

# **Analysis of Nutrients in Hog Manure by Field-portable Near-infrared Spectroscopy: Development of a Mobile Laboratory and Results for Foss NIRSystems Inc. Model 6500 Spectrophotometer in the Laboratory**



## **Final Report 1 of 3 to CETAC-West on Manure Demo Project**

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## Executive Summary

The overall purpose of this project was to develop a field protocol for testing two field-portable near-infrared (NIR) spectrophotometers as on-site, free-standing (not in-line), measurement tools for nutrients in hog manure at the time of application of manure to agricultural land. This project was a developmental step between the analysis of hog manure in the laboratory using near-infrared spectroscopy (NIRS) and the deployment of NIR instruments in the manure stream for real-time measurement of composition of manure during application to land. The field-portable instruments included the Textron Systems Corp (USA)/Case NH (USA) ProSpectra™ Spectrometer and the Carl Zeiss (Germany) Corona® Spectrometer.

The first step in this project was the design and construction of a mobile laboratory mounted on the bed of a 1/4-ton pick-up truck. Considerations in designing and building this system included reliable power supply for the instruments and notebook computers, security of the equipment against movement during transit and against theft, protection from the elements, and worker safety.

Secondly, the project involved sampling of manure (n = 121) at 13 application operations in the vicinity of Winnipeg MB during between 28 September and 4 November 2000. All but two of these operations held the manure in earthen stores, one had a slurry store and a secondary lagoon, and one had above ground storage. Six of the operations were visited once and seven were visited from two to seven times during pump-out from agitated lagoons. Using conventional physical and chemical methods, the samples were analyzed by the Freshwater Institute Analytical Laboratory for pH, conductivity, density, ammonium-nitrogen (NH<sub>4</sub>-N), total dissolved nitrogen (TDN), particulate nitrogen, dissolved phosphorus (dissolved P), particulate P, and particulate carbon (particulate C, i.e., a measure of the particular organic matter). Eighty of the 121 samples of manure were analyzed for 31 minor elements and metals by inductively coupled plasma spectrometry and for moisture by drying by Norwest Labs.

Thirdly, the project involved operating the two field-portable NIR instruments on the mobile laboratory for the scanning of the manure samples. As well, all of the samples were scanned with a laboratory instrument, the Foss NIRSystems Inc. (USA) model 6500 visible/near-infrared scanning spectrophotometer. The NIR spectral data from the 6500 and field-portable instruments were statistically correlated with the chemical data on the same samples to develop calibrations, or statistical models, for each constituent on each instrument. The success of calibrations was evaluated statistically as a measure of the performance of the instruments and their suitability for on-site manure analysis. Successful calibrations can be used with the respective instruments in the field or laboratory to predict composition of future manure samples.

This is the first of six reports describing the results from the overall project. It describes the design and construction of the mobile laboratory, the collection and analysis hog manure samples from 13 hog operations in the vicinity of Winnipeg from September to November 2000, and the calibration results achieved with the laboratory model 6500 NIR instrument.

The mobile laboratory was constructed to fit the bed of a compact 1/4 ton pickup. It consisted of an instrumentation and power deck, tonneau cover, and tent assembly. The instrument deck was easily installed or removed, and required no drilling or other modification of the pickup truck bed. The deck provided an easily accessible work surface and was very stable under severe driving conditions. The tonneau cover provided lockable, out-of-view security, as well as protection from wind and rain in transit or when parked. The tent assembly provided all weather protection to both the equipment and the operator during laboratory function.

Overall, the manure samples ranged in pH from 6.7 - 8.1, conductivity from 6.8 - 27.2 mS/cm, density from 1.002 - 1.049 g/mL, ammonium-N from 0.56 - 5.54 g/L, total dissolved N from 0.59 - 6.11 g/L, suspended N from 0.01 - 4.08 g/L, total N from 0.61 - 10.14 g/L, soluble reactive P (phosphate-P) from 0.05 - 3.81 g/L, total dissolved P from 0.06 - 3.86 g/L, suspended P from 0.003 - 2.65 g/L, total P from 0.06 - 6.51 g/L, and suspended C from 0.09 - 54.60 g/L.

This study showed that manure sampled from three types of manure stores from 13 hog operations was inherently variable for a number of constituents, including ammonium-N, and dissolved P. For a two-celled manure store sampled 7 times during pump-out,  $\text{NH}_4\text{-N}$  varied over 2.4-fold, particulate N varied 38-fold, and total N ranged over 3.5-fold. More remarkable was the variation in P during pump-out. Dissolved P varied 9.5-fold; particulate P, 230-fold; and total P varied 20-fold. Organic nutrients, N and P, bound to particles were most variable because of the high variability of particulate content from sample to sample. Because of variable particulate content, the N:P ratio in manure can vary widely during pump-out, and therefore significantly affect the application of manure as a fertilizer. A few constituents, most importantly K, did not change during the pump-out cycle

The calibrations developed for pH, conductivity, and the nutrients based on spectra from the model 6500 were excellent. These results provide baseline calibration performance against which to compare the results from each field-portable NIR instrument.

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The photo on the cover shows the mobile NIR lab set up for operation in the field. Photo is the property of PDK Projects, Inc.

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## Introduction

Hog manure has become a recognized and valued fertilizer resource, largely because the N it contains is mostly in the form of  $\text{NH}_4\text{-N}$  that binds to soil and is less prone to leaching to groundwater than  $\text{NO}_3\text{-N}$ . Furthermore, as inorganic fertilizer costs rise, the low costs and the availability of manure in agricultural areas make the use of manure increasingly attractive. Nevertheless, management of manure from hog production is a particular challenge because of the associated odor, the large volume, high water content, and variable nutrient content.

The management of the nutrients in manure has implications not only for agronomy and water pollution, but also for the emission of greenhouse gases. Agriculture and land use are important sources of the major greenhouse gases,  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ . Agricultural practices, particularly including the use and overuse of fertilizers, influence emissions of the most potent  $\text{N}_2\text{O}$  (310 times the global-warming potential of  $\text{CO}_2$ , compared with  $\text{CH}_4$  that has 21 times the potential of  $\text{CO}_2$ ). The agricultural emission of these gases is mediated by microbial communities in the soil, influenced by amounts of fertilizer added, land use practices (such as cultivation), soil type, and weather.

Measuring nutrient loading to land reliably is more difficult with manure than with inorganic fertilizer. Manure is variable in composition from one store to another, and virtually impossible to maintain in a homogeneous state due to rapid settling of particulate material. Material drawn from the top of a storage tank or earthen store is highly liquid and contains low suspended solids and low P concentrations, while that from the bottom can have a high particulate content and associated high levels of P and organic N. Ammonium-N and K are fairly uniform regardless of the particulate content, but total N varies with particulate content. It is unlikely that the manure in a store can be adequately mixed by agitation. Thus, little is known about actual N and P loading with time during application, even if the manure is constantly agitated as it is applied. Determination of nutrient concentrations at numerous times during application is desirable.

A method of analytical testing that is rapid, cost effective, field-portable, and, if possible, operating in-stream, that has the capability to analyze N, P, and salts in liquids and slurries would have wide use for monitoring and guiding manure application to land. This would be useful not only for maximizing the agronomic use of the nutrients but also provide data useful for the calculation of greenhouse gas emissions from manured lands.

### *Near-infrared Spectroscopy (NIRS)*

Near-infrared spectroscopy is a 30-year old technology that has the capability of determining quantities of organic constituents in liquids, slurries, and solids. It is used globally for determination of a wide variety of constituents, composition, and functionality in agricultural products, feeds, food, forages, petrochemicals, cosmetics, polymers, (including waste plastic streams for recycling), pharmaceuticals, textiles and other materials. Medical and environmental applications are emerging areas.

The technique is based on measurement of the intensity of the absorption of near-infrared radiation (780 to 2500 nm) by a sample. Radiant energy in this range may excite molecular vibrations to higher energy levels. Absorbance occurs at wavelengths that match the frequency of the molecular vibrations. Commonly, NIRS is used for quantitative measurement of constituents containing organic functional groups, such as covalent O-H, C-H, N-H, C=O, and C-N and for prediction of functional properties of samples resulting from the organic composition. Nevertheless, NIRS has been successfully used for the determination of inorganic substances, such as NH<sub>4</sub>-N in an industrial *Escherichia coli* fermentation broth (Hall et al. 1996). It has been used to determine simultaneously the concentrations of electrolytes such as NaNO<sub>3</sub>, NaNO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> in liquids based on the perturbation of the water spectrum (Espinoza et al. 1999).

NIRS is not a stand-alone analytical technique. Its ability to provide rapid analyses depends on the prior preparation of mathematical calibrations used to predict constituents, parameters, or functionality in unknown samples. Calibrations are based on statistical relationships developed between NIR spectra of a set of samples and values for constituents, parameters, or functions of interest that have been determined by conventional methods on the same samples. The calibrations are then entered into the instrument's computer and are used to predict the parameters of interest in the unknown samples within 2 minutes or less, depending on the NIR technology used. Accuracy and precision are maintained by periodical, on-going analysis by the conventional methods of a sub-sample, e.g., 5-10%, of the unknown samples.

NIRS has the capability of measuring constituents in liquids (e.g., Gatin et al. 1995) and slurries (Wust et al. 1996, Malley and Currie 1999) through the use of one of two methods, transmission and reflectance, or their combination, known as transreflectance. NIRS technology is used in-line in industrial applications where fibre optic probes are inserted into the industrial process stream (e.g., Brookes et al. 1996), or focussed on to an industrial flow such as waste plastic articles.

Considerable experience exists in the measurement of constituents in hog manure by NIRS using the bench-top laboratory NIR instrument, the Foss NIRSystems Inc. model 6500 visible/near-infrared scanning spectrophotometer (Silver Spring MD) (Malley 1999; Malley and Currie 1999; Malley et al. 1999; Malley and Vandenbyllaardt 1999; Millmier et al. 2000; Malley et al. submitted for publication).

The recent development of field portable NIR instrumentation for on-the-go analysis of forage (Zeiss Corona® by Zeiss, Germany) (Rode 2001) and protein in grains (ProSpectra™ by Case NH/Textron Systems Corporation) (Case IH 1999) provides potential for on-site and/or on-the-go (in-stream) analysis that may be useful in the testing of hog manure at the time of application. Also on the market is the field-portable, self-contained LabSpec Pro NIR Analyzer (Analytical Spectral Devices, Inc., Colorado). In-stream capability would also permit hog manure to be augmented with inorganic fertilizer and applied to land as a complete custom fertilizer as patented in Canada, the U.S., and Europe (Guyot: US 5,907,925; CA 2,192,898; EP 0846408 A1) by Ag Waste Management Corp (Lyseng 1999).

Some experience has been gained with the use of a Textron/Case NH ProSpectra prototype model for manure analysis in the laboratory (Malley, Badiou and Williams 2000).

### ***Sample Requirements for NIRS Calibration***

The sample requirements for developing an NIR calibration are that:

- there is a minimum of 50 samples, but preferably at least 100-150 samples that have been analyzed for the constituents or parameters of interest by conventional (i.e., reference) methods with a high degree of accuracy
- samples represent a range of values in each constituent, e.g., highest values should be at least twice and preferably ten times the lowest values
- samples represent the full range of concentration of the constituents of interest anticipated in future samples to be predicted by the calibration
- samples represent the range of physical and chemical composition anticipated in future samples to be predicted by the calibration
- samples are chemically unchanged between the time they are scanned by NIRS and analyzed chemically by reference methods
- samples are physically uniformly mixed so that the aliquots analyzed by reference methods and those scanned by NIRS are truly representative.

### ***Purpose***

This field demonstration project had three major goals and several subgoals:

- A. Development of mobile laboratory
  - 1) design and build a truck-mounted laboratory to operate two field-portable NIR instruments, the Textron ProSpectra prototype instrument and the Zeiss Corona, in the field
  - 2) provide for safely and securely transporting instruments and computers; supply correct power requirements in the field; establish a weatherproof, level working area; and provide a safe working environment for the operator
- B. Development of field sampling and scanning protocol
  - 1) sample and scan hog manure in the field with the portable instruments operating in a free-standing mode at a range of ambient temperatures
  - 2) obtain compositional data from manure applicators in the field obtained with hand-held equipment
  - 3) obtain data from the on-board nutrient monitoring system of the Ag Waste Management Corp TR 6000 manure injection truck during field operation.
- C. Evaluation of the performance of the portable instruments
  - 1) have the manure samples analyzed by conventional chemical methods for moisture, nutrients, metals, and minor elements

- 2) develop and evaluate calibrations for each constituent from the spectra recorded from the ProSpectra prototype and the Corona together with the reference chemical data
- 3) scan manure samples with the model 6500 instrument and develop and evaluate calibrations using this instrument as a baseline of known performance
- 4) evaluate the predictions of the portable instruments against the performance of the 6500, the hand-held instruments, and the on-board nutrient monitoring system.

This report is first in a series of six reports on the field-testing of the mobile instruments. It describes the development and construction of the truck-mounted NIR laboratory. It describes the procedures for sampling and analyzing the manure for physical and chemical parameters and nutrients. Results are given for the composition of the manure and evaluation of the success of predicting physical and chemical parameters and nutrients using the Foss NIRSystems Inc. model 6500. Results for predicting physical and chemical parameters and nutrients in the manure samples with the Textron ProSpectra prototype are reported in the second report by Malley, Martin and Moffatt (2001a) and with the Zeiss Corona in the third report by Malley, Martin and Dettman (2001a). Analysis of the manure for minor elements and metals and the prediction of these by the 6500, the ProSpectra and the Corona are reported in the fourth to sixth reports by Malley, Martin, Woods and Dettman (2001), Malley, Martin and Moffatt (2001b) and Malley, Martin and Dettman (2001b), respectively.

Goals B(2), B(3), and part of C(4) above were not completed. The compositional data was not obtained from the manure applicators in the field and the on-board nutrient monitoring system was not operating during the period of this study.

# Methods

## *Design and Construction of Truck-mounted Laboratory*

Project requirements were provision for remote power, stability in transit, convenient access, protection from inclement weather, and security when not in use. The mobile lab was developed by building a frame, deck, and movable bench in the bed of a 1/4 ton pick-up truck. A custom tent was designed and built. Preparation of the truck was required as shown in Table 1. Tables 2 to 4 provide parts list for the tent, frame, deck, bench, and power supply.

Table 1. Steps in the preparation of the 1/4 ton pick-up truck for the mounting of the mobile laboratory

Application of a polyurethane liner to the bed of the truck to protect the bed from the installation of the wood frame and to provide a non-slip surface for the frame
Purchase of a tonneau cap to cover and protect the laboratory when not in use
Installation of an air assist suspension kit on the truck to provide additional suspension under the heavy load, especially on rough roads

Table 2. Parts list for tent assembly

Tent designed in-house and custom built by a Winnipeg company
Aluminum A-frame assembly; to provide support for awning extension work area: <ul style="list-style-type: none"><li>• 1 inch aluminum hollow square tubing for poles</li><li>• 1/4 inch aluminum plate for joint assemblies and tailgate fasteners (proprietary)</li><li>• hardwood square plug inserts for connections and adjustable pole lower extensions</li></ul>
Aluminum support struts for rigid support of tonneau: <ul style="list-style-type: none"><li>• 3/4 inch aluminum hollow square tubing</li></ul>

Table 3. Parts list for frame, deck and bench designed and built in-house

Wooden frame base, ladder construction: <ul style="list-style-type: none"><li>• rubber footings</li><li>• 2x4 (optional) construction</li></ul>
Plywood deck surface with high density foam rubber shock pads for equipment

<p>Tension assembly (proprietary):</p> <ul style="list-style-type: none"> <li>• tension pads for rigidly securing frame to truck box (wood with high density foam rubber interface)</li> <li>• two-way tensioner bolts and associated hardware</li> </ul>
<p>Extendible bench assembly:</p> <ul style="list-style-type: none"> <li>• arborite/plywood laminated tabletop</li> <li>• high density foam rubber shock mounting for table-mounted equipment</li> <li>• Velcro strapping for securing of notebook computer and Zeiss Corona</li> <li>• wooden extension arms connected to 22 inch heavy-duty, ball-bearing drawer slides</li> <li>• four point leveling bolts</li> <li>• removable wetworks basin (pan)</li> <li>• spring-loaded tabletop extension locking assemblies</li> <li>• Velcro strapping for securing of tabletop from motion in transit (retracted position)</li> </ul>

Table 4. Parts list for instrument power supply.

<p>Battery power bank:</p> <ul style="list-style-type: none"> <li>• 600 Amp-hour battery bank consisting of 6 -100 Amp-hour sealed (gel cell) batteries</li> <li>• intercell and bank to terminal block connection cables</li> <li>• weather resistant plastic battery cases for safety and securing of batteries to deck</li> </ul>
<p>Power distribution:</p> <ul style="list-style-type: none"> <li>• twin (one positive, one negative) terminal blocks, one piece, solid alloy construction</li> <li>• 6 inch weatherproof PVC terminal housing</li> <li>• 10 gauge stranded cable leads to equipment</li> </ul>
<p>Charging system:</p> <ul style="list-style-type: none"> <li>• voltage sensing, multistage battery charger, with 13 amp maximum output</li> <li>• extendible assembly providing a.) manufacturer recommended clearance regarding thermal properties/airflow requirements of charger (extended) and b.) efficient use of limited space (retracted)</li> <li>• extension cord (to AC power outlet input)</li> </ul>
<p>Power regulation:</p> <ul style="list-style-type: none"> <li>• 4 individual 150 watt DC to AC power inverters, to provide a.) AC power to equipment specific AC to DC power regulators, b.) double redundancy protection of equipment from power surges, and c.) inverter redundancy (in case of inverter failure)</li> <li>• Manufacturer supplied AC to DC power regulators specific to equipment in use (ie. laptops and spectrophotometers)</li> </ul>
<p>Alternate power supply:</p> <ul style="list-style-type: none"> <li>• portable power generator (gasoline powered)</li> <li>• booster cables for connection to terminal blocks of vehicle battery and charging system</li> </ul>

## ***Sampling and Analysis of Hog Manure***

### **Sampling**

Between 28 September and 4 November 2000, 121 samples of hog manure were collected from 13 hog operations near Winnipeg. All but two of these operations had manure in earthen stores, one had a slurry store and a secondary lagoon, and one had above ground storage. Six of the operations were visited once and seven were visited from two to seven times during pump-out. Several of these were visited at the start and the finish of pump-out, as well as periodically in between. This was intended to provide data on the range of concentrations of nutrients that are applied during the emptying of a manure store. Variability data are not generally available and are of interest to hog producers, farmers and regulators. This sampling strategy also provided the wide range of concentrations of constituents that is desirable in NIRS.

Most samples were taken from manure collected in a 10-L pail from a dropout valve located on the pump itself during land application by professional applicators using an umbilicus system between the manure store and the tractor. The contents of the pail were stirred and four sub-samples were transferred to 1-L polyethylene bottles with stirring between each sub-sample. Some samples were collected as grab samples by manually dipping the pail below the surface of the manure store from a position atop the agitator boom. The agitator was shut off during this process for safety reasons. Sub-samples were transferred to 1-L bottles as above.

### **Chemical Analysis**

Using the methods of Stainton et al. (1977), the samples were analyzed by the Freshwater Institute Analytical Laboratory for pH, conductivity, density, ammonium-nitrogen ( $\text{NH}_4\text{-N}$ ), total dissolved nitrogen (TDN), suspended nitrogen (susp N), soluble reactive phosphorus (SRP, i.e., phosphate or inorganic P), total dissolved phosphorus (TDP, i.e., dissolved inorganic and organic P), suspended P (susp P), and suspended carbon (susp C, i.e., a measure of the particular organic matter).

Total N was calculated from the sum of total dissolved N and suspended N. Total P was calculated from the sum of total dissolved P and suspended P.

### ***Density***

The density of hog manure samples at room temperature was determined by weighing 100 mL of manure in a graduated cylinder to the nearest 0.01 g. Samples were shaken well before they were poured into the cylinder. The density of distilled water at room temperature was measured. If the density of water was not exactly 1.00 g/mL, a correction factor was established.

### ***Total Dissolved Nitrogen and Ammonia Nitrogen***

The manure samples were filtered through Whatman GF/C filters and filtrates were diluted until they were in the 5 to 2000  $\mu\text{g/L}$  N range. For the determination of total dissolved N, organic N compounds are decomposed by a 1-hour exposure to short, high intensity UV radiation under conditions of pH 2 and adequate oxygen supply. The products of combustion

were  $\text{NH}_4\text{-N}$ ,  $\text{NO}_2\text{-N}$  and  $\text{NO}_3\text{-N}$ . Samples were passed through a zinc reduction column where  $\text{NO}_2\text{-N}$  and  $\text{NO}_3\text{-N}$  were reduced to  $\text{NH}_4\text{-N}$ . Total dissolved N was then measured as  $\text{NH}_3$  using a Technicon Auto-Analyzer. Ammonium-N reacts with phenol and hypochlorite to form indophenol blue measured at 640 nm.

Ammonium-N was determined by directly analyzing the diluted filtrates without the UV decomposition and reduction steps.

### ***Particulate or Suspended Carbon and Nitrogen***

Particles were collected on pre-ignited glass fiber filter papers so that filters contained 0.1 to 100  $\mu\text{g N}$  or 1 to 500  $\mu\text{g C}$ . Filter papers with particulates were vacuum desiccated in the dark to dryness and stored at  $-10^\circ\text{C}$  until analysis. The particulate material was combusted in an oxygen helium atmosphere at  $950\text{-}975^\circ\text{C}$ . Helium gas is used to carry the combustion products through different stages of the procedure. The combustion gas passes over a heated bed of special packing that oxidizes the combustion gases to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and oxides of N, and removes interfering compounds. The hot gas stream then passes over hot Cu ( $625\text{-}650^\circ\text{C}$ ) to reduce nitrogen oxides to  $\text{N}_2$  and to remove excess  $\text{O}_2$ . The gas mixture passes through thermal conductivity detectors and traps that sequentially remove  $\text{H}_2\text{O}$  and  $\text{C}_2\text{O}$ . The remaining gas contains only  $\text{N}_2$  and He. Signals from the detectors at various stages in the process are standardized using known reference materials.

### ***Soluble Reactive Phosphorus***

Filtrates from manure samples were diluted until they were in the 1 to 500  $\mu\text{g/L P}$  range. Soluble reactive P, i.e., orthophosphate ( $\text{PO}_4\text{-P}$ ), was determined by reaction with ammonium molybdate under acidic conditions. This produces a blue-colored complex that is measured by absorbance at 885 nm.

### ***Total Dissolved Phosphorus***

Filtrates from manure samples were diluted until they were in the 5 to 250  $\mu\text{g/L P}$  range. Organic P in the samples was photo-oxidized over a 1 to 4 h period to  $\text{PO}_4\text{-P}$  using short UV radiation under acidic conditions and the presence of oxygen. Orthophosphate was analyzed as soluble reactive P in the method given below.

### ***Particulate or Suspended Phosphorus***

Particles were collected on pre-ignited glass fiber filter papers so that filters contained 0.05 to 20  $\mu\text{g P}$ . Filters were ignited at  $550^\circ\text{C}$  to destroy organic matter. The filters were then heated at  $104^\circ\text{C}$  with dilute HCl (0.165 N) to extract the P and convert it to orthophosphate ( $\text{PO}_4\text{-P}$ ). Phosphorus was determined by the soluble reactive P method.

### ***Near-infrared Spectroscopy in the Laboratory Using the Foss NIRSystems 6500***

NIR spectra were recorded using a Foss NIRSystems Inc (Silver Spring MD) Model 6500 visible/NIR scanning spectrophotometer operated with Near-infrared Spectral Analysis Software (NSAS). Manure sub-samples were well shaken and aliquots removed and dispensed into a liquid sample cell with path length of 2 mm. The cell had quartz glass on two sides, a non-absorbing opaque ceramic fastened over one glass side, and a gasket to make the cell watertight.

For thin samples, light passed (was transmitted) through this cell and reflected back to the detector from the ceramic. For thick samples, most of the light was reflected back from the particles. This is referred to as a transreflectance cell.

The NIR instrument was equipped with a standard sample transport but was turned on its back so that the transport operated horizontally, instead of vertically as is normal. In this way, any settling particles stayed in the path of the light, rather than falling out of it.

Absorbance was recorded every 2 nm from 400 to 2500 nm. Between each sample scan, a reference ceramic was scanned and the reference spectrum was automatically subtracted from each sample scan. Sub-samples were loaded into the cell twice. For each loading, triplicate scans were recorded, with the cell being turned 120° between scans.

### ***Principal Component Analysis***

Using multivariate analysis software, Unscrambler® (CAMO ASA Oslo, Norway), principal component analysis (PCA) was performed on the pH, conductivity, density, and nutrient chemical data. The data were centered, all 12 constituents were weighted using a transformation, 1/SD. On a two-dimensional scatter plot, loadings of individual constituents on the first two principal components (PC) explaining the variance in constituents were examined. The plot shows the importance of various constituents, i.e., the extent to which their variability is explained by PC1 or PC2, and the extent to which they are interrelated. Variables close to each other in the loading plot will have a high positive correlation if the two variables explain a large proportion of the variance in composition. Variables in diagonally-opposed quadrants will tend to be negatively correlated. Variables close to the center of the plot will be poorly explained by the plotted PCs.

On a second scatter plot, scores for individual samples on the first two PCs explaining the variance in the constituent data were plotted. The plot gives information about patterns among the samples. The closer samples were in the score plot, the more similar they were with respect to composition. Conversely, samples far away from each other were different from each other. The loading and score plots can be viewed together. Samples in one quadrant of the score plot will usually have high values for the variables in that quadrant in the loading plot.

### ***Calibration Procedure by Multiple Linear Regression Using NSAS***

The ability of NIRS to provide rapid analyses depends on the prior preparation of mathematical calibrations used to predict constituents, parameters or functionality in unknown samples. A calibration is a statistical correlation model relating the spectral data for a set of samples to its compositional data determined by conventional methods.

To remove the calibration software as a variable in the evaluation of the laboratory and field-portable instruments in this initial feasibility study it was intended to perform all calibrations using the multiple linear regression option of NSAS. This software is efficient in examining many pre-treatments of the spectral data before they are correlated with the

constituent data. For example, many combinations of smoothing interval, derivative (first or second) and derivative size can be developed quickly. Once an NIR instrument is considered as a candidate for field use, nevertheless, calibrations for constituents of interest must be developed in the operating software of the instrument.

The six replicate spectra for each sample were averaged to give one spectrum per sample. The reference chemical results for all the constituents for each sample were added to the NIR spectral file. Concentrations of constituents in the manure were on a wet weight basis.

For each constituent, the spectra were sorted from lowest to highest constituent value and divided equally into two sets. Every other sample was allocated to the calibration set ("A"), and the remaining samples to the validation set ("B"). Each set therefore represented the full range of constituent concentrations. Using the calibration set, up to 288 calibration equations were developed for the wavelength range 400-2498 nm using the stepwise multiple linear regression (MLR) option in the NSAS software. For example, separate calibration equations were computed using the raw optical data ( $\log 1/R$ ) smoothed over 4, 10, 20, or 40 wavelength points, termed "segments" (where wavelength points were 2 nm apart). The optical data were then transformed using first or second derivative and derivative ("gap") sizes of 4, 10, 20, or 40 wavelength points. As for the raw optical data, the derivatized data were smoothed using the above wavelengths segments. For each combination of segment and gap, equations for one to 8 wavelengths were calculated.

Each of the calibration equations developed from the calibration set was used to predict the constituent values for the independent spectra in the validation set. The NIR-predicted values for the validation set were correlated to their chemically-measured reference values. The calibration process was completed when one equation was selected as giving the best results. This is referred to as "A/B" in Table 6. The procedure was repeated by using the validation set ("B") to develop the calibrations and the calibration set (A) for the validation process. This is referred to as "B/A" in Table 6. The procedure was repeated for each constituent.

### ***Statistical Evaluation of Calibrations***

The best calibration was the one with the highest  $r^2$  (coefficient of determination) between NIR-predicted and reference values, and lowest SEP (standard error of performance, i.e., the standard deviation of the residuals about the 1:1 line). Other statistics used to evaluate the calibration were the RPD, i.e., the ratio of the SD of the reference values for the validation set to the SEP; and the RER, i.e., the ratio of the range of the reference values for the validation set to the SEP.

In the successful analysis of agricultural commodities, usually  $r^2$  is  $> 0.95$ , RPD is  $> 5$  and RER is  $> 20$ . Nevertheless, for samples such as manure that are more variable than commodities, several levels of performance are defined and used in this study. Excellent calibrations were those with  $r^2 > 0.95$  and RPD  $> 4$ . Successful calibrations had  $r^2 = 0.9 - 0.95$  and RPD = 3 - 4. Moderately successful calibrations had  $r^2 = 0.8 - 0.9$  and RPD = 2.25 - 3 and moderately useful ones had  $r^2$  from 0.7 - 0.8 and RPD from 1.75 - 2.25. Calibrations with lower statistical performance may still be useful depending on the accuracy required in the field

situation and the lack of availability of better alternative field methods. They are useful for screening purposes, such as for distinguishing among low, medium, and high values, or for selecting samples for costly conventional chemical analysis.

## Results

### *Development of the Truck Lab*

The lab consisted of an instrumentation and power deck, tonneau cover and tent assembly. The mobile laboratory was designed and constructed in-house by PDK Projects, Inc. to fit the bed of a compact pickup (Fig. 1, 2). The lab was built upon a 1999 Chevrolet S-10 Extended Cab Shortbox chassis. The design is easily transferable to other makes and models of pickup trucks. An air-assist suspension was installed at the rear axle to allow for ride attitude adjustment under load.

An after-market custom-fit fibreglass tonneau cover provided protection from wind and rain and out-of-view security while in transit or when the vehicle is parked (Fig. 3). The cover was locked manually. When locked, the cover did not allow the tailgate to be opened.

A custom designed Tonnotent™ assembly (Fig. 1, 2) provided protection from the elements to both the operator and the equipment. The tent attached to the underside of the tonneau cover, and extended out and over the sides of the vehicle to the ground (Fig. 1, 2). The tent also extended over the back tailgate, where it was supported by an aluminum A-frame (Fig. 4). Two arms of the A-frame assembly attached directly to the tailgate of the truck, while the other two rested on the ground. The latter two also acted as a door frame to the resulting enclosure.

The batteries and instruments were mounted on a wooden deck. The deck consisted of a plywood surface above a ladder frame assembly. Integral to the frame was a tension assembly, which fastened the deck to the truck bed. Also integral to the deck was a self-supporting sliding lab bench. The bench pulled out and locked in place over the tailgate of the truck (Fig. 5, 6) and could be leveled manually. The deck provided an easily accessible work surface (Fig. 6) and was very stable under severe driving conditions. The instrument deck was easily installed or removed, and required no drilling or other modification of the pickup truck bed.

Power was supplied to the instruments via a 600-amp/hour battery bank consisting of 6 100-amp/hour gel-cell batteries (Fig. 7). The power distribution system included a charging system, a power regulation system, and provision for an alternate power supply (Fig. 8).



Fig. 1. Custom-designed tent using the tonneau cap as part of the roof of the tent



Fig. 2. Tent has windows on the sides and entry at the back



Fig. 3. Truck lab is secure when the tonneau cap is closed and locked.



Fig. 4. Tent poles fasten in soft ground around tail gate for operation.



Fig. 5. Moveable lab bench (see Table 3) slides back over tailgate for operation



Fig. 6. Moveable bench over tailgate provides a convenient working area



Fig. 7. Power supply and regulation system (see Table 4) in place on the deck



Fig. 8. Battery charger (left), converters (red) for DC to AC conversion and inverters (black) to convert AC to DC for instruments and notebook computers

## Composition of the Manure

In this set of 121 hog manure samples, pH varied from 6.7 to 8.1, conductivity from 6.8 to 27.2 mS/cm and density from 1.002 to 1.049 g/mL (Table 5). On average, 90.9 % of the TDN was NH<sub>4</sub>-N, and 80.0 % of the total N was TDN. Therefore most (72.7 %) of the total N was NH<sub>4</sub>-N. Total dissolved P was 96.9 % SRP, i.e., inorganic phosphate, and TDP was 60.4 % of the total P (Table 5). Therefore, just over half (58.5 %) of the total P was inorganic phosphate.

Suspended C was the most concentrated constituent and the most variable, i.e., had the highest coefficient of variation. Suspended P, and the other P fractions, and suspended N were also highly variable in concentration. Ammonium-N and TDN were the least variable of the nutrients (Table 5).

In this set of samples, NH<sub>4</sub>-N and TDN were very highly correlated as were SRP and TDP (Table 6). Ammonium-N and TDN were highly correlated with total N but less highly correlated with suspended N. All the P fractions were highly inter-correlated with one another and with suspended N and suspended C (Table 6). Most constituents were somewhat negatively

Table 5. Average chemical composition of the 121 hog manure samples analyzed in this study

Constituent	Mean $\pm$ SD	Range	Median	CV* %
pH		6.66 - 8.10	7.71	4.7
Conductivity, mS/cm	15.14 $\pm$ 4.73	6.84 - 27.20	15.28	31.3
Density, g/mL	1.023 $\pm$ 0.010	1.002 - 1.049	1.022	1.0
NH <sub>4</sub> -N, g/L	2.18 $\pm$ 1.11	0.56 - 5.54	1.95	51.0
Total Dissolved N, g/L	2.40 $\pm$ 1.21	0.59 - 6.11	2.11	50.6
Suspended N, g/L	0.602 $\pm$ 0.798	0.014 - 4.083	0.306	132.7
Total N, g/L	3.00 $\pm$ 1.89	0.61 - 10.14	2.46	62.9
Soluble Reactive P, g/L	0.562 $\pm$ 0.703	0.047 - 3.813	0.363	125.1
Total Dissolved P, g/L	0.580 $\pm$ 0.716	0.055 - 3.86	0.378	123.3
Suspended P, g/L	0.380 $\pm$ 0.573	0.003 - 2.650	0.125	150.9
Total P, g/L	0.960 $\pm$ 1.268	0.055 - 6.512	0.579	132.0
Suspended C, g/L	6.10 $\pm$ 10.007	0.092 - 54.602	2.4	164.0

\* Coefficient of variation = (standard deviation/mean) \* 100

correlated with pH. Only  $\text{NH}_4\text{-N}$  and TDN were correlated with conductivity. No constituents were appreciably correlated with density (Table 6).

Figure 9 shows that PC 1, explaining 74 % of the variation in the constituent data, expressed the inverse relationship between pH and the other constituents that is seen in Table 6. We interpret that PC2, explaining an additional 15 % of the variation, was related to ionic strength. More or less, the constituents above the horizontal line are ionic or associated with ion strength and those below are non-ionic. Consistent with Table 6, this plot shows that suspended C, N, and P were all highly inter-correlated and that these were highly correlated with TDP and SRP. The high correlation between  $\text{NH}_4\text{-N}$  and TDN from Table 2 is readily seen. The latter two constituents were not highly correlated with conductivity and density (Table 6).

Figure 10 shows the relationships among the samples based on composition. There is a central grouping comprised of most of the samples. To the lower right is a set of four samples that was from the thickest manure in the study. Clearly, these samples are outliers in this sample set in terms of composition. At the top of the plot is a set of 10 samples that were the only ones in the study from an above-ground store. Considering Fig. 9 and 10 together, it can be seen that the samples at the lower right differ from the others primarily in having high suspended and P contents. The above-ground store samples at the upper part of the plot differ from the others in having little particulate content and high conductivity.

Table 6. Correlation, r, matrix among pH, conductivity, density, and the nutrients in the 121 samples of hog manure in this study.

	<b>pH</b>	<b>Cond</b>	<b>Density</b>	<b>NH<sub>4</sub>-N</b>	<b>TDN</b>	<b>Susp N</b>	<b>Total N</b>	<b>SRP</b>	<b>TDP</b>	<b>Susp P</b>	<b>Total P</b>	<b>Susp C</b>
<b>pH</b>	1.000											
<b>Cond</b>	-0.028	1.000										
<b>Density</b>	-0.384	0.384	1.000									
<b>NH<sub>4</sub>-N</b>	-0.488	0.749	0.411	1.000								
<b>TDN</b>	-0.478	0.759	0.397	0.998	1.000							
<b>Susp N</b>	-0.690	0.158	0.296	0.763	0.746	1.000						
<b>Total N</b>	-0.600	0.555	0.381	0.965	0.960	0.904	1.000					
<b>SRP</b>	-0.643	0.236	0.249	0.811	0.798	0.980	0.928	1.000				
<b>TDP</b>	-0.643	0.243	0.258	0.814	0.803	0.978	0.930	0.999	1.000			
<b>Susp P</b>	-0.608	0.109	0.342	0.705	0.685	0.973	0.853	0.938	0.935	1.000		
<b>Total P</b>	-0.638	0.187	0.300	0.778	0.763	0.992	0.911	0.988	0.987	0.980	1.000	
<b>Susp C</b>	-0.701	0.105	0.175	0.728	0.714	0.984	0.878	0.978	0.976	0.935	0.973	1.000

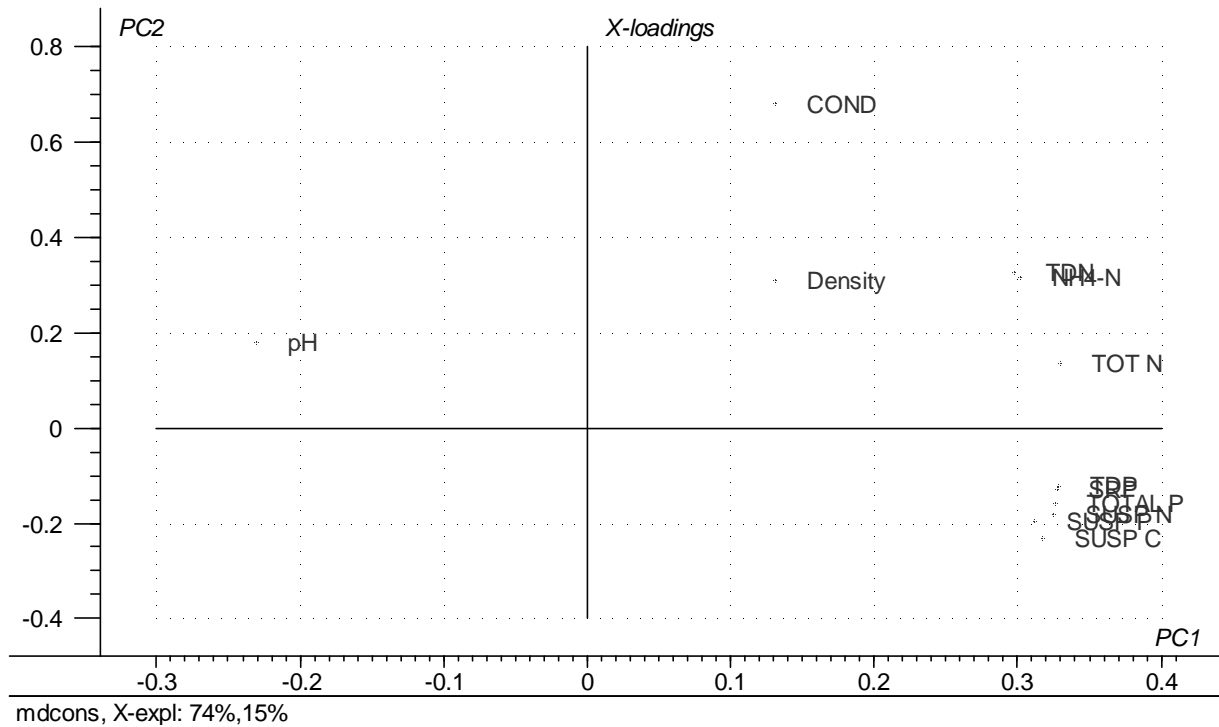


Fig. 9. Loadings plot for pH, conductivity, density, and the nutrients in the 121 samples of hog manure on the first two principal components explaining the variance in the constituent data

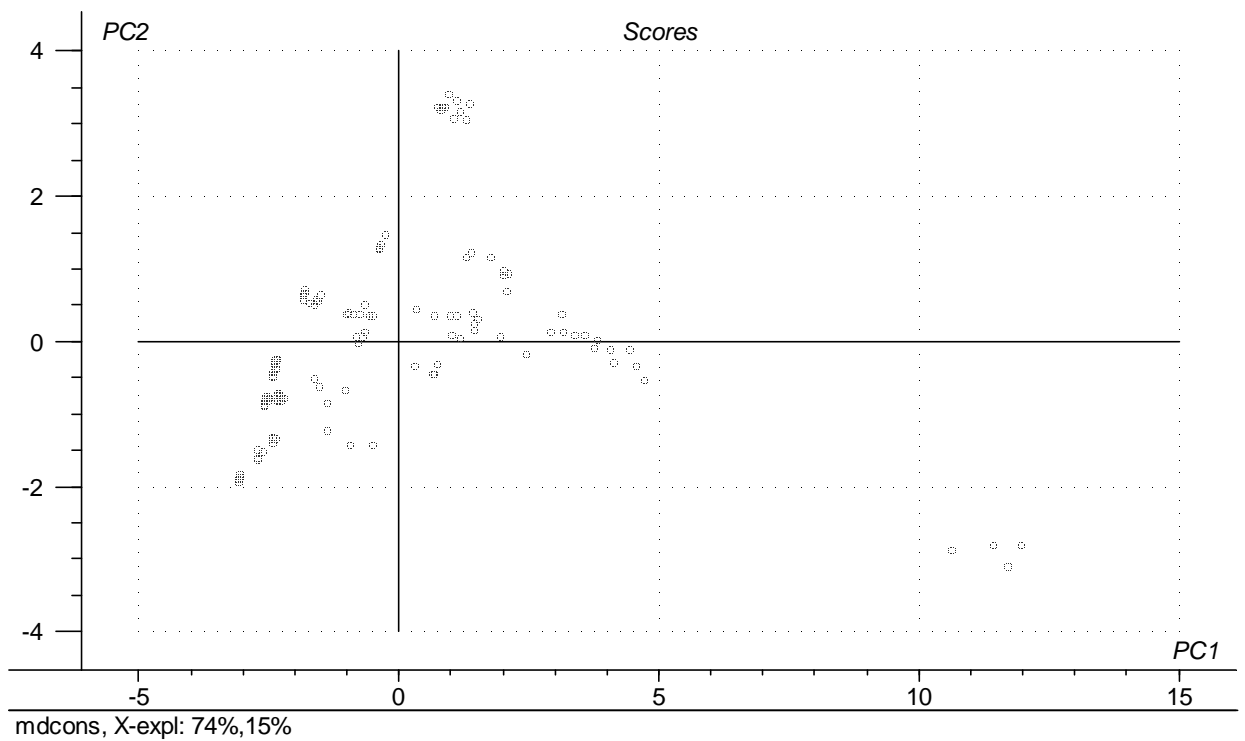


Fig. 10. Score plot of 121 samples of hog manure on the first two principal components explaining variance in the constituent data

### ***Variability in Composition with Depth in a Manure Store***

Figure 11 shows the change in composition of an above ground manure store with sampling depth. The samples (from left to right) were taken in duplicate at 2', 5', 11', 12', and at the bottom of the store. Except for suspended C that was variable, composition showed little change with depth. The lack of significant stratification with depth is attributed to the low suspended solids content of this manure. Suspended C averaged 3.52 mg/L compared with the overall mean in the sample set of 6.10 mg/L.

These samples are the outliers at the top of Fig. 10. As speculated, they are higher in conductivity (26.5 mS/cm) than the average (15.1 mS/cm). The behaviour of this manure with depth is not considered to represent thicker manures that are expected to stratify with depth.

### ***Variability in Composition over Time during Pump-out***

Some operations sampled in this study were visited only once. Others were visited up to 7 times. For the operation shown in Fig. 12, there were dramatic changes in nutrient concentrations in the manure over the 8 days of the pump-out, despite the fact that the manure store was continuously agitated. Ammonium-N varied over 2.4-fold during pump-out, particulate N varied 38-fold, and total N ranged over 3.5-fold. More extreme was the variation in P during pump-out. Dissolved P varied 9.5-fold; particulate P, 230-fold; and total P varied 20-fold. Potassium varied little (not shown).

### ***Spectra***

Figure 13 shows representative spectra obtained with the model 6500 spectrophotometer from manure samples with a variety of particulate content. The spectral range was 400 to 2498 nm. The discontinuity at 1100 nm is the division between two detectors. The spectra are dominated by water that absorbs at 1400 and 1900 nm. Most of the spectra above 1900 nm are saturated by water. To be useful, absorbances should be below 2. Therefore, the region above 1900 nm is likely to be less useful for prediction than below 1900 nm. The spectrum that is upper most on the left side of the figure (blue) was recorded by a sample with high particulate content. It has the highest colour (absorbance in the 400 - 700 nm region) consistent with its dark appearance and the lowest absorbance at 1400 and 1900 nm consistent with its lower water content.

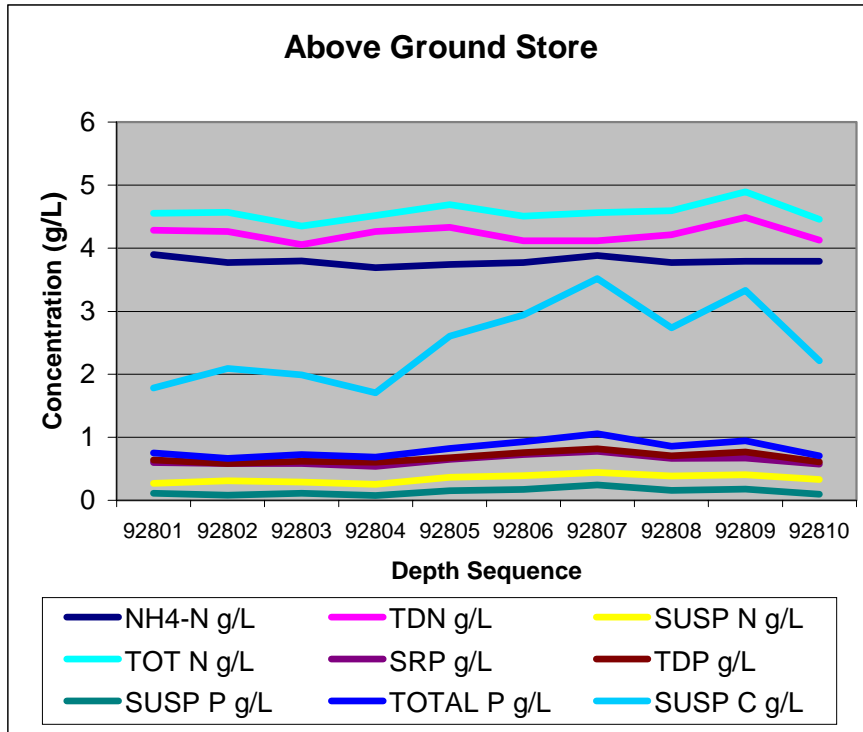


Figure 11. Changes in composition of manure with sampling down (left to right) an above ground tank

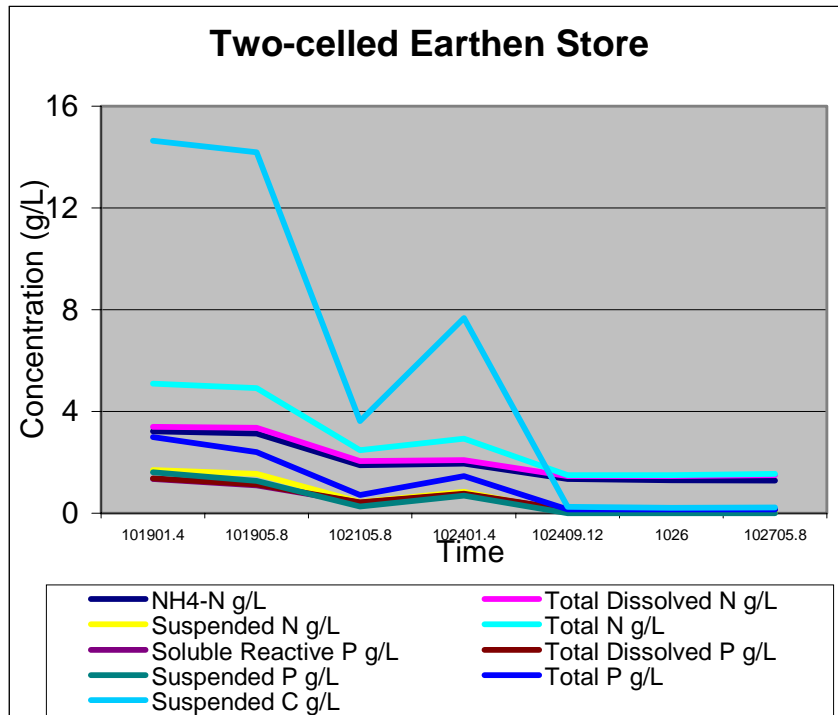


Figure 12. Changes in composition of manure over time during pump-out of a two-celled earthen store

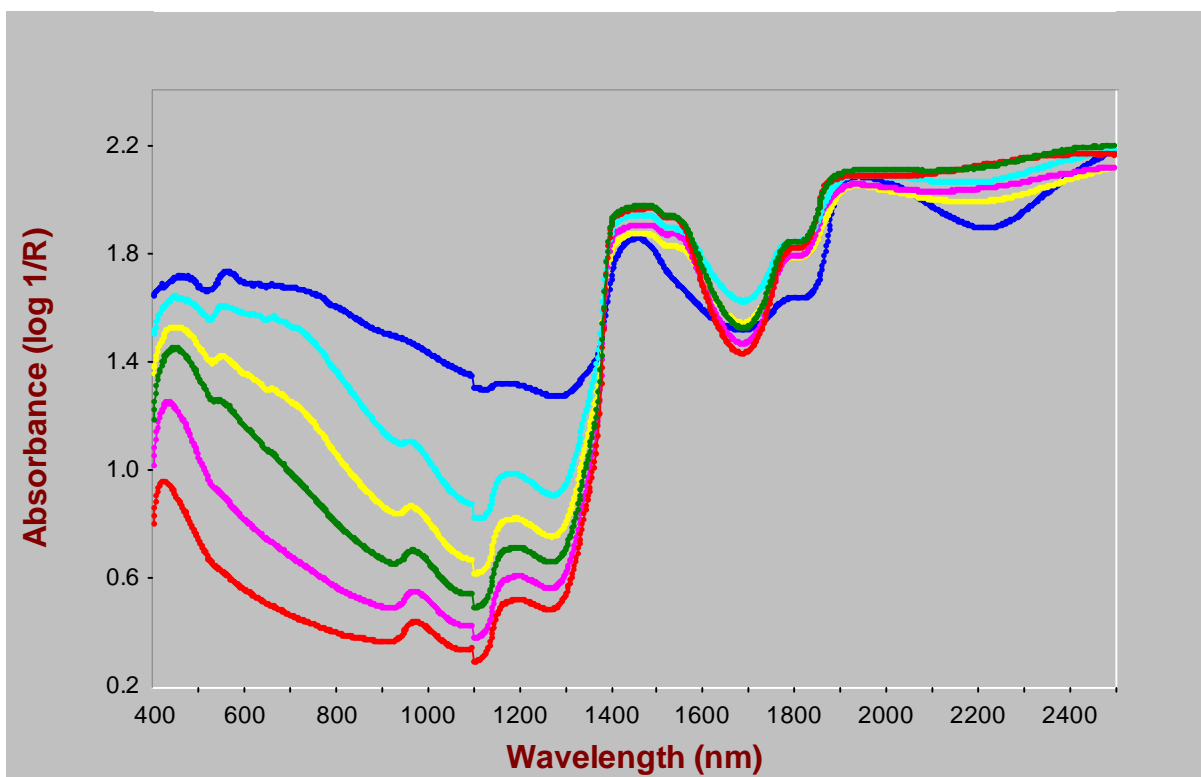


Fig. 13. Representative spectra from hog manure samples in this study recorded with the Foss NIRSystems Inc. Model 6500 spectrophotometer.

### ***NIR Prediction of pH, Conductivity, and Nutrients in Hog Manure***

Table 7 shows the statistical results for the "A/B" and "B/A" calibrations. Figure 14 shows the results of the "A/B" calibrations graphically. Most of the constituents had discontinuous distributions consistent with the groupings of samples seen in Fig. 10. Nevertheless, both high and low concentrations were modeled well by the calibrations. Using the criteria indicated in Methods for statistical evaluation of calibrations, those developed for all of the constituents were excellent with  $r^2 \sim > 0.95$  and  $RPD > 4$ .

Table 7. Accuracy of prediction for NIR calibrations for nutrients in 121 samples of hog manure collected in fall 2000. Calibrations were developed using NSAS. A, B, SEP, RPD, and RER are defined in the text.

Statistic	pH		Conductivity mS/cm		NH <sub>4</sub> -N g/L	
	A/B	B/A	A/B	B/A	A/B	B/A
<b>r<sup>2</sup></b>	0.96	0.96	0.94	0.94	0.95	0.95
<b>SEP</b>	0.069	0.078	1.21	1.17	0.244	0.255
<b>RPD</b>	5.21	4.64	3.91	4.08	4.55	4.42
<b>RER</b>	20.67	18.49	16.37	17.41	20.04	19.52

Statistic	TDN g/L		Suspended N g/L		SRP g/L	
	A/B	B/A	A/B	B/A	A/B	B/A
<b>r<sup>2</sup></b>	0.94	0.95	0.98	0.97	0.98	0.97
<b>SEP</b>	0.293	0.280	0.113	0.149	0.099	0.119
<b>RPD</b>	4.10	4.42	7.02	5.43	7.08	6.02
<b>RER</b>	18.36	19.73	35.52	27.31	37.33	31.64

Statistic	TDP g/L		Suspended P g/L		Suspended C g/L	
	A/B	B/A	A/B	B/A	A/B	B/A
<b>r<sup>2</sup></b>	0.98	0.97	0.96	0.95	0.97	0.98
<b>SEP</b>	0.104	0.133	0.112	0.141	1.57	1.56
<b>RPD</b>	6.78	5.50	4.98	4.21	6.25	6.59
<b>RER</b>	36.17	28.66	23.03	18.77	33.35	34.94

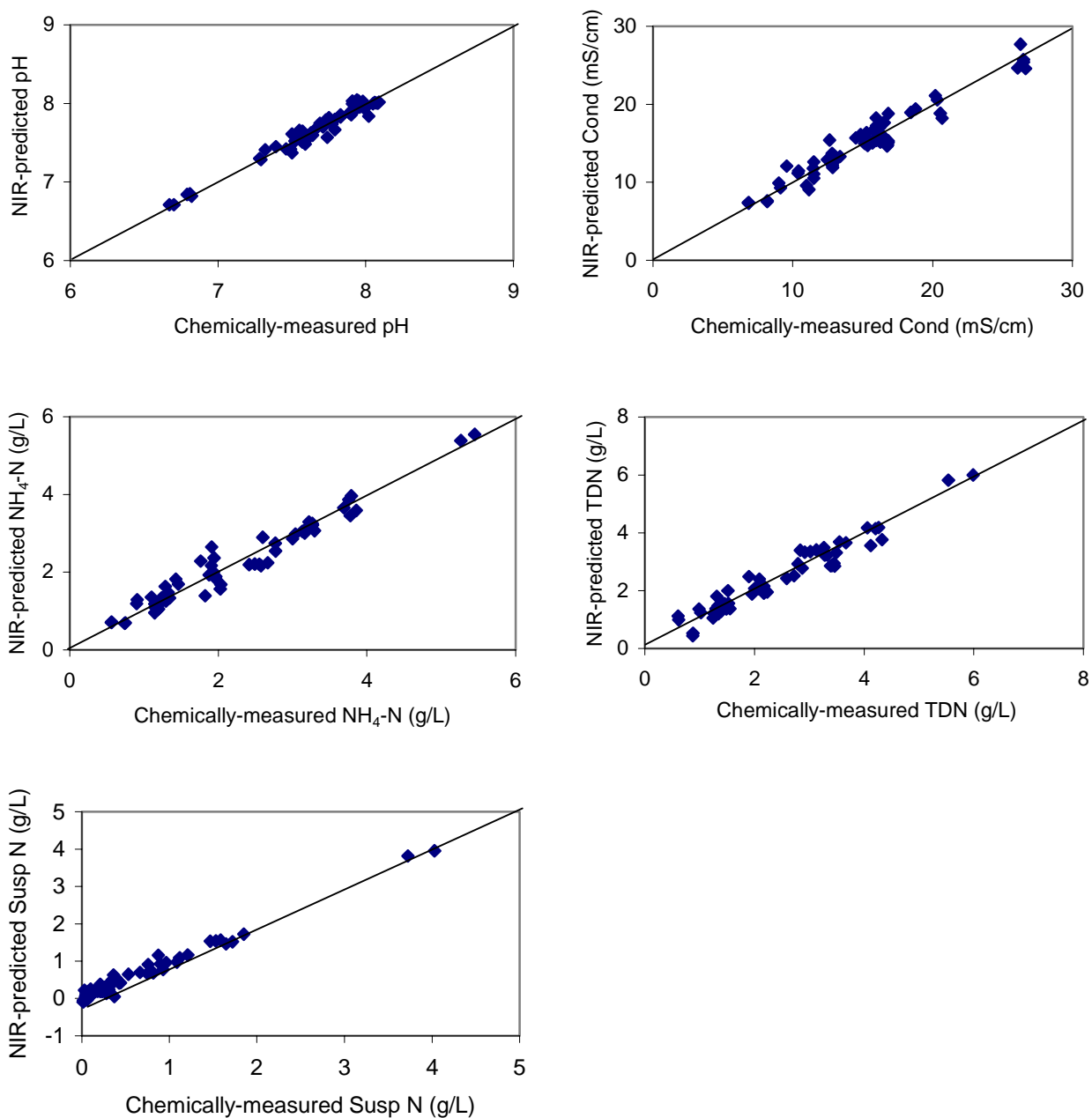


Figure 14. Linear regression relationships between the NIR-predicted and the chemically-determined values for each constituent in the manure samples collected in fall 2000. The line is 1:1 and goes through the origin.  $R^2$  and other statistics are given in Table 5.

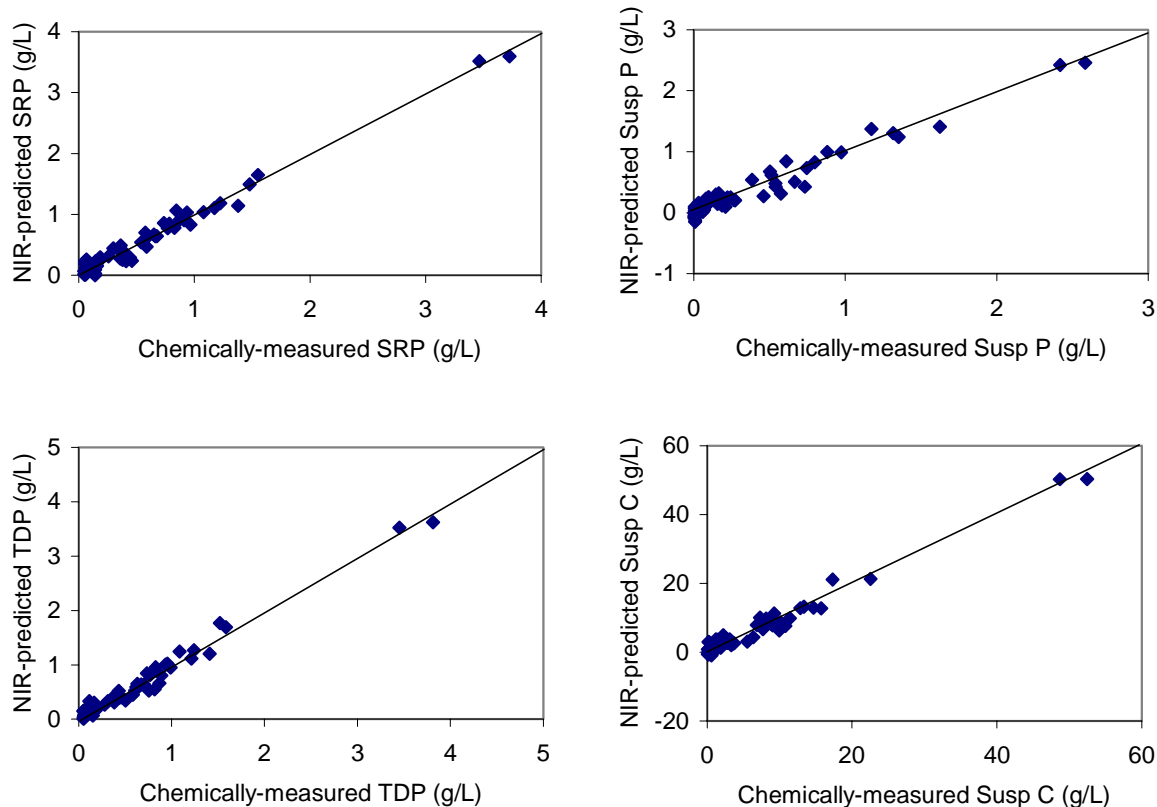


Fig. 14 cont'd

## Discussion

Few data exist on the variability in composition of hog manure during pump-out of earthen stores for land application. The data presented here suggest that  $\text{NH}_4\text{-N}$  can vary more than two to three-fold during emptying. Determination of the  $\text{NH}_4\text{-N}$  using a hand-held gas gauge at the beginning of pump-out to guide the rate of application would provide a rough guide to  $\text{NH}_4\text{-N}$  loading over time but would not be very accurate. Of greater concern is the much larger variability in total P in the manure over time that can be as much as 10 to 20-fold. The particulate content varies greatly over the pump-out cycle of a manure store even when it is agitated. Particles contain organic N and P and other constituents such as metals. Variable particulate content contributed to highly variable N:P ratio. In this sample set overall, the N:P ratio varied from 1.5 to 33. Potassium varied little during the pump-out and may be adequately measured by a point-in-time sampling of the manure store before pump-out. In this sample set, mean total N:mean total P was 4.3. Therefore, on the average, the manure samples had more P than agronomically desirable. Thus, even highly effective agitation of the manure stores would not eliminate the problem of excess P. Possibly separation and separate handling of the liquid and semi-solid portions of the manure is one possible solution. Alternatively, in-stream

measurement of the nutrients and augmentation with inorganic fertilizer as in the patented process held by Ag Waste Management Corp is another solution (Lyseng 1999).

The two groups of samples identified in this study as outliers represent manure samples different from the composition of the majority of the samples. To obtain more robust calibrations more samples of these types should be added to the data set and the calibrations re-developed.

Based on the spectral data collected by the 6500 on the samples in this study, excellent calibrations were developed for pH, conductivity, and the forms of N and P. The quality of results is similar to those obtained by Malley and Currie (1999) on 64 samples from 7 manure stores. Calibrations developed for nutrients for the set of 64 samples and the 121 samples from 13 manure stores in this study tend to be more successful than those from studies on two sets of manure samples representing 25 or more manure stores (Malley and Vandenbyllaardt 1999; Malley, Badiou and Williams 2000). The quality of calibrations for nutrients in hog manure by NIRS tend to vary inversely with sample heterogeneity (Malley and Vandenbyllaardt 1999). This indicates that it may be useful to explore developing calibrations for constituents based on samples with lesser heterogeneity, such as by type of hog operation or type of feed.

This study is a developmental stage between laboratory analysis of hog manure samples by NIRS and in-stream, real-time measurement during land application. It involved the deployment of a pre-commercial NIR instrument, the ProSpectra, and a commercial instrument, the Corona. Both instruments were being evaluated in applications new to them. The evaluation of a new NIR instrument is a complex process (Table 8). The evaluation of instruments to meet the additional needs of field deployment involves further considerations as well (Table 9). We demonstrated that two NIR instruments can be mounted on a mobile laboratory and operated in a free-standing mode. Several steps are necessary to complete the evaluation of the free-standing operation of these instruments. The calibrations developed by NSAS and The Unscrambler in this study need to be exported to the software that operates the instruments. This is Delight in the case of the ProSpectra, and Aspect Plus in the case of the Corona. In the field, future manure samples need to be scanned and the composition predicted using the calibrations from this initial study has to be compared with the results of conventional chemical analyses on the same samples. Once calibrations have been demonstrated to be reliable and robust, the instruments could be available in a free-standing mode for commercial or regulatory use. Considerations at that point will include benefit:cost and whether the instruments perform for the most important constituents at the level of precision required

The major challenges to moving from the free-standing mode to in-stream operation are sample presentation and communication between the NIR instrument and the controller for the application of manure and monitoring of loading rates.

Table 8. Factors involved in evaluation of a new near-infrared instrument. From Williams and Labossiere (2000).

<b>Factors</b>	<b>Comments</b>
Instrument purpose	<ul style="list-style-type: none"> <li>• What measurements are needed?</li> <li>• In what samples?</li> <li>• What accuracy/precision are needed?</li> </ul>
Instrument size	<ul style="list-style-type: none"> <li>• How large?</li> <li>• How portable?</li> <li>• What services are needed?</li> </ul>
Spectral range	<ul style="list-style-type: none"> <li>• Relates to the measurements that are needed.</li> </ul>
Sample size	<ul style="list-style-type: none"> <li>• Should be flexible</li> </ul>
Sample access/presentation	<ul style="list-style-type: none"> <li>• Sample type</li> <li>• Sample size</li> <li>• Access/presentation mechanism</li> <li>• Sample cell design</li> <li>• Cell cleaning</li> </ul>
Operating manual	<ul style="list-style-type: none"> <li>• Often not adequate</li> </ul>
Simplicity in use	<ul style="list-style-type: none"> <li>• Are calibrations developed in the operating software of the instrument?</li> <li>• Time per test</li> <li>• Instrument diagnostics</li> </ul>
Durability	<ul style="list-style-type: none"> <li>• Life-span of energy (light) source</li> <li>• Life-span of detector</li> <li>• Durability of sample access system</li> </ul>
Calibration transferability	<ul style="list-style-type: none"> <li>• Ease of transfer among instruments of the same type</li> <li>• Ease of monitoring. Is there a reference or master instrument?</li> <li>• Reference testing</li> <li>• Reference samples</li> </ul>
Spectral quality	<ul style="list-style-type: none"> <li>• Are there noisy areas at the ends of elsewhere in the spectra?</li> </ul>
Precision, and its contribution to overall performance	<ul style="list-style-type: none"> <li>• Day-to-day and operator-to-operator</li> <li>• Instrument precision</li> </ul>
Consistency of accuracy	<ul style="list-style-type: none"> <li>• Process control</li> <li>• Value of bias</li> </ul>

Table 9. Additional factors in the selection of an NIR instrument for a field-portable, agricultural application

<b>Factor</b>	<b>Comments</b>
suitability for type of field operation	<ul style="list-style-type: none"> <li>• free-standing</li> <li>• in-stream</li> </ul>
ease of integration into field/agricultural equipment	<ul style="list-style-type: none"> <li>• physical size and shape</li> </ul>
ease of integration into the overall application	<ul style="list-style-type: none"> <li>• includes software compatibility, communication with GPS/GIS systems</li> </ul>
availability and performance of fibre optic probes	<ul style="list-style-type: none"> <li>• includes sample presentation</li> </ul>
simplicity of operation	<ul style="list-style-type: none"> <li>• suitable for agricultural workers</li> </ul>
weather resistant	<ul style="list-style-type: none"> <li>• temperature</li> <li>• rain and snow</li> <li>• dust</li> <li>• vibration and shock</li> </ul>
stability	<ul style="list-style-type: none"> <li>• electronic stability</li> <li>• durability under field conditions</li> </ul>
application support	<ul style="list-style-type: none"> <li>• on-going performance evaluation and support</li> <li>• provision of calibrations</li> <li>• monitoring of calibrations</li> <li>• updating of calibrations</li> </ul>
instrument technical support	<ul style="list-style-type: none"> <li>• problem-solving, trouble-shooting</li> <li>• repair</li> <li>• maintenance</li> </ul>
cost	<ul style="list-style-type: none"> <li>• more important when the material to be measured is a waste/by-product than a commodity</li> </ul>

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