season.

Carrot production system responses

Early in the growing season shortly after fertilizing, the soil NO₃-N level for the IF treatment was nearly three times higher than for the LDM treatment, while for the remainder of the growing season, it remained in the order of two times higher. There

was a significant increase in soil $\text{NO}_3\text{-N}$ for both the IF and LDM treatments after harvest at the end of the study period in late-Fall. It is suspected that these late-Fall increases were due to a 'tillage effect' from mechanical harvesting in combination with a short-term increase in soil temperature typical for the geographic area.

There was no significant difference in mean plant tissue-sap $\text{NO}_3\text{-N}$ response to the IF and LDM treatments; however a significant Day effect was detected. During mid-growth stage, plant tissue-sap $\text{NO}_3\text{-N}$ levels were sufficient for maximum top-biomass growth and root yield and then dropped of dramatically during active root bulking until homeostasis was reached. The level remained unchanged between homeostasis and the time the roots were harvested.

Tissue Total N level for the IF treatment dropped significantly during active root bulking and then stabilized for the remainder of the growing season. During this same period for the LDM treatment, tissue Total N level also dropped significantly, but unlike for the IF treatment, continued to drop dramatically instead of stabilizing.

There was no significant difference in fresh root yield (IF = 40.5 t ha^{-1} , LDM = 39.8 t ha^{-1}) or root Total N (IF = 1.53%, LDM = 1.59%) between the treatments. These results suggest that the plants took up enough N during shoot growth to sustain root bulking, thereby utilizing stored N for root bulking rather than relying on available N in the soil. These results further suggest that although there were significant changes in soil $\text{NO}_3\text{-N}$ levels over the growing season, and between the IF and LDM treatments, they did not affect very much what was happening in the carrot plants. This finding stresses the environmental implications of managing soil $\text{NO}_3\text{-N}$ in a carrot production system.

CHAPTER 8

General discussion

The research program conducted and presented in this thesis has resulted in the development of an automated on-the-go soil nitrate mapping system (SNMS). In this general discussion, the SNMS is briefly described and the significance of its development is discussed. Next, the achievements of the research program are presented and discussed. Closing remarks commenting on the practicality, innovativeness, and potential for future use of the SNMS are then made, followed by several recommendations for further research.

Brief description of the soil nitrate mapping system

The SNMS is an electro-mechanical machine that automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyzes it electrochemically for nitrate concentration in real-time (6 s) using a nitrate ion-selective electrode (NO_3^- -ISE) as the analysis instrument. Additionally, global positioning system (GPS) geo-referenced position data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field being sampled. The SNMS consists of six sub-assemblies: (1) soil sampler, (2) soil metering and conveying, (3) nitrate extraction and measurement, (4) auto-calibration, (5) control, and (6) GPS.

The SNMS can be used to analyse soil samples automatically while on-the-go or manually while stationary by hand-placing samples into its nitrate extraction and measurement sub-assembly. It is envisioned that the system will eventually be used in practice as (i) a tractor-mounted version and (ii) as a ‘suitcase’ (portable) version. The SNMS currently has the ability to sample (i) with lab-grade accuracy, (ii) at any desired spacing down to approximately one meter (very fine scale) when operated in manual mode, (iii) at the rate of approximately two samples per minute, and (iv) at approximately $1/10^{\text{th}}$ the cost of conventional lab analysis.

Significance of the development of the soil nitrate mapping system

The development of the SNMS is significant from several perspectives. These perspectives include (i) linking soil $\text{NO}_3\text{-N}$ variation to crop growth, (ii) environmental monitoring of soil $\text{NO}_3\text{-N}$, (iii) developing site-specific crop management practices, and (iv) assessing soil nitrate variation. These perspectives are discussed below.

Linking soil nitrate variation to crop growth

Soil $\text{NO}_3\text{-N}$ in agricultural fields is highly variable spatially and temporally, and at different measurement scales and level of aggregation (Heuvelink and Pebesma, 1999). This variation of $\text{NO}_3\text{-N}$ in the soil depends on many soil forming, chemical, microbial, plant growth, environmental, and management factors that influence soil nitrogen dynamics (Addiscott, 1983; Wagenet and Rao, 1983; Trangmar et al., 1985).

Much research has been dedicated to assessing and characterizing this variation to improve our understanding of the effects of soil $\text{NO}_3\text{-N}$ on crop growth and yield within agro-ecosystems (Almekinders et al., 1995). For approximately the last 20 years in particular, many researchers have been attempting to study the levels of nitrogen in plants at the various phenological stages in correlation with availability and distribution of soil $\text{NO}_3\text{-N}$ levels at the same times, and on a small-scale, to develop better site-specific nitrogen management practices. However, the high costs and high labor intensity of collecting this data at the required sampling intensity, in addition to the time-lag involved between sampling and analysis have been cited by these researchers as impediments to being able to conduct this work (Engel et al., 1999; Birrell and Hummel, 2000; Schröder et al., 2000; Ehsani et al., 2001; Adamchuk et al., 2004a). The SNMS overcomes these impediments by providing a way to quickly, accurately, and affordably collect the data necessary to analyze the small-scale variation in soil nitrate in space and over time, and while crops are being grown thus enabling this variation to be linked to crop growth and yield.

Environmental monitoring of soil nitrate

The importance of dealing with environmental issues associated with the use of nitrogen fertilizers is increasing. Water sources contamination and associated socio-economic costs indicate a great need for precise soil fertility management practices – using the right form of fertilizer, applied at the right time, in the right amount, and in the right way (Power and Schepers, 1989; Dinnes et al., 2002). As such, better soil nitrogen management practices, including more accurate placement of fertilizers with application equipment, could help minimize the contribution by agriculture to the NO_3^- pollution problem.

The seriousness and extent of NO_3^- contamination of water sources and its effect on drinking water quality has prompted policy makers to revise laws to ensure the safety of public water supplies. These include amendments to the Water Pollution Control Acts in Canada and the United States, the European Community Nitrate Directive, and the Mineral Policy in the Netherlands.

The SNMS provides the ability to quickly, accurately, and affordably collect the data necessary for environmental monitoring of NO_3^- levels in agricultural fields and

water sources. In this way, regulators can more closely monitor NO_3^- status and thus take quicker action when needed. Farmers will be able to measure and document soil $\text{NO}_3\text{-N}$ levels in their fields thus improving traceability and improving their ability to be compliant with any current and future legislation requiring control of nitrogen fertilizers.

Developing site-specific crop management practices

Researchers and farmers involved with *precision agriculture* are working to develop site-specific crop management (SSCM) practices which offer the potential for increased production efficiencies to farmers, while at the same time offering assurances to the public those practices are being conducted in the most environmentally friendly way (Birrell and Hummel, 2000; Ehsani et al., 2001; Adamchuk et al., 2004a; Bongiovanni and Lowenberg-DeBoer, 2004; Bourenanne et al., 2004).

The inability to assess soil and plant data rapidly and inexpensively in the field has been identified as one of the biggest limitations of *precision agriculture* (Ehsani et al., 2001; Adamchuk et al., 2004b). In particular the lack of a soil $\text{NO}_3\text{-N}$ measurement system is a major roadblock (Ehsani et al., 1999). The SNMS overcomes this roadblock by providing an economical, automated, on-the-go technology that can be used to intensely and accurately collect data on the current status of soil $\text{NO}_3\text{-N}$ any time during the growing season.

Assessing soil nitrate variation

Geostatistical techniques have been developed to provide practically useful mathematical tools for assessing the spatial and temporal variation and spatial structure of soil properties including soil $\text{NO}_3\text{-N}$ (Journel and Huijbregts, 1978; Burgess and Webster, 1980; Webster and Burgess, 1984; Isaaks and Srivastava, 1989; Webster and McBratney, 1989; Cressie, 1991; Van Noordwijk and Wadman, 1992; McBratney and Pringle, 1997, 1999).

Research applying these tools on a field-scale, such as through SSCM-experimentation (Pringle et al., 2004), has led to the development of a multitude of methods for determining minimum soil sample spacing, sampling grid layout and cell size (Vieira et al., 1981; Russo, 1984; Webster and Burgess, 1984; Han et al., 1994; Van Meirvenne, 2003; Lauzon et al., 2005), optimum number of samples (Webster and Burgess, 1984), sampling schemes and protocols for pre-planning experimental designs (Trangmar et al., 1985; Chang et al., 1999; Ruffo et al., 2005) and sample bulking strategies (Webster and Burgess, 1984). However, when using these methods for implementing *precision agriculture* practices related to soil nitrogen management,

the “most serious obstacles” are still the need to know the spatial structure in advance and the cost of obtaining this information even though the sampling effort required is much less than for full-scale sampling (Webster and Burgess, 1984; Lark, 1997; McBratney and Pringle, 1999; Jung et al., 2006). The SNMS overcomes these serious obstacles by providing a rapid and cost effective technology for researchers interested in more closely studying soil $\text{NO}_3\text{-N}$ variation and its effects, either on crop growth or the environment.

Achievements of the research program

The research work presented in this thesis has resulted in several significant achievements in meeting the objectives of the program. These achievements include (i) determining that a NO_3^- -ISE could be used in a soil-slurry solution and under what operating variables, (ii) developing a fully-functioning prototype of the SNMS, (iii) testing the performance of the soil sampler on a field scale, (iv) validating the accuracy of the nitrate extraction and measurement sub-assembly on a field scale, (v) demonstrating that the SNMS can be a useful tool to assist soil scientists with experimental investigations of the spatial and temporal aspects of soil $\text{NO}_3\text{-N}$, and (vi) demonstrating that the SNMS can be a useful tool to assist crop scientists with experimental investigations of plant and soil nitrate responses under a variety of field management conditions. These achievements are presented and discussed under the corresponding chapter titles below.

Laboratory evaluation of the ion selective electrode for use in an automated soil nitrate monitoring system

Laboratory work conducted determined that a NO_3^- -ISE could be used in a soil-slurry solution and under what operating variables (Chapter 2). Typically in the laboratory, these electrodes were inserted into a clarified extract solution during NO_3^- measurement. As such, the first prototype SNMS, developed by Adsett (1990), used a specially designed unit wherein the soil was mixed with deionized water and then the solution was clarified before being presented to the electrode for NO_3^- measurement. Difficulties in getting a clear solution often caused clogging of the unit. Operating variables investigated included soil/extractant ratios and solution clarity, electrode response time, repeatability, and output signal stability.

Laboratory tests conducted using a Chaswood clay loam soil indicated NO_3^- concentrations did not vary significantly with soil:extractant ratio or extract clarity. As well, reliable estimates of NO_3^- concentration were made in less than 4 s using normalized response time curves. As a result of the work, it was concluded that the

NO_3^- -ISE was well suited for use in an automated on-the-go system provided regular calibration of the electrode was performed. A successful system, however, would depend not only on a properly functioning electrode, but also on properly functioning mechanical components and the ability to collect and analyze samples quickly.

Development of an automated on-the-go soil nitrate monitoring system

Developmental research work used bench-top models and lab testing of the various new mechanical components (units) to create a fully-functioning second-generation prototype (Chapter 3). The new units developed enabled the functions of soil sampling, soil metering and conveying, nitrate extraction and measurement, and electronic control of the system's operation to be performed in the field on-the-go. These units were integrated together, mounted on a tractor, and subjected to preliminary field testing. This research work also included successful development of a field (soil) calibration method for speeding up the measurement process to facilitate quick sample analysis while on-the-go.

Overall, the performance of the prototype in the lab was found to be very satisfactory. The lab testing confirmed that the NO_3^- -ISE was suitable for rapid in-field soil $\text{NO}_3\text{-N}$ measurement with proper calibration procedures and its repeatability was excellent. The criterion developed for speeding up the measurement process showed that in silty clay loam soil, the actual, or final $\text{NO}_3\text{-N}$ concentration of a sample could be sufficiently predicted within 6 s of the commencement of extraction.

The preliminary field testing showed that more work needed to be done before using the system extensively in the field. Several mechanical and electronic issues were identified that were not obvious during the lab testing. Despite these issues, however, the prototype worked well enough that it was deemed worthwhile for development work to continue. This continued work resulted in the third-generation prototype which was demonstrated to Greenland Nieuw-Vennep BV and European researchers in the Netherlands in 1996 as part of commercialization efforts. For various business reasons, these efforts were not successful. Development work continued resulting in a fourth-generation prototype in 2001 which included a GPS unit. This prototype was used to successfully map soil $\text{NO}_3\text{-N}$ levels in fields located on the farm of the Nova Scotia Agricultural College (data not reported) and confirmed that the SNMS was ready for extensive field-scale testing.

Field performance testing of an on-the-go soil sampler for an automated soil nitrate mapping system

The soil sampler was subjected to extensive field-scale performance testing in five field conditions to determine the validity of its 'uniform bulk density' design principle,

the uniformity of pocket fullness, the relationship between pocket fullness and delivered ‘weight’ (mass), and the uniformity of delivered weight (Chapter 4). An essential requirement of the sampler is the ability to reliably collect a soil sample of known ‘weight’ (mass). The design principle of the sampler is based on the hypothesis that if a uniform bulk density sample could be collected in a device of fixed volume, then the mass of the sample would be known and constant. As such, indirect estimation of the sample mass could be accomplished thus avoiding the extreme mechanical difficulties associated with trying to directly measure the mass of a small sample while on-the-go.

The results of the field-scale testing revealed that for all field conditions tested, the overall uniformity of sample bulk density was 92.9%. The practical effect of this level of uniformity on delivered weight was determined to cause less than a 5.5% deviation in delivered weight in 83.6% of the cases. It was concluded that the sampler’s main design principle of ‘uniform bulk density’ was valid for all intents and purposes of field use.

Among fields, pocket fullness means ranged between 80.9–100.8% and the coefficient of uniformity ranged between 81.3–90.1%. For all field conditions data combined, the mean pocket fullness was 89.9% and the coefficient of uniformity was 83.6%. Pocket fullness uniformity was found to be field-condition specific, related mostly to localized high clay content at several sampling locations in three of the fields.

Delivered weight was found to be consistently very highly correlated to pocket fullness over all field conditions. The linear relationship between delivered weight and pocket fullness for all field conditions data combined was determined to be:

$$\text{Delivered Weight} = -1.186 + 16.804 \times \text{Pocket Fullness} \quad (R^2 = 0.979, n = 140).$$

Overall, the sampler had a mean delivered weight error of 10.9% and a coefficient of uniformity of 82.0%. Delivered weight uniformity was found to be field-condition specific as well, again related mostly to localized high clay content at several sampling locations in three of the fields. It was concluded that delivered weight uniformity of the sampler, particularly when used in clayey soils, should be increased by improving the design.

How to improve the design now becomes a question for debate. Should improvements strive to obtain a consistently delivered known ‘weight’ (mass) of soil at some percentage of pocket fullness (i.e. a not quite full pocket), or a consistently full pocket of known weight? In either case it does not really matter what the relative magnitude of the weight is as long as it is known and consistent. Therefore, it is important that the current design of the sampler be improved to either (i) ensure better consistency in delivered weight if the ‘uniform bulk density’ design principle is

continued to be used, or (ii) incorporate a method of ‘weighing’ individual samples as they are being delivered. In the first case it may also be possible to incorporate a vision system into the design and use the pocket fullness and delivered weight relationship to estimate the weight based on a measurement of pocket fullness. In the second case, it is expected that mechanical difficulties with weighing a small sample while on-the-go would still be an issue.

Field-scale validation of an automated soil nitrate measurement system

Extensive field-scale testing of the nitrate extraction unit to validate its accuracy in the field (Chapter 5) was performed. The field conditions under which the unit was tested included wheat and carrot crops, conventional tillage vs. no tillage, inorganic vs. organic fertilization, four soil groups, and three time points throughout the season.

This field-scale testing determined the level of agreement between SNMS soil $\text{NO}_3\text{-N}$ measurements and standard lab soil $\text{NO}_3\text{-N}$ measurements was excellent and resulted in the development of regression equations to enable field measurements using the SNMS to be obtained with lab-grade accuracy. The results obtained strongly suggest that the SNMS is so robust that it can be used for both wheat and carrot crops, as well as in different soil groups, fertility levels, tillage conditions, and at any time throughout the season.

It was also determined as a result of this testing that at the field-scale there was little practical difference in results obtained when using either integer math or whole math data processing methods. The implication of this result is that future designs of the SNMS’ control system can continue to use cheaper integer math chip technology for processing the NO_3^- -ISE readings.

In answer to the question of whether a soil moisture content sensor is necessary for achieving accurate results in the field, it was determined that accurate predictions of lab values can be obtained by simply using either of the integer math or whole math data processing regression equations developed for processing the NO_3^- -ISE readings. Therefore, future designs of the SNMS would not need a soil moisture sensor, ultimately saving on manufacturing cost and keeping the system simpler.

Using an automated on-the-go mapping system to assess the spatial and temporal aspects of soil nitrate

Using data collected by the SNMS on a fine-scale sampling grid and a combination of classical and geostatistical analytical techniques and tools, the spatial and temporal aspects of $\text{NO}_3\text{-N}$ variation in a wheat production system at seven time points covering pre-seeding, growing season, and post-harvest soil conditions, as well as the intrinsic spatial structure of $\text{NO}_3\text{-N}$ present in the field, were assessed (Chapter 6).

This research work was conducted to demonstrate that, as a proof-of-concept, the SNMS could be used as an effective tool to assist soil scientists with experimental investigations of the spatial and temporal aspects of soil NO₃-N.

Being able to analyze samples with the SNMS on a fine-scale sampling grid much quicker, as accurately as, and more affordably than conventional lab analysis means, in practical terms, that the SNMS can provide a long-awaited solution to the problem of conducting soil NO₃-N variation assessment experiments at an affordable cost. In addition, the SNMS provides a way to collect data so that the spatial structure of the NO₃-N in a field of interest is “known in advance” of the experimental planning. With this knowledge, the experimental sampling scheme and optimal sample size required for statistical analysis reliability can be prior determined with confidence.

The SNMS was successfully used to measure soil NO₃-N level during the study period and to monitor spatial and temporal variation over time. As well, accurate, high resolution posted values (contour) maps were generated that give excellent visual pictures of the NO₃-N spatial variation that was evident just prior to, at peak nitrogen release, during, and just after the growing season.

The SNMS was able to be used to assess the spatial structure soil NO₃-N variation. Very strong proportional effect relationships were found between the data sets mean and standard deviation values ($R^2 = 0.972$) and the squared mean and variance values ($R^2 = 0.996$). These relationships can be used for predicting high-quality average and proportional variograms, which in turn can be used for determining NO₃-N soil sampling schemes for the field to a desired level of accuracy.

It was found that soil NO₃-N levels exhibited significant positive autocorrelation at separation distances ≤ 20 m in the test field. Consequently, for accurate estimation of levels in un-sampled locations by kriging, the sample spacing in this field should be limited to no more than 20 m. Further, it was found that the separation distance at which no autocorrelation was evident varied between approximately 20–45 m. This result indicates that the range of intrinsic spatial structure beyond which NO₃-N values did not have spatial dependency was likely approximately 45 m. This distance, then, would be the minimum sample spacing for conducting soil NO₃-N experiments in this field that require analyses by classical statistical methods.

Spatial autocorrelograms of NO₃-N levels exhibited a high degree of similarity in their shapes indicating a high likelihood that the intrinsic spatial structure of NO₃-N variation was temporally stable over the study period. At first blush, this finding seemed to be a paradox – how could stability and variation co-exist? However, upon closer reflection, it was concluded that temporal stability of spatial structure indicates that the variation of NO₃-N level followed a similar pattern of change over time, not

that the level was the same everywhere and at all times.

Variogram models of soil NO₃-N spatial structure were developed for each of the sampling dates. These were of the isotropic spherical type and had high R² values ranging between 0.904–0.999 combined with very low RSS values. These very high goodness-of-fit measures for all models indicated that they describe the spatial structure of NO₃-N variation very well. Similarities in the spatial structure of soil NO₃-N on the sampling dates were evident as these models had similar slopes, nuggets, ranges, and nugget-to-sill ratios. Spatial dependency was found overall to be moderate. Since the models represent data from time-spaced sampling dates, their similarity, as does the similarity in the spatial autocorrelograms, indicates a high likelihood that the intrinsic spatial structure of soil NO₃-N in this field exhibited temporal stability over the study period.

A scaled average variogram model that very likely accurately represents the intrinsic spatial structure present in the field was created having a sill of 1.005, a nugget of 0.331, and a range of 44 m. Future researchers working in this field could apply this model to this field as a “known in advance” variogram for experimental planning purposes.

Using an automated on-the-go soil nitrate mapping system to investigate plant and soil nitrate responses in wheat and carrot production systems

Using data collected by the SNMS on small-scale sampling grids at seven time points before, during, and after crops were being grown, the variation in soil NO₃-N levels in wheat and carrot production systems over time were linked to crop performance (Chapter 7). This research work was conducted to demonstrate that, as a proof-of-concept, the SNMS could be used as an effective tool to assist crop scientists with their experimental investigations of plant and soil nitrate responses under a variety of field management conditions. In wheat under organic fertilizer management, the effect of conventional tillage vs. no tillage on soil nitrate, plant nitrogen and yield responses were determined. In carrot under conventional tillage management, the effect of inorganic fertilizer vs. organic fertilizer on soil nitrate, plant nitrogen and yield responses were determined.

The SNMS was successfully used to measure soil NO₃-N level at any time during the study period in both wheat and carrot when the plants were not growing using fully automatic mode, and when plants were growing using manual-sampling and auto-analysis mode.

In wheat, it was determined that the only significant difference in mean soil NO₃-N level between the conventional tillage and no tillage treatments occurred early in the growing season shortly after fertilizing, when the level for the conventional

tillage treatment was nearly two times higher than for the no tillage treatment.

There was no significant difference in the response of plant tissue Total N to the conventional tillage and no tillage treatments; however a significant Day effect was detected. Significant differences were found in mean tissue Total N level between grain set, grain filling, and maturity, but no significant difference thereafter. Mean plant tissue-sap $\text{NO}_3\text{-N}$, grain yield and grain Total N all showed no significant difference in response to the conventional tillage and no tillage treatments. These results suggest that the plants responded equally well at producing final grain yield under either the conventional tillage or no tillage management practice and despite there being significant changes in soil $\text{NO}_3\text{-N}$ level over the growing season.

In carrot, early in the growing season shortly after fertilizing, the soil $\text{NO}_3\text{-N}$ level for the inorganic fertilizer treatment was nearly three times higher than for the liquid dairy manure treatment, while for the remainder of the growing season it remained in the order of two times higher. There was a significant increase in soil $\text{NO}_3\text{-N}$ for both the inorganic fertilizer and liquid dairy manure treatments after harvest at the end of the study period in late-Fall. It is suspected that these late-Fall increases were due to a 'tillage effect' from mechanical harvesting in combination with a short-term increase in soil temperature typical for the geographic area.

There was no significant difference in mean plant tissue-sap $\text{NO}_3\text{-N}$ response to the inorganic fertilizer and liquid dairy manure treatments; however a significant Day effect was detected. During mid-growth stage, plant tissue-sap $\text{NO}_3\text{-N}$ levels were sufficient for maximum top-biomass growth and root yield and then dropped dramatically during active root bulking until homeostasis was reached. The level remained unchanged between homeostasis and the time the roots were harvested.

Plant tissue Total N level for the inorganic fertilizer treatment dropped significantly during active root bulking and then stabilized for the remainder of the growing season. During this same period for the liquid dairy manure treatment, tissue Total N level also dropped significantly, but unlike for the inorganic fertilizer treatment, continued to drop dramatically instead of stabilizing. This dramatic drop was attributed to a combination of factors including weakness of the liquid dairy manure treated plants at that time resulting in a higher rate of leaf senescence that enabled sufficient N re-translocation to meet the needs of the bulking roots, rainfall-induced nitrification in the soil which was limiting N availability to the plants, and a leaching effect of the heavy rains on the senescing leaves.

There was no significant difference in fresh root yield or root Total N between the treatments. These results suggest that the plants took up enough N during shoot growth to sustain root bulking, thereby utilizing stored N for root bulking rather than relying on available N in the soil. These results further suggest that although there

were significant changes in soil NO₃-N levels over the growing season, and between the inorganic fertilizer and liquid dairy manure treatments, they did not affect very much what was happening in the carrot plants. This finding stresses the environmental implications of managing soil NO₃-N in a carrot production system.

Closing remarks

The SNMS as presented in this thesis is both practical and innovative. The SNMS is practical in that the system's operation has been completely automated so it can be easily used, it has a variety of field uses, and it is an expandable platform technology that can be easily modified to enable simultaneous use of other types of ion-selective electrodes available for measurement of plant nutrients present in the soil. With simple modifications to the control system, it is also possible to directly vary a fertilizer spreader's application rate while on-the-go in response to variation in soil NO₃-N measurements by sending a control signal to the spreader. The SNMS is innovative in that to the best of my knowledge as of this writing, despite several attempts by others to develop such a system over the last 20 years or so (Adamchuk et al., 2004a), it is the only working tractor-mounted, real-time, in-field soil nitrate mapping system in the world. The majority of research work by others has not progressed past laboratory feasibility studies and testing in soil-bins, and none has resulted in a fully-functioning prototype used for conducting field experiments demonstrating their practical usefulness as has been done with the SNMS as part of the research of this thesis (presented in Chapters 6 and 7).

The SNMS overcomes many of the impediments, roadblocks, and serious obstacles cited by many researchers of measuring and assessing soil NO₃-N variation using conventional methods in terms of sample analysis lag time, high labor requirements, and high costs. It has been demonstrated that soil NO₃-N measurements using the SNMS can be obtained on a fine scale and with lab-grade accuracy. It has been demonstrated that data collected using the SNMS can be used by soil scientists for assessing the spatial and temporal aspects of soil NO₃-N variation, and by plant scientists to assess variation in soil NO₃-N levels in space and over time and link this variation to crop performance.

The SNMS offers the potential to assist researchers working in *precision agriculture* to develop better soil nitrogen practices for agricultural production. It offers farmers the potential to more intensely and precisely analyze variations in soil NO₃-N levels throughout the growing season in correlation with environmental and crop response data in order to make the most sound and site- and time-specific management decisions possible. As well for farmers, it offers the potential for them to

measure and document soil $\text{NO}_3\text{-N}$ levels in their fields thus improving traceability and their ability to be compliant with any current and future legislation requiring control of nitrogen fertilizers. It offers regulators the potential to conduct environmental monitoring of NO_3^- levels in agricultural fields and water sources. Ultimately as a result of its use, the public may be assured that soil nitrogen management practices in agriculture are being conducted in the most environmentally friendly way.

Recommendations for further research

Research work it seems is never completely done. It is inherent to research that when working to answer ones current questions, new questions arise. It was no different during the work conducted for this thesis. Thus, several recommendations for further research are presented below.

Since the beginning of *precision agriculture*, it has been a goal of many researchers to develop variable rate fertilizer spreaders. Several types have been developed and are commercially available. These spreaders are useful to a certain degree, but the missing link to their full effectiveness is still the ability to vary fertilizer application rate in response to precisely what the plant needs; particularly in response to the plant's need for nitrate, but more generally to several nutrient needs (potassium, calcium, magnesium, etc.) as a 'package' and other soil variables, such as pH, that determine their availability. This was the initial vision for the SNMS. Thus, it has been designed as an expandable platform technology that can be easily modified to incorporate the simultaneous use of several different types of ion-selective electrodes. In the immediate term, research should be conducted to develop the agronomic-based algorithms linking soil $\text{NO}_3\text{-N}$ availability to crop performance to enable effective on-the-go control of a fertilizer spreader by the SNMS. In the near term, research should be conducted in combination with plant-related experiments to begin to build in the capability of the SNMS to measure and respond to the availability of a 'soil nutrient package'.

Currently, the SNMS is a tractor-mounted version. It has been mentioned above that it is envisioned that the system will eventually be used in practice also as 'suitcase' (portable) version. During 1996–1997 a bench-top suitcase version was developed and lab-tested (data not reported) that successfully measured NO_3^- and pH in soil-slurry samples. Further research should be conducted to continue development of a fully-functional suitcase version of the SNMS.

The method used in Chapter 7 for measuring plant tissue-sap $\text{NO}_3\text{-N}$ with the NO_3^- -ISE was purposefully developed as a precursor to building in the capability of

the SNMS to measure tissue-sap $\text{NO}_3\text{-N}$ while operated in manual mode. During this research a few samples were put into the SNMS' nitrate extraction and measurement sub-assembly and analyzed. The results obtained indicate that this use of the SNMS is entirely possible. Future research should be conducted to develop this capability for the 'suitcase' version of the system in addition to the capability to analyze soil samples.

Results from the work of Chapter 4 indicate that the delivered weight uniformity of the SNMS' soil sampler, particularly when used in clayey soils, should be increased by improving the design. Some of the other mechanical components could also use some design refinement to improve their reliability and also to speed up their operation to reduce the overall cycle time of the system when operated in automatic mode. This work should be done immediately.

More research should be conducted using the SNMS to investigate further the spatial and temporal variation and spatial structure of soil $\text{NO}_3\text{-N}$ under a wide variety of field conditions. The work presented in Chapter 6 clearly demonstrates that the SNMS can be used for this type of work. Additionally, research should be conducted using the SNMS to investigate further the links between soil $\text{NO}_3\text{-N}$ variation and availability and crop growth and yield under a wide variety of field conditions and crops. The work presented in Chapter 7 clearly demonstrates that the SNMS can be used for this type of work.

The above are but a few of the possibilities for further research now that a technology such as the SNMS is available. I invite readers of this thesis to open their minds to the many possibilities for future research and applications that this technology could be used for in helping them with their search for answers to the many questions they have.

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Summary

The research program conducted at the Nova Scotia Agricultural College, Truro, Nova Scotia, Canada over a 16-year period, and presented in this thesis, has resulted in the development of an automated on-the-go soil nitrate mapping system (SNMS). The research work started in 1991 with laboratory experiments aimed at refining the initial nitrate monitoring system prototype and culminated in 2006–07 with extensive field-scale validation testing of a fully-functioning prototype and the conduct of field experiments demonstrating its practical usefulness in spring wheat (*Triticum aestivum* L.) and carrot (*Daucus carota* L.) crops.

Brief description of the soil nitrate mapping system

The SNMS is an electro-mechanical machine that automatically collects a soil sample (0–15-cm depth), mixes it with water, and directly analyzes it electrochemically for nitrate concentration in real-time (6 s) using a nitrate ion-selective electrode (NO_3^- -ISE). Additionally, global positioning system (GPS) geo-referenced position data are simultaneously recorded at each sampling location to enable a nitrate map to be created for the field being sampled. The SNMS consists of six sub-assemblies: (1) soil sampler, (2) soil metering and conveying, (3) nitrate extraction and measurement, (4) auto-calibration, (5) control, and (6) GPS.

The SNMS can be used to analyse soil samples automatically while on-the-go or manually while stationary by hand-placing samples into its nitrate extraction and measurement sub-assembly. It is envisioned that the system will eventually be used in practice as a tractor-mounted version and as a ‘suitcase’ (portable) version. The SNMS currently has the ability to sample (i) with lab-grade accuracy, (ii) at any desired spacing down to approximately 1 m when operated in manual mode, (iii) at the rate of approximately two samples per minute, and (iv) at approximately 1/10th the cost of conventional lab analysis.

Significance of the soil nitrate mapping system

The development of the SNMS is significant from several perspectives: (i) linking soil NO_3 -N variation to crop growth, (ii) environmental monitoring of soil NO_3 -N, (iii) developing site-specific crop management practices, and (iv) assessing soil nitrate variation.

Many researchers over the last 20 years or so have been attempting to study the levels of nitrogen (N) in plants at the various phenological stages in correlation with availability and distribution of soil NO_3 -N levels at the same times, and on a small-scale,

to develop better site-specific N management practices. However, the high costs and high labor intensity of collecting this data at the required sampling intensity, in addition to the time-lag involved between sampling and analysis are significant constraints to being able to conduct this work. The SNMS overcomes these constraints by providing a way to quickly, accurately, and affordably collect the data necessary to analyze small-scale variation in soil nitrate in space and over time while crops are being grown, thus enabling this variation to be linked to crop growth and yield.

The importance of dealing with environmental issues associated with the use of N fertilizers in agriculture is increasing. The seriousness and extent of NO_3^- contamination of water sources by agriculture and the negative effect on drinking water quality has prompted policy makers to revise laws to ensure the safety of public water supplies. The SNMS provides the ability to quickly, accurately, and affordably collect the data necessary for environmental monitoring of NO_3^- levels in agricultural fields and water sources. In this way, regulators can more closely monitor NO_3^- status and, thus, take quicker action when needed. Farmers will be able to measure and document soil $\text{NO}_3\text{-N}$ levels in their fields thus improving traceability and improving their ability to be compliant with any current and future legislation requiring control of N fertilizers.

Researchers and farmers involved with *precision agriculture* are working to develop site-specific crop management (SSCM) practices which offer the potential for increased production efficiencies to farmers, while at the same time offering assurances to the public those practices are being conducted in the most environmentally friendly way. The lack of a soil $\text{NO}_3\text{-N}$ measurement system is a major roadblock. The SNMS overcomes this roadblock by providing an economical, automated, on-the-go technology that can be used to intensely and accurately collect data on the current status of soil $\text{NO}_3\text{-N}$ any time during the growing season.

Geostatistical techniques and tools have been used by many researchers for assessing the spatial and temporal variation and spatial structure of soil $\text{NO}_3\text{-N}$. Research applying these tools on a field scale, such as through SSCM experimentation, has led to the development of a multitude of methods for determining minimum soil sample spacing, sampling grid layout and cell size, optimum number of samples, sampling schemes and protocols for pre-planning experimental designs, and sample bulking strategies. However, when using these methods for implementing *precision agriculture* practices related to soil nitrogen management, the “most serious obstacles” are still the need to know the spatial structure in advance and the cost of obtaining this information even though the sampling effort required is much less than for full-scale sampling. The SNMS overcomes these serious obstacles by providing a rapid and cost effective technology for researchers interested in more closely studying soil $\text{NO}_3\text{-N}$ variation and its effects, either on crop growth or the environment.

Major achievements

The major achievements of the research program include: (i) determining that an ion selective electrode could be used in a soil-slurry solution, (ii) development of a tractor-mounted version of the SNMS, (iii) field-scale performance testing of the soil sampler, (iv) field-scale validation testing of the nitrate extraction and measurement sub-assembly, (v) using the SNMS to assess the spatial and temporal aspects of soil nitrate, and (vi) using the SNMS to investigate plant and soil nitrate responses in wheat and carrot production systems.

Chapter 2 describes laboratory work conducted to determine if a NO_3^- -ISE could be used in a soil-slurry solution and under what operating variables. Tests using a Chaswood clay loam soil indicated NO_3^- concentrations measured with the NO_3^- -ISE did not vary significantly with soil:extractant ratio or extract clarity. As well, reliable estimates of NO_3^- concentration were made in less than 4 s using normalized response time curves. Therefore, it was concluded that the NO_3^- -ISE was well suited for use in an automated on-the-go system provided regular calibration of the electrode was performed. A successful system, however, would depend not only on a properly functioning electrode, but properly functioning mechanical sub-assemblies and the ability to collect and analyze samples quickly.

Chapter 3 describes the development of bench-top models and testing of the various mechanical sub-assemblies needed for a fully-functioning system. This work resulted in the development of sub-assemblies that enabled the functions of soil sampling, soil metering and conveying, nitrate extraction and measurement, and electronic control of the system's operation to be performed while on-the-go. These sub-assemblies were integrated together, mounted on a tractor, and subjected to preliminary field testing. Overall, the performance of the system was found to be very satisfactory but several mechanical and electronic issues were identified. Development work continued resulting in a fully-functioning prototype in 2001 which included a GPS unit. This prototype was used to successfully map soil $\text{NO}_3\text{-N}$ levels in fields located on the farm of the Nova Scotia Agricultural College and confirmed that the SNMS was ready for extensive field-scale testing. This research work also included development of a field (soil) calibration method for speeding up the measurement process to facilitate quick sample analysis while on-the-go.

The soil sampler was subjected to extensive field-scale performance testing in five field conditions to determine the validity of its 'uniform bulk density' design principle, the uniformity of pocket fullness, the relationship between pocket fullness and delivered 'weight' (mass), and the uniformity of delivered weight (Chapter 4). For all field conditions tested, the overall uniformity of sample bulk density was 92.9%. The practical effect of this level of uniformity on delivered weight was determined to

cause less than a 5.5% deviation in delivered weight in 83.6% of the cases. Overall, the sampler had a mean delivered weight error of 10.9% and a coefficient of uniformity of 82.0%. Among fields, pocket fullness means ranged between 80.9–100.8% and the coefficient of uniformity ranged between 81.3–90.1%. For all field conditions data combined, the mean pocket fullness was 89.9% and the coefficient of uniformity was 83.6%. Delivered weight was found to be consistently very highly linearly correlated to pocket fullness over all field conditions ($R^2 = 0.979$, $n = 140$). Pocket fullness and delivered weight uniformity were found to be field-condition specific, related mostly to localized high clay content at several sampling locations in three of the fields. It was concluded that the sampler's main design principle of 'uniform bulk density' was valid for all intents and purposes of field use and that delivered weight uniformity of the sampler, particularly when used in clayey soils, should be increased by improving the design.

Extensive field-scale testing of the nitrate extraction and measurement sub-assembly to validate its accuracy in the field was performed (Chapter 5). The field conditions under which the sub-assembly was tested included wheat and carrot crops, conventional tillage vs. no tillage, inorganic vs. organic fertilization, four soil groups, and three time points throughout the season. The agreement between SNMS soil $\text{NO}_3\text{-N}$ measurements and standard lab soil $\text{NO}_3\text{-N}$ measurements was excellent and using regression equations field measurements with the SNMS could be obtained with lab-grade accuracy. There was little practical difference in results obtained when using either integer math or whole math data processing methods. It was concluded that (i) the SNMS is so robust that it can be used for both wheat and carrot crops, as well as in different soil groups, fertility levels, tillage conditions, and at any time throughout the season, (ii) future designs of the SNMS' control system can continue to use cheaper integer math chip technology for processing the $\text{NO}_3\text{-ISE}$ readings, and (iii) future designs of the SNMS would not need a soil moisture sensor, ultimately saving on manufacturing cost and keeping the system simple.

Using data collected by the SNMS on a fine-scale sampling grid and a combination of classical and geostatistical analytical techniques and tools, the spatial and temporal aspects of $\text{NO}_3\text{-N}$ variation in a wheat production system at seven time points covering pre-seeding, growing season, and post-harvest soil conditions, as well as the intrinsic spatial structure of $\text{NO}_3\text{-N}$ present in the field, were assessed (Chapter 6). This research work was conducted to demonstrate that, as a proof-of-concept, the SNMS could be used as an effective tool to assist soil scientists with experimental investigations of the spatial and temporal aspects of soil $\text{NO}_3\text{-N}$. The SNMS was successfully used to measure soil $\text{NO}_3\text{-N}$ level during the study period and to monitor spatial and temporal variation over time. As well, accurate, high resolution posted

values (contour) maps were generated that give excellent visual pictures of the $\text{NO}_3\text{-N}$ spatial variation that was evident just prior to, at peak nitrogen release, during, and just after the growing season. The spatial structure soil $\text{NO}_3\text{-N}$ variation present in the field had a very strong linear proportional effect. Relationships were found between the data sets mean and standard deviation values ($R^2 = 0.972$, $n = 7$) and the squared mean and variance values ($R^2 = 0.996$, $n = 7$). Soil $\text{NO}_3\text{-N}$ levels exhibited significant positive autocorrelation at separation distances ≤ 20 m in the test field and the separation distance at which no autocorrelation was evident varied between approximately 20–45 m. Variogram models of soil $\text{NO}_3\text{-N}$ spatial structure were developed for each of the sampling dates. These models were of the isotropic spherical type and had high R^2 values ranging between 0.904–0.999 combined with very low RSS values. Similarities in the spatial structure of soil $\text{NO}_3\text{-N}$ on the sampling dates were evident as these models had similar slopes, nuggets, ranges, and nugget-to-sill ratios. Spatial dependency was found overall to be moderate. A scaled average variogram model was created that very likely accurately represents the intrinsic spatial structure of soil $\text{NO}_3\text{-N}$ variation present in this field. This model had a sill of 1.005, a nugget of 0.331, and a range of 44 m. It was concluded that the soil $\text{NO}_3\text{-N}$ levels over the study period had large variation spatially and temporally, however the locations of several of the ‘hot spots’ and the ‘swale’ identified in the field were relatively consistent and strikingly corresponded to low areas in the field even though $\text{NO}_3\text{-N}$ level, generally, did not correlate with elevation. The intrinsic spatial structure of $\text{NO}_3\text{-N}$ variation exhibited temporal stability.

Using data collected by the SNMS on small-scale sampling grids at seven time points before, during, and after crops were being grown, the variation in soil $\text{NO}_3\text{-N}$ levels in wheat and carrot production systems over time were linked to crop performance (Chapter 7). This research work was conducted to demonstrate that, as a proof of concept, the SNMS could be used as an effective tool to assist crop scientists with their experimental investigations of plant and soil nitrate responses under a variety of field management conditions. In wheat under organic fertilizer management, the effect of conventional tillage vs. no tillage on soil nitrate, plant nitrogen and yield responses were determined. In carrot under conventional tillage management, the effect of inorganic fertilizer vs. organic fertilizer on soil nitrate, plant nitrogen and yield responses were determined. The SNMS was successfully used to measure soil $\text{NO}_3\text{-N}$ level at any time during the study period in both wheat and carrot when the plants were not growing using fully automatic mode, and when plants were growing using manual-sampling and auto-analysis mode. In wheat, it was determined that the only significant difference in mean soil $\text{NO}_3\text{-N}$ level between the conventional tillage and no tillage treatments occurred early in the growing season shortly after fertilizing,

Summary

when the level for the conventional tillage treatment was nearly two times higher than for the no tillage treatment. There was no significant difference in the response of plant tissue Total N to the conventional tillage and no tillage treatments; however a significant Day effect was detected. Significant differences were found in mean tissue Total N level between grain set, grain filling, and maturity, but no significant difference thereafter. Mean plant tissue-sap $\text{NO}_3\text{-N}$, grain yield and grain Total N all showed no significant difference in response to the conventional tillage and no tillage treatments. In carrot, early in the growing season shortly after fertilizing, the soil $\text{NO}_3\text{-N}$ level for the inorganic fertilizer treatment was nearly three times higher than for the liquid dairy manure treatment, while for the remainder of the growing season it remained in the order of two times higher. There was a significant increase in soil $\text{NO}_3\text{-N}$ for both the inorganic fertilizer and liquid dairy manure treatments after harvest at the end of the study period in late-Fall. There was no significant difference in mean plant tissue-sap $\text{NO}_3\text{-N}$ response to the inorganic fertilizer and liquid dairy manure treatments; however, a significant Day effect was detected. During mid-growth stage, plant tissue-sap $\text{NO}_3\text{-N}$ levels were sufficient for maximum top-biomass growth and root yield and then dropped dramatically during active root bulking until homeostasis was reached. The plant tissue-sap $\text{NO}_3\text{-N}$ level remained unchanged between homeostasis and the time the roots were harvested. Plant tissue Total N level for the inorganic fertilizer treatment dropped significantly during active root bulking and then stabilized for the remainder of the growing season. During this same period for the liquid dairy manure treatment, tissue Total N level also dropped significantly, but unlike for the inorganic fertilizer treatment, continued to drop dramatically instead of stabilizing. There was no significant difference in fresh root yield or root Total N between the treatments. It was concluded that the wheat plants responded equally well at producing final grain yield under either the conventional tillage or no tillage management practice and despite there being significant changes in soil $\text{NO}_3\text{-N}$ level over the growing season. For carrot, the plants took up enough N during shoot growth to sustain root bulking, thereby utilizing stored N for root bulking rather than relying on available N in the soil. And further, although there were significant changes in soil $\text{NO}_3\text{-N}$ levels over the growing season and between the inorganic fertilizer and liquid dairy manure treatments, they did not affect very much what was happening in the carrot plants. This finding stresses the environmental implications of managing soil $\text{NO}_3\text{-N}$ in a carrot production system.

Closing remarks

The SNMS as presented in this thesis is both practical and innovative. The SNMS is practical in that the system's operation has been completely automated so it can be

easily used, it has a variety of field uses, and it is an expandable platform technology that can be easily modified to enable simultaneous use of other types of ion-selective electrodes available for measurement of plant nutrients present in the soil. The SNMS is innovative in that it is the only working tractor-mounted, real-time, in-field soil nitrate mapping system in the world.

The SNMS overcomes many of the constraints, roadblocks, and serious obstacles cited by many researchers of measuring and assessing soil $\text{NO}_3\text{-N}$ variation using conventional methods in terms of sample analysis lag time, high labor requirements, and high costs. It has been demonstrated that soil $\text{NO}_3\text{-N}$ measurements using the SNMS can be obtained on a fine scale and with lab-grade accuracy. It has been demonstrated that data collected using the SNMS can be used (i) by soil scientists for assessing the spatial and temporal aspects of soil $\text{NO}_3\text{-N}$ variation and (ii) by plant scientists to assess variation in soil $\text{NO}_3\text{-N}$ levels in space and over time and link this variation to crop performance.

The SNMS offers the potential to assist researchers working in *precision agriculture* to develop better soil nitrogen practices for agricultural production. It offers farmers the potential to more intensely and precisely analyze variations in soil $\text{NO}_3\text{-N}$ levels throughout the growing season in correlation with environmental and crop response data in order to make the most sound and site- and time-specific management decisions possible. As well for farmers, it offers the potential for them to measure and document soil $\text{NO}_3\text{-N}$ levels in their fields thus improving traceability and their ability to be compliant with any current and future legislation requiring control of nitrogen fertilizers. It offers regulators the potential to conduct environmental monitoring of NO_3^- levels in agricultural fields and water sources. Ultimately as a result of its use, the public may be assured that soil nitrogen management practices in agriculture are being conducted in the most environmentally friendly way.

Samenvatting

Het onderzoek dat in dit proefschrift wordt beschreven, werd uitgevoerd gedurende een periode van 16 jaar en vond plaats aan het Nova Scotia Agricultural College, in Truro, Nova Scotia, Canada. Het programma heeft geresulteerd in de ontwikkeling van een geautomatiseerd apparaat, dat al rijdend bodemnitraat in kaart brengt (afgekort: het SNMS). Het onderzoek begon in 1991 met laboratoriumproeven gericht op het verfijnen van het oorspronkelijke prototype van een nitraat-monitorsysteem. Het onderzoek culmineerde in 2006–2007 in uitgebreide proeven op veldschaal om te testen of het volledig operationele prototype voldeed en om in veldproeven met de gewassen zomertarwe (*Triticium aestivum* L.) en peen (*Daucus carota* L.) aan te tonen hoe nuttig het systeem in de praktijk kan zijn.

Korte beschrijving van het systeem om bodemnitraat in kaart te brengen

Het SNMS is een elektromechanisch apparaat dat automatisch een bodemmonster neemt (op 0–15 cm diepte), dat monster mengt met water, en in dat monster rechtstreeks, ter plekke en in “real time” (6 s) de nitraatconcentratie meet met een nitraat-ion-selectieve electrode (NO_3^- -ISE). Bovendien worden tegelijkertijd op elke bemonsteringsplek met een global positioning system (GPS) gegevens verzameld omtrent de exacte geografische positie zodat voor het bemonsterde veld een nitraatkaart kan worden gemaakt. Het SNMS bestaat uit 6 onderdelen: (1) een bodembemonsteringsapparaat, (2) een systeem dat grond afmeet en transporteert, (3) een apparaat dat de nitraatextractie en de nitraatbepaling uitvoert, (4) een systeem voor auto-calibratie, (5) een control panel, en (6) een GPS.

Het SNMS kan worden gebruikt om al rijdend automatisch bodemmonsters te analyseren. Het kan echter ook opereren met handbediening en dan stationair worden gebruikt om monsters te analyseren die handmatig worden ingevoerd in het onderdeel dat de nitraatextractie en -bepaling uitvoert. Ik stel mij voor dat het apparaat uiteindelijk in de praktijk in twee verschillende modules zal worden gebruikt: als rijdend systeem gemonteerd op een tractor en als draagbare koffer-versie. Het SNMS is thans in staat te bemonsteren (a) met een nauwkeurigheid die ook in het laboratorium kan worden gehaald, (b) op elke willekeurige afstand tot op een dichtheid van 1 m afstand indien het apparaat met de hand bediend wordt, (c) met een snelheid van ongeveer twee monsters per minuut, en (d) tegen ongeveer één tiende van de kosten van de conventionele laboratoriumanalyse.

Belang van het systeem om bodemnitraat in kaart te brengen

De ontwikkeling van het SNMS is vanuit verschillende perspectieven van belang: (i) het koppelen van de variatie in $\text{NO}_3\text{-N}$ in de bodem aan gewasgroei, (ii) het monitoren van $\text{NO}_3\text{-N}$ in de bodem vanuit een milieudoelstelling, (iii) het ontwikkelen van locatiespecifieke teeltpraktijken, en (iv) het vaststellen van variatie in bodemnitraat.

Gedurende de laatste 20 jaar pogen vele onderzoekers al onderzoek te doen naar de stikstofgehalten in planten gedurende verschillende fenologische stadia en deze gehalten te koppelen aan de beschikbaarheid en verdeling van $\text{NO}_3\text{-N}$ in de bodem op hetzelfde tijdstip. Op kleine schaal is ook gepoogd teeltmaatregelen te ontwikkelen die kunnen leiden tot een beter locatiespecifiek stikstofbeheer. Echter, het verzamelen van gegevens met een voldoende hoge bemonsteringsintensiteit is duur en vergt veel arbeid. Bovendien blijft de analyse in de tijd (te) veel achter bij de bemonstering. Dit soort aspecten maakt dat het niet eenvoudig is dergelijk onderzoek uit te voeren. Met het SNMS kunnen deze problemen worden overwonnen. Het SNMS is immers in staat om snel, nauwkeurig en tegen betaalbare kosten de data te verzamelen die nodig zijn om variatie in bodemnitraat over kleine afstanden in tijd en ruimte te analyseren. Bovendien kunnen deze data gedurende de gewasgroei worden verzameld zodat de variatie in bodemnitraat rechtstreeks kan worden gekoppeld aan gewasgroei en opbrengst.

Het wordt steeds belangrijker om op een juiste wijze de milieu-aspecten van het gebruik van stikstofmeststoffen in de landbouw te adresseren. Nitraatvervuiling van waterbronnen door de landbouw is ernstig en grootschalig, en deze vervuiling heeft een negatief effect op de kwaliteit van het drinkwater. Daarom hebben beleidsmakers besloten om de wetgeving te herzien teneinde de veiligheid van de publieke waterbronnen te verzekeren. Het SNMS maakt het mogelijk om snel, nauwkeurig en tegen lage kosten de gegevens te verzamelen die nodig zijn om de nitraatniveaus op akkers en in waterbronnen te monitoren. Op deze wijze kunnen ambtenaren die belast zijn met het handhaven van de regelgeving de nitraattoestand nauwlettender in de gaten houden en sneller tot actie komen mocht dat nodig zijn. Telers zullen de $\text{NO}_3\text{-N}$ in de bodem van hun akkers kunnen meten en documenteren en dat zal de naspeurbaarheid bevorderen en de telers in staat stellen de huidige en toekomstige wetgeving rond het beheersen van stikstofmeststoffen na te leven.

Onderzoekers en telers die betrokken zijn bij *precisielandbouw*, werken aan het ontwikkelen van teeltmaatregelen voor locatiespecifieke teelt (LST). Met dergelijke teeltmaatregelen kan enerzijds de efficiëntie van de productie worden verhoogd en anderzijds het publiek er van worden verzekerd dat de gewassen zo milieuvriendelijk mogelijk zullen worden geteeld. Het ontbreken van een systeem om $\text{NO}_3\text{-N}$ in de bodem te meten is een belangrijke hinderpaal. Het SNMS neemt deze belemmering

weg door een economisch verantwoorde, geautomatiseerde, rijdende technologie te leveren die kan worden gebruikt om intensief en nauwkeurig gegevens te verzamelen betreffende de heersende toestand van $\text{NO}_3\text{-N}$ in de bodem voor elk tijdstip gedurende het groeiseizoen.

Vele onderzoekers hebben geostatistische technieken en instrumenten gebruikt om de ruimtelijke en temporele variatie en de ruimtelijke structuur van $\text{NO}_3\text{-N}$ in de bodem vast te stellen. Onderzoek dat deze instrumenten op veldschaal heeft toegepast (zoals via LST proeven) heeft geleid tot een veelheid van methoden voor het vaststellen van de minimale bodembemonsteringsdichtheid, opzet voor een bemonsteringsraster, celgrootte, optimaal aantal monsters, schema's voor bemonstering en protocollen voor het vooruitplannen van proefontwerpen, en strategieën voor het bij elkaar doen van monsters. Als men echter deze methoden toepast bij het implementeren van teeltmaatregelen voor het beheersen van bodemstikstof in precisielandbouw zijn er nog steeds zeer belangrijke obstakels: men moet vooraf de ruimtelijke structuur kennen, en de kosten die gemoeid zijn met het verkrijgen van informatie hieromtrent zijn hoog, zelfs als de inspanning om te bemonsteren veel kleiner is dan bij een volledige bemonstering. Het SNMS kan een oplossing bieden, omdat het onderzoekers die interesse hebben in het nader bestuderen van variatie in $\text{NO}_3\text{-N}$ in de bodem en de effecten daarvan op gewasgroei of het milieu, een technologie verschaft die snel en kosteneffectief is.

Belangrijkste wapenfeiten

Het onderzoek heeft het volgende tot stand gebracht: (i) er is vastgesteld dat een ion-selectieve elektrode gebruikt kan worden in een modderige oplossing, (ii) er is een versie van het SNMS ontwikkeld die op een tractor kan worden gemonteerd, (iii) het systeem voor bodembemonstering is getest om te bezien of het ook onder veldomstandigheden naar behoren presteert, (iv) het onderdeel voor extractie en meting van nitraat is onder veldomstandigheden gevalideerd, (v) het SNMS is gebruikt om de ruimtelijke en temporele aspecten van bodemnitraat vast te stellen, en (vi) het SNMS is gebruikt om nitraat in plant en bodem te onderzoeken in productiesystemen met zomertarwe en peen.

Hoofdstuk 2 beschrijft werk dat in het laboratorium werd uitgevoerd om vast te stellen of een nitraat-ion-selectieve elektrode (een NO_3^- -ISE) in een modderige oplossing kon worden gebruikt en onder welke operationele variabelen dat mogelijk is. In testen met een Chaswood bodem (een kleiachtige leem) bleken de nitraatconcentraties die met de NO_3^- -ISE werden gemeten niet significant te verschillen bij verschillende verhoudingen tussen bodem en extract of bij verschillende niveaus van helderheid van het extract. Betrouwbare schattingen van nitraatconcentraties konden

binnen 4 seconden worden gemaakt met behulp van genormaliseerde responstijd curven. De conclusie luidde daarom dat de NO_3^- -ISE prima geschikt is om in een geautomatiseerd, rijdend systeem te gebruiken mits de elektrode regelmatig gekalibreerd wordt. Een succesvol systeem moet echter niet alleen beschikken over een goed functionerende elektrode, maar ook over een goed functionerende mechanische onderdelen en moet de monsters snel kunnen nemen en analyseren.

Hoofdstuk 3 beschrijft de ontwikkeling van modellen op laboratoriumschaal en het testen van verschillende mechanische onderdelen die nodig zijn voor een volledig functionerend systeem. Dit deel van het onderzoek leidde tot de ontwikkeling van onderdelen die het mogelijk moeten maken al rijdend de volgende functies uit te voeren: het bemonsteren van de bodem, het afmeten en transporteren van het bodemmonster, de nitraatextractie en -meting, en de elektronische aansturing van het opereren van het gehele systeem. Deze onderdelen werden geïntegreerd, op een tractor gemonteerd, en aan voorlopige testen in het veld blootgesteld. In het algemeen functioneerde het systeem heel behoorlijk, al werden er verscheidene mechanische en elektronische probleempjes geconstateerd. Het ontwerp werd verder ontwikkeld totdat uiteindelijk in 2001 een volledig functioneel prototype tot stand kwam dat met een GPS unit werd uitgerust. Dit prototype werd vervolgens met succes benut om in akkers van de proefboerderij van het Nova Scotia Agricultural College de $\text{NO}_3\text{-N}$ van de bodem in kaart te brengen. Daarmee werd aangetoond dat het prototype van het SNMS gereed was voor een uitgebreide test in het veld. Dit deel van het onderzoek omvatte tevens de ontwikkeling van een veld- (bodem-)calibratiemethode om het meetproces te versnellen zodat de bodemanalyse al rijdend kon plaatsvinden.

Het bodembemonsteringsonderdeel werd uitgebreid in het veld getest op verschillende akkers om vast te stellen of het toegepaste ontwerpprincipe van uniforme volumedichtheid wel valide was. Bovendien werd getest of de mate waarin de vakjes op de transportband gevuld waren wel uniform was, werd de relatie tussen mate van vulling en de massa geleverde bodemmonster onderzocht, en werd de uniformiteit van het geleverde gewicht getest (Hoofdstuk 4). Voor alle geteste veldomstandigheden werd waargenomen dat de algehele uniformiteit of de volumedichtheid van het monster 92,9% was. Het praktische effect van dit niveau van uniformiteit op het geleverde gewicht bleek te zijn dat er minder dan 5,5% afwijking in geleverd gewicht was in 83,6% van de gevallen. Over het geheel genomen had de bemonsteringsmodule een gemiddelde fout in geleverd gewicht van 10,9% en een uniformiteitscoëfficiënt van 82,0%. De mate van vulling van de vakjes varieerde tussen 90,9 en 100,8% voor de verschillende velden en de uniformiteitscoëfficiënt varieerde van 83,1 tot 90,1%. Wanneer alle veldomstandigheden op een hoop werden gegooid dan was de gemiddelde vulling van de vakjes 89,9% en de uniformiteitscoëfficiënt 83,6%. Er was

stelselmatig over alle veldcondities een zeer hoge, lineaire correlatie tussen het geleverde gewicht en de mate van vulling van de vakjes ($R^2 = 0,979$; $n = 140$). Uniformiteit van mate van vulling en van geleverd gewicht hing af van de specifieke veldcondities. Het effect van deze condities was meestal gerelateerd aan het kleigehalte dat lokaal hoog kon zijn op de verschillende bemonsteringsplekken van de drie bij het onderzoek betrokken akkers. Geconcludeerd werd dat het belangrijkste ontwerpprincipie van uniforme volumedichtheid van het bemonsteringsonderdeel valide was voor alle intenties en gebruiksdoelen in het veld, maar dat de uniformiteit van geleverd gewicht van het bemonsteringsonderdeel, vooral bij gebruik op kleiige bodems, verbeterd dient te worden teneinde tot een nog beter ontwerp te komen.

Uitgebreide tests werden uitgevoerd in het veld om de nauwkeurigheid in het veld van het onderdeel voor nitraatextractie en -meting te valideren (Hoofdstuk 5). Dit meetonderdeel werd onder veldomstandigheden getest in tarwe- en peengewassen, met conventionele grondbewerking en zonder grondbewerking, bij organische bemesting en bij kunstmestgift, bij vier bodemgroepen en op drie tijdstippen gedurende het groeiseizoen. De overeenstemming tussen de bodemnitraatmetingen van het SNMS en de standaardmetingen van nitraat in het lab was uitstekend en met behulp van regressievergelijkingen konden veldmetingen met het SNMS worden verkregen met een nauwkeurigheid die vergelijkbaar was met die in het lab. Voor de resultaten maakte het weinig uit of de data werden verwerkt op basis van gehele getallen of met getallen in decimalen. Geconcludeerd werd dat (i) het SNMS zo robuust was dat het zowel voor tarwe als voor peen kon worden gebruikt, (ii) dat in toekomstige ontwerpen van het controlesysteem van het SNMS de goedkopere chiptechnologie op basis van gehele getallen kan worden gebruikt voor het verwerken van de aflezingen van de NO_3^- -ISE, en (iii) dat toekomstige ontwerpen van het SNMS geen bodemvochtsensor nodig hebben, waardoor op kosten kan worden bespaard en het systeem eenvoudig kan worden gehouden.

Met behulp van het SNMS werden gegevens verzameld in een fijnmazig bemonsteringsraster. Deze data werden met behulp van een combinatie van klassieke en van geostatistische analysemethoden en -technieken geanalyseerd. Op deze manier konden ruimtelijke en temporele aspecten van variatie in $\text{NO}_3\text{-N}$ worden vastgesteld. Data werden verzameld voor een tarweproductiesysteem waarin de temporele aspecten werden onderzocht door op zeven momenten in de tijd monsters te nemen (namelijk zowel voor het zaaien, als tijdens het groeiseizoen als ook na de oogst); tevens werd de intrinsieke ruimtelijke structuur van $\text{NO}_3\text{-N}$ in het veld vastgesteld (Hoofdstuk 6). Dit onderzoek werd uitgevoerd om aan te tonen dat, als een “proof-of-concept”, het SNMS kon worden benut als een effectief instrument om bodemkundigen te assisteren bij experimenteel onderzoek naar de ruimtelijke en temporele aspecten van $\text{NO}_3\text{-N}$ in de

bodem. Het SNMS werd met succes gebruikt om het niveau van $\text{NO}_3\text{-N}$ in de bodem te meten gedurende de onderzoeksperiode en om ruimtelijke en temporele variatie in de tijd te meten. Bovendien konden nauwkeurige contourkaarten met een hoge resolutie worden gegenereerd. Deze kaarten konden op uitstekende wijze de variatie in $\text{NO}_3\text{-N}$ in kaart brengen die aanwezig was net voor en tijdens de piek in het vrijkomen van stikstof, alsmede gedurende en na het groeiseizoen. De ruimtelijke structuur in de variatie in $\text{NO}_3\text{-N}$ in de bodem zoals die in het veld aanwezig was, bleek een sterk lineair proportioneel effect te vertonen. Er werden relaties gevonden tussen de gemiddelden en de standaardafwijkingen van de data ($R^2 = 0,972$, $n = 7$) en tussen de gemiddelden in het kwadraat en variantiewaarden ($R^2 = 0,966$, $n = 7$). $\text{NO}_3\text{-N}$ waarden in de bodem vertoonden significante auto-correlatie bij scheidingsafstanden kleiner dan 20 m op de testakker en de scheidingsafstanden waarbij geen autocorrelatie optrad varieerden tussen ongeveer 20 en 45 m. Variogrammodellen van de ruimtelijke structuur van de $\text{NO}_3\text{-N}$ in de bodem werden voor elk van de bemonsteringsdagen ontwikkeld. Deze modellen kwamen overeen met het isotropisch-sferisch type en hadden hoge R^2 waarden, variërend van 0,904 tot 0,999 en tegelijkertijd heel lage waarden voor de residuele som van de kwadraten. Overeenkomsten in de ruimtelijke structuur van de $\text{NO}_3\text{-N}$ in de bodem op de bemonsteringsdagen waren evident aangezien deze modellen vergelijkbare hellingshoeken, “nuggets”, ranges, en “nugget-to-sill” verhoudingen hadden. De ruimtelijke afhankelijkheid bleek in het algemeen slechts beperkt. Een op basis van schaalcorrecties gemiddeld variogrammodel werd gemaakt en dit model gaf met een zeer grote waarschijnlijkheid de intrinsieke ruimtelijke structuur van de variatie in bodem- $\text{NO}_3\text{-N}$ die in dit veld aanwezig was, weer. Dit model had een “sill” van 1,005, een “nugget” van 0,331, en een range van 4 m. Geconcludeerd werd dat de niveaus van $\text{NO}_3\text{-N}$ in de bodem gedurende de onderzoeksperiode een grote ruimtelijke en temporele variatie vertoonden. Echter, de locaties van de verschillende “hot spots” en van de plek met lage waarden die op het veld werden geïdentificeerd, bleken relatief consistent en vertoonden een grote overeenkomst met de lagere gebieden in het veld, ook al vertoonde het niveau van $\text{NO}_3\text{-N}$ in het algemeen geen verband met elevatie. De intrinsieke ruimtelijke structuur van $\text{NO}_3\text{-N}$ bleek in de tijd stabiel.

Met behulp van de gegevens die met het SNMS werden verzameld over een dicht raster en op zeven tijdstippen voor, gedurende en na het telen van de gewassen, werd de variatie in $\text{NO}_3\text{-N}$ in de bodem in de productiesystemen met de gewassen tarwe en peen over de tijd gekoppeld aan de prestaties van het gewas (Hoofdstuk 7). Dit deel van het onderzoek werd uitgevoerd om te laten zien dat, als een “proof-of-concept”, het SNMS kan worden gebruikt als een effectief instrument om agronomen te helpen bij het uitvoeren van hun experimenteel onderzoek naar plant- en bodemnitraat-

responses bij een reeks van teeltcondities. In tarwe werd, bij een organische bemesting, de effecten van bodembewerking (conventioneel versus geen) op bodemnitraat, stikstof in de plant en opbrengst bepaald. Het SNMS bleek met succes het niveau van $\text{NO}_3\text{-N}$ in de bodem te kunnen meten, en wel op elk tijdstip tijdens de teelt van tarwe of peen. Als er geen gewas te velde stond werd de volledig geautomatiseerde module gebruikt. Met een gewas te velde werd met de hand bemonsterd en werd de auto-analyse vorm gebruikt. Voor het tarwegewas werd gevonden dat het enige significante verschil in gemiddelde waarde voor de $\text{NO}_3\text{-N}$ in de bodem tussen de conventionele grondbewerking en geen grondbewerking vroeg in het groeiseizoen werd gevonden, d.w.z. kort na de bemesting. Op dat moment was het niveau voor conventionele bodembewerking bijna twee keer zo hoog als voor de behandeling zonder grondbewerking. Er werd geen significant verschil gevonden tussen de twee grondbewerkingsbehandelingen ten aanzien van het totale stikstofgehalte van het plantenweefsel. Er werd wel een significant effect van tijdstip gevonden. Er werden significante verschillen gevonden in de gemiddelde waarden van totaal stikstof in het plantenweefsel tussen de tijdstippen van korrelzetting, korrelvulling en rijpheid. Na rijping werden geen significante verschillen meer gevonden. Gemiddelde waarden voor $\text{NO}_3\text{-N}$ in het sap van plantenweefsel, voor korrelopbrengst en voor totaal stikstof in de korrel waren niet significant verschillend voor de beide bodembewerkingsbehandelingen. In het peengewas bleek het $\text{NO}_3\text{-N}$ niveau in de bodem vroeg in het groeiseizoen kort na de bemesting bijna drie keer zo hoog te zijn voor de behandeling met kunstmeststikstofbemesting als voor de behandeling met drijfmest. Gedurende de rest van het seizoen waren de waarden voor de kunstmestbehandeling ongeveer twee keer zo hoog als voor de drijfmestbehandeling. Voor beide bemestingsbehandelingen was er sprake van een significante toename in het gehalte aan $\text{NO}_3\text{-N}$ in de bodem na de oogst aan het eind van de onderzoeksperiode in de late herfst. Er werd geen significant verschil tussen beide bemestingsvarianten gevonden voor de gemiddelde waarden van de $\text{NO}_3\text{-N}$ -gehalten in het plantenweefsel. Er werd echter wel een effect van tijdstip waargenomen. Gedurende het midden van het groeiseizoen waren de $\text{NO}_3\text{-N}$ -gehalten in het sap van het plantenweefsel voldoende voor een maximale bovengrondse en ondergrondse groei, maar daarna namen de gehalten tijdens de peengroei zeer sterk af totdat een homeostase werd bereikt. Het niveau van $\text{NO}_3\text{-N}$ in het plantenweefsel bleef onveranderd tussen de homeostase en het tijdstip waarop de penen werden geoogst. Het niveau van totaalstikstof in de plant nam voor de kunstmestbehandeling significant af gedurende de periode van actieve peengroei en stabiliseerde zich vervolgens voor de rest van het groeiseizoen. Gedurende deze zelfde periode nam het gehalte van totaalstikstof in het plantenweefsel voor de behandeling met drijfmest ook sterk af, maar in dit geval ging de afname door

en het gehalte stabiliseerde zich niet. De behandelingen verschilden niet significant in peenopbrengst of in totaalstikstofgehalte van de peen. Voor het tarwegewas werd geconcludeerd dat de bodembewerkingsbehandeling niet leidde tot verschillen in uiteindelijke korrelopbrengst ondanks significante verschillen in het niveau van $\text{NO}_3\text{-N}$ in de bodem gedurende het groeiseizoen. Voor peen bleken de planten voldoende stikstof op te nemen tijdens de bovengrondse groei om daarmee de groei van de penen te onderhouden en aldus opgeslagen stikstof gebruikend voor peengroei in plaats van te vertrouwen op beschikbare stikstof in de bodem. Bovendien, hoewel er significante veranderingen optraden in $\text{NO}_3\text{-N}$ in de bodem gedurende het groeiseizoen en deze gehalten ook werden beïnvloed door de bemestingsbehandelingen, was er weinig effect op het gedrag van de peenplanten. Daarmee worden wel de milieu-implicaties onderstreept van het nauwkeurig beheersen van $\text{NO}_3\text{-N}$ in de bodem.

Ten slotte

Het SNMS zoals dat in dit proefschrift is gepresenteerd, is zowel praktisch als innovatief. Het SNMS is praktisch omdat het een volledig geautomatiseerd systeem is zodat het gemakkelijk kan worden gebruikt, omdat het op veel verschillende wijzen kan worden gebruikt in het veld, en omdat het een platformtechnologie is die nog verder kan worden uitgebouwd en makkelijk kan worden aangepast voor gelijktijdig toepassing van andere typen ion-selectieve elektrodes die beschikbaar zijn voor het meten van in de grond aanwezige plantenvoedingsstoffen. Het SNMS is innovatief omdat het het enige operationele systeem in de wereld is dat op een trekker kan worden gebouwd, en dan ter plekke en in “real-time” het bodemnitraat van een akker in kaart kan brengen.

Het SNMS kan een oplossing zijn voor de vele beperkingen, belemmeringen en obstakels die door vele onderzoekers vermeld worden inzake het meten en vaststellen van variatie in $\text{NO}_3\text{-N}$ in de bodem met behulp van conventionele methoden in termen van verlate beschikbaarheid van resultaten van de bodemanalyse ten opzichte van het moment van bemonstering, hoge arbeidsbehoefte en hoge kosten. Het is aangetoond dat de metingen van de $\text{NO}_3\text{-N}$ in de bodem met behulp van het SNMS kunnen worden verkregen een fijnmazige schaal en met een nauwkeurigheid die vergelijkbaar is met die van laboratoriumanalyses. Het is tevens aangetoond dat de data die met het SNMS zijn verzameld zowel door bodemkundigen kunnen worden gebruikt voor het vaststellen van de ruimtelijke en temporele aspecten van variatie in $\text{NO}_3\text{-N}$ in de bodem als door agronomen kunnen worden gebruikt voor het vaststellen van variatie in de niveaus van $\text{NO}_3\text{-N}$ in de bodem in ruimte en tijd en om deze variatie te koppelen aan gewasprestaties.

Het SNMS biedt de mogelijkheid onderzoekers ten dienste te zijn die werken aan precisielandbouw bij het ontwikkelen van betere praktijken om bodemstikstof te beheersen in de teelt van gewassen. Het SNMS biedt telers de mogelijkheid om variaties in NO₃-N-gehalten in de bodem met een grotere intensiteit en precisie te analyseren gedurende het gehele groeiseizoen, en deze variatie te correleren aan milieugegevens en gegevens betreffende gewasprestaties teneinde de beste, locatie- en tijdspecifieke managementbeslissingen te nemen. Het SNMS biedt telers ook de mogelijkheid om de gehalten aan NO₃-N in de bodem van hun akkers te meten en te documenteren. Dat is van belang voor de traceerbaarheid en voor het vermogen van deze telers om tegemoet te komen aan thans geldende en toekomstige wetgeving ten aanzien van de beheersing van stikstofmeststoffen. Het biedt regelgevers de mogelijkheid de nitraatgehalten op akkers en in waterbronnen te monitoren. Uiteindelijk zal als gevolg van dit alles het publiek de verzekering kunnen krijgen dat de praktijken voor het beheersen van bodemstikstof op de meest milieuvriendelijke wijze zullen worden uitgevoerd.

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Curriculum vitae

Kevin Sibley was born in Woodstock, New Brunswick, Canada on August 6, 1960. He graduated with honors from the Nova Scotia Agricultural College (NSAC), Truro, Nova Scotia in 1980 with a Degree Diploma in Agricultural Engineering. He subsequently enrolled at Macdonald College of McGill University, graduating in 1982 with a BSc (Agr. Eng.) with distinction and an MSc (Agr. Eng.) in 1984. From 1983 to 1986, he worked for Cherryfield Foods Inc., Maine, USA, until 1985 as their farm supervisor. He was responsible for the company's 2,000 hectare commercial wild blueberry farming operation and blueberry grower service network. From 1986 to 1989, he worked as a project engineer for the Atlantic Farm Mechanization Institute, Halifax, Nova Scotia where he was responsible for research, development, testing and evaluation of agricultural, food processing, and fisheries machinery. He began his academic career in 1989 when he joined NSAC as an assistant professor in the Agricultural Engineering Department. He has taught many courses at the technician, technology and undergraduate level in the areas of agricultural machinery, mechanized systems, horticultural equipment, mechanics of materials, engineering design, and research methods. He has conducted research and development in the fields of wild blueberry and rhubarb mechanization along with his work in precision agriculture developing the automated on-the-go soil nitrate mapping system. He was promoted to Associate Professor in 1996 and to Department Head in 2003. In addition to his work as a university professor, he has been involved in private industry as a consultant in agricultural engineering and business development, and part-owner of several companies in the food service, machinery manufacturing, and plant biotechnology sectors. He has completed over 70 scientific research & development and business development projects in a variety of areas including agricultural mechanization, freeze processing, productivity assessments, technical and economic feasibility studies, strategic plans, business plans, and market studies. He has completed 36 continuing education and professional development programmes in engineering, business, and leadership skills. He has been a leadership coach to business people at a variety of levels from line supervisors up to Presidents/CEOs. He has provided leadership on over 30 committees and boards within the private sector, academia, and volunteer organizations – mostly at the executive level as president, chair, or secretary. He has received 21 awards for professional and personal excellence, and community service. He holds double professional designations as an engineer and agrologist. He is currently a faculty member in the Engineering Department at the NSAC and Chief Operating Officer of the Atlantic Bio-Venture Center, Truro, Nova Scotia.

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