

Analysis of Minor Elements and Metals in Hog Manure by Field-portable Near-infrared Spectroscopy: Results for Foss NIRSystems Inc. Model 6500 Spectrophotometer in the Laboratory



Final Report 1 of 3 to Manitoba Livestock Manure Management Initiative on Project 00-02-03

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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 is 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 laptop 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 at 13 application operations during September to November 2000. A total of 121 manure samples were collected. Using conventional physical and chemical methods, the samples were analyzed for moisture, pH, density, conductivity, nutrients, metals and minor elements.

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 to predict composition of future manure samples.

This is the third of six reports describing the results from the overall project. It reports the concentrations of minor elements and metals in the manure samples collected in fall 2000. It also reports the results from developing calibrations for each of these constituents from the spectra obtained with the Model 6500 NIR instrument in the laboratory. Finally, it provides calibration results for a separate set of manure samples from another study collected in 1999 for the Agricultural Research Development Initiative (ARDI) Project 98-124 and scanned with the 6500. The calibration results for fall 2000, ARDI 1999 and ARDI 1998 samples are compared.

Moisture was predicted very successfully. Based on calibrations for the three years of data, successful calibrations were developed for Cu and Cd and moderately successful calibrations were developed for Ca, Fe, Mg, Mn, Mo, S, and Sn. Based on two of three sets, the

elements Al, Ba, Be, Cr, Ni, Se, Sr and Ti were predicted successfully or moderately successfully. Calibrations were inconsistent for Co, K, Na, Pb, Si, V, and Zn. Of these elements in this report, S is the most important as a nutrient. The metals Cu, Cr, and Zn are important as micro-nutrients. When they are in high concentrations in the manure and at risk of accumulating in soil, Cd, Cu, Cr, Pb, and Zn are important as potentially-toxic metals. The most important elements that were not reliably predicable by NIRS were K and B.

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Foss NIRSystems Inc. (Silver Spring, MD) is acknowledged for in-kind support with instrumentation, software, supplies, and technical support.

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

Economically and environmentally-sustainable operation of the hog production industry in Manitoba requires a life cycle approach to the management of all inputs and outputs. Acceptable management of the manure wastes from the operations is a particular challenge not only because of the associated odour, their large volume and high water content, but also because they are highly variable in nutrient composition (Malley, Martin and Woods, 2001). The practice of using the manure as a raw material as a crop fertilizer can be ecologically-sound, both solving a waste management problem and reducing the cost of chemical fertilizer, providing precautions are taken to avoid over-fertilization of soils; leaching of nutrients into ground and surface water; and accumulation of salts, heavy metals, and minor elements in the manure by the soil.

Hog manure is a complex mixture with three sources of inputs. It is primarily a collection of excretory products and non-digested food that have passed through the hogs, including metabolites of food, pharmaceuticals, and, potentially, pathogens and parasites. It also contains materials washed from the barns, including wasted feed, wash water, cleaning products, spilled drinking water, and water from staff showers. Finally, it contains materials such as clay and minerals scoured from the storage facility, particularly when manure is stored in earthen ponds. The composition of manure varies depending upon the type and age of animal, food, water content, storage and handling procedures, and climate (Prairie Swine Centre Inc. Factsheet, undated).

Determination of constituent concentrations in the hog manure before application to land is desirable because the concentration of total solids and the chemical composition of the manure vary from one production facility to another, over time within a facility, and most importantly, with settling. Material drawn from the top of a non-agitated truck, tank, or earthen manure store will be highly liquid and contain high ammonia and low phosphate concentrations, while that from the bottom can be highly concentrated in phosphorus, organic nitrogen and other particle-bound constituents. Manure sampled from typical hog operations in Manitoba contains a wide range of concentrations of minor elements and metals (Fitzgerald and Racz 2001) as well as of nutrients. Thus, one-time mixing and sampling of a manure store some time in advance of pump-out will not provide accurate compositional information on the manure during the application of the manure to fields or pastures.

A method of chemical analysis of the manure that is rapid, cost effective, versatile, field-portable and, if possible, operating in-stream would have wide applicability.

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 composed of light atoms, such as covalent O-H, C-H, N-H, C=O, and C-N bonds and for prediction of functional properties of samples resulting from the organic composition. Although organic substances are typically analyzed by NIRS, it has been used to determine the concentration of electrolytes such as NaNO_3 , NaNO_3 , Na_2CO_3 in liquids based on the perturbation of the water spectrum (Espinoza et al. 1999). Metals, themselves, do not absorb NIR light, but may be predictable by NIRS by their association with NIR absorbers, such as organic matter or clay, or possibly by their effects on water. Predictability of six heavy metals in sediments by NIRS was attributed to their association with naturally-occurring organic matter (Malley and Williams, 1997).

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 statistical models developed between NIR spectra from 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 NIR instrument's computer and are used to predict the parameters of interest in the unknown samples within 1 minute or less. Accuracy and precision are maintained by periodical, on-going analysis by the conventional methods of some proportion, 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). 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; Wust et al. 1996), or focused on to an industrial flow such as waste plastic articles.

Considerable experience exists in the measurement of constituents in hog manure by NIRS using bench-top laboratory NIR instruments (Malley 1999; Malley and Currie 1999; Malley et al. 1999; Malley and Vandenbyllaardt 1999; Millmier et al. 2000). Some experience has been gained with the use of a field portable NIR instrument, the Textron/Case NH ProSpectra™ in the laboratory (Malley, Badiou and Williams 2000).

Mobile NIR Laboratory

As a developmental stage between laboratory analysis of hog manure and in-stream, real-time measurement of composition of manure during application to land, a mobile laboratory was built carrying two field-portable NIR instruments (Malley, Martin and Woods, 2001). The instruments were the Textron Systems Corp (USA)/Case NH (USA) ProSpectra™ Spectrometer and the Carl Zeiss (Germany) Corona® Spectrometer. The capability of these instruments for the analysis of nutrients in hog manure is reported by Malley, Martin and Moffat (2001a) and Malley, Martin and Dettman (2001a), respectively.

The model 6500 laboratory instrument serves as a baseline instrument with a wide wavelength range and well-known performance throughout all of our studies on hog manure analysis by NIRS. It is expected that it provides a performance target against which to measure the performance of the field-portable instruments. Nevertheless, a number of factors other than instrument electronic performance affect the success of calibrations. Calibrations are highly dependent on the accuracy and precision of the chemically-measured reference data. Sample presentation affects the success of calibrations. The algorithms and the software package used for the development of calibrations have an influence as well.

Measurement of Minor Elements and Metals with NIRS

Malley and Vandenbyllaardt (1999) reported on the feasibility of estimating a number of metals and minor elements by NIRS in 75 hog manure samples collected in 1998 from 25 manure stores affiliated with Elite Swine Ltd. The samples and analytical data were obtained from a two-year study funded by the Agricultural Research Development Initiative (ARDI project 98-124) on the long-term effects of hog manure on soil quality and productivity (Fitzgerald and Racz 2001). Useful calibrations were developed for Ca, Mg, Ba, Be, Cd, Cu, Cr, Fe, Mn, Mo, Ni, Se, Sr, S, Ti, V, and Zn. Unsuccessful results were obtained for Na, K, Cl, Al, As, B, and Li (Malley and Vandenbyllaardt 1999). Malley, Badiou and Williams (2000) scanned the year 2 (1999) samples from the ARDI study using the model 6500 spectrophotometer and the ProSpectra™ spectrometer and developed calibrations for nutrients.

Purpose

The goals of this project were:

1. Development of calibrations for up to 28 metals and minor elements from the year 2 (1999) ARDI samples scanned with the model 6500 instrument.
2. Development of calibrations for up to 28 metals and minor elements from the year 2 (1999) ARDI samples scanned with the Textron/Case NH ProSpectra™ spectrometer.
3. Analysis of 100 of up to 150 hog manure samples collected in the fall of 2000 for 32 elements by inductively-coupled plasma emission spectroscopy (ICP-ES).
4. Development of calibrations for up to 28 metals and minor elements in the fall 2000 samples from the scans from three instruments:
 - a. Foss NIRSystems Inc. model 6500
 - b. Textron/Case NH ProSpectra™ spectrometer
 - c. Zeiss Corona® spectrometer.

This report describes the results of developing calibrations for the ARDI year 2 (1999) samples for metals and minor elements (goal 1) and compares the results with those for the ARDI year 1 (1998). It reports the concentrations of minor elements and metals in the manure samples collected in 2000 (goal 3), and the success of developing calibrations for the year 2000 samples for metals and minor elements (goal 4a). Results for the ProSpectra™ (goals 4b) are given in Malley, Martin, and Moffatt (2001b) and for the Corona® (goal 4c) are given in Malley, Martin, and Dettman (2001b). Based on further work with sample presentation to the

ProSpectra™ spectrometer (Malley, Martin and Moffat 2001a), it was decided not to pursue goal 2 at this time.

This report is fourth in a series of six reports on the field-testing of the mobile instruments where Malley, Martin, and Woods (2001), Malley, Martin and Moffat (2001a) and Malley, Martin and Dettman (2001a) describe the results for nutrients. This report and Malley, Martin and Moffat (2001b) and Malley, Martin and Dettman (2001b) describe results for the minor elements and metals.

Methods

Mobile Laboratory and Sampling of Manure

The design and construction of the mobile laboratory are described by Malley, Martin and Woods (2001). They also report on the collection of hog manure samples for this study from 13 hog operations in the vicinity of Winnipeg from September to November 2000.

The collection of hog manure for the two-year ARDI study is described by Fitzgerald and Racz 2001).

Chemical Analyses

The 1998 ARDI manure samples (n = 75) were analyzed by Norwest Labs by four tests: 1) liquid manure physical properties - moisture, electrical conductivity; 2) liquid manure nutrients - total N, NH₄-N, total P, K and Na; 3) salts - Ca, Mg, Na, Cl, and 4) inductively-coupled plasma (ICP) spectroscopy for 32 elements including Ca, Mg, K, Na, P, Al, Sb, As, Ba, Be, Bi, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Se, Si, Ag, Sr, S, Ti, Tl, V, Sn, and Zn.

The 1999 ARDI samples (67 of 137 samples) were analyzed by Norwest Labs for: 1) liquid manure physical properties - moisture, pH, electrical conductivity and 2) trace inductively-coupled plasma emission spectroscopy (ICP-ES) for 32 elements including Ca, Mg, K, Na, P, Al, Sb, As, Ba, Be, Bi, B, Cd, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Se, Si, Ag, Sr, S, Ti, Tl, V, Sn, and Zn.

In both years, values for Sb, As, Ag, and Tl were all or mostly below the limits of detection of the method. They were not considered further here.

Eighty of 121 samples of manure collected from September to November 2000 were analyzed for moisture, and for 32 metals and minor elements by Norwest Labs. All or many of the values for Ag, As, Bi, Sb, Se, and Ti were below the limits of detection for the method. These were not considered further.

For the ICP analysis, 500 mL of manure sample was preserved with 5 mL of 20% nitric acid preservative and stored at 4° C until measured. Samples were presented to the spectrometer using an ultrasonic nebulizer. Detection limits varied with the element.

Recording Spectra in the Laboratory Using the NIRSystems Model 6500

NIR spectra were recorded in the laboratory using a Foss NIRSystems Inc. (Silver Spring, MD) Model 6500 visible/NIR scanning spectrophotometer fitted with a standard sample transport. Absorbance was recorded every 2 nm from 400 to 2498 nm using DOS-based Near-infrared Spectral Analysis Software (NSAS). An electronic noise test was carried out prior to scanning on each day. Once a week a bandwidth test was performed using internal standards in the instrument. The NIR instrument with the standard sample transport was turned on its back so that the transport operated horizontally, instead of vertically as is normal (Fig. 1, from Malley and Currie 1999). In this way, settling particles stayed in the path of the light, rather than falling out of it.

Manure samples were well shaken and aliquots removed and dispensed into a liquid sample cell with quartz glass on two sides, an opaque ceramic fastened over one glass side, and a gasket to make the cell watertight. Path length of the cell was 2 mm.

Between each sample scan, a non-absorbing reference ceramic was scanned and the resulting reference spectrum was automatically subtracted from each sample scan. Samples were



Fig. 1. Foss NIRSystems model 6500 visible/near-infrared scanning spectrophotometer on its back so that the sample transport (uppermost) operated horizontally instead of vertically.

loaded into the cell twice. For each loading, triplicate scans were recorded, with the cell being turned 120° between scans. This resulted in 6 scans per sample.

Principal Component Analysis of Constituent Data

Using multivariate analysis software, Unscrambler® (CAMO ASA Oslo, Norway), principal component analysis (PCA) was performed on the metal and minor element chemical data. The data were centered, all 27 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 are in the score plot, the more similar they will be with respect to composition. Conversely, samples far away from each other will be 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.

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 prediction 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 values 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 chemically-determined values for the validation set to the SEP; and the RER, i.e., the ratio of the range of the chemically-determined 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 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

Composition of the Manure

Tables 1 to 3 report the composition of three years of manure samples in this study. Median concentrations are given as the concentrations at the 50th percentile of the samples. The two years of samples from the ARDI study were similar ranging from 85 to almost 100 % water and averaging 97.0 %. Conductivity ranged from 8 to 28 mS/cm (Tables 1, 2).

In the 121 samples from fall 2000, moisture ranged from 89 to nearly 100%. pH varied from 6.7 to 8.1, conductivity from 7 to 27 mS/cm and density from 1.002 to 1.049 (Malley, Martin, and Woods 2001) (Table 3). On average, 90.9 % of the TDN was $\text{NH}_4\text{-N}$, and 84.9 % of

the total N was TDN. Therefore most, 77.2 %, of the total N was $\text{NH}_4\text{-N}$. Total dissolved P was 95.8 % SRP, or inorganic phosphate, and TDP was 73.2 % of the total P (Table 3). Therefore, most of the total P was inorganic phosphate. Suspended C was the most concentrated nutrient. Coefficient of variability (CV) was calculated for each constituent in these samples as a comparative measure of variation in concentrations. Suspended C was the most variable nutrient, i.e., had the highest coefficient of variation. Suspended P, the other P fractions, and suspended N were also highly variable in concentration. Potassium, $\text{NH}_4\text{-N}$, and TDN were the least variable of the nutrients (Table 3).

Concentrations of metals and minor constituents were similar among the three sets of samples. Silicon was the most variable constituent among the three years (Table 1-3).

Comparing CVs among minor elements and metals in Table 3, it can be seen that Zn, Cu, Mn, and Cr were the most variable. Of the important metals, Pb varied the least (Table 3).

Figure 2 shows the relationships among the constituents from the principal component analysis of the compositional data for the samples collected in fall 2000. The first principal component explained 72 % of the variance in the composition, was dominated by water, and reflects the particulate content of the samples. As expected there was an inverse relationship between water content and the concentrations of the elements, except for Pb that was correlated with water and inversely correlated with the remaining elements. The second principle component explained an additional 8 % of the variance in the composition. It was dominated by Na and possibly reflects the degree to which the elements were dissolved (ionic) vs particulate.

Elements that are close together in Fig. 2 were highly correlated. This includes most of the metals. Lead, Sn, and Na were not correlated with any other elements. Potassium, Si, Co, and Li were correlated. Correlations are important in explaining why spectrally-inactive constituents can be predicted by NIRS. More data on inter-correlations for the samples collected in fall 2000 are provided in Table 4. Correlations are reported for all of the constituents, including the nutrients. There were numerous correlations among constituents. In particular, a number of constituents were highly correlated ($r \sim 0.9$) with dry matter, i.e., particulate content of the manure, namely, suspended N, SRP, TDP, suspended P, total P, suspended C, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P (by ICP), Sr, Zn, and Zr (Table 4). These include the most variable constituents in the manure consistent with the knowledge that compositional variability in manure is largely a function of particulate content.

Figure 3 shows the relationships among the samples collected in fall 2000 with respect to their composition. It shows that there are two sets of outliers, a group of samples in the lower, right hand corner, and a second group at the top of the PC2 axis. The samples in the lower right hand corner are in the same quadrant as most of the constituents and opposite to water. They are samples with the highest particulate content.

Table 1. Chemical composition of the 75 samples of hog manure sampled for the ARDI study in 1998. Data provided by Norwest Labs. Samples with concentrations less than the limits of detection were omitted.

Parameter	Analysis	No. of samples	Value		
			Median	Mean \pm SD	Range
Moisture, %		74 ¹	98.6	97.2 \pm 2.7	88.4 - 100
Conductivity, mS/cm		75	14.2	15.24 \pm 4.36	9.01 - 27.5
NH ₄ -N, g/L		74	1.90	2.00 \pm 0.79	0.82 - 3.68
Total N, g/L		75	2.40	2.77 \pm 1.32	0.90 - 6.50
Total P, g/L	Nutrients	75	0.47	0.87 \pm 0.96	0.05 - 5.51
Phosphorus, g/L	ICP	75	0.56	1.04 \pm 1.16	0.06 - 6.19
Potassium, g/L	Nutrients	75	1.32	1.35 \pm 0.52	0.26 - 3.5
Potassium, g/L	ICP	75	1.22	1.48 \pm 0.50	0.68 - 2.6
Sodium, g/L	Salts	75	0.35	0.42 \pm 0.20	0.15 - 1.07
Sodium, g/L	Nutrients	75	0.36	0.45 \pm 0.22	0.20 - 1.23
Sodium, mg/L	ICP	75	0.43	0.51 \pm 0.26	0.18 - 1.5
Calcium, g/L	Salts	75	0.69	1.18 \pm 1.18	0.07 - 5.37
Calcium, g/L	ICP	75	0.63	1.07 \pm 1.09	0.06 - 4.51
Magnesium, g/L	Salts	75	0.32	0.65 \pm 0.70	0.02 - 3.59
Magnesium, g/L	ICP	75	0.33	0.58 \pm 0.67	0.01 - 3.70
Chloride, g/L (Cl)	ICP	75	1.02	1.11 \pm 0.45	0.42 - 2.22
Sulfur, mg/L (S)	ICP	75	153	226 \pm 186	23 - 727
Aluminum, mg/L (Al)	ICP	75	33.6	84.2 \pm 117.8	1.52 - 683
Antimony, mg/L (Sb)	ICP	most <0.05			
Arsenic, mg/L (As)	ICP	33 ²	0.18	0.20 \pm 0.08	0.10 - 0.44
Barium, mg/L (Ba)	ICP	75	0.90	1.86 \pm 2.20	0.06 - 11.00
Beryllium, mg/L (Be)	ICP	37 ³	0.016	0.021 \pm 0.014	0.006 - 0.058
Bismuth, mg/L (Bi)	ICP	all <0.07			
Boron, mg/L (B)	ICP	75	1.50	2.09 \pm 1.48	0.59 - 7.34

Cadmium, mg/L (Cd)	ICP	70 ⁴	0.036	0.049 ± 0.045	0.006 - 0.198
Chromium, mg/L (Cr)	ICP	74	0.16	0.37 ± 0.42	0.012 - 1.67
Cobalt, mg/L (Co)	ICP	64 ⁵	0.015	0.050 ± 0.058	0.008 - 0.340
Copper, mg/L (Cu)	ICP	75	19.7	33.5 ± 35.8	1.1 - 169.0
Iron, mg/L (Fe)	ICP	75	67.7	138.6 ± 169.6	4.7 - 988.0
Lead, mg/L (Pb)	ICP	40 ⁶	0.13	0.16 ± 0.12	0.03 - 0.48
Lithium, mg/L (Li)	ICP	75	0.19	0.24 ± 0.15	0.05 - 0.96
Manganese, mg/L (Mn)	ICP	75	9.2	19.3 ± 22.0	0.5 - 96.0
Molybdenum, mg/L (Mo)	ICP	73	0.26	0.40 ± 0.38	0.02- 2.02
Nickel, mg/L (Ni)	ICP	75	0.31	0.42 ± 0.38	0.06 - 1.88
Selenium, mg/L (Se)	ICP	67 ⁷	0.21	0.26 ± 0.18	0.04 - 0.85
Silicon, mg/L (Si)	ICP	75	124	255 ± 272	46 - 1520
Silver, mg/L (Ag)	ICP	most <0.01			
Strontium, mg/L (Sr)	ICP	75	1.40	2.14 ± 2.06	0.14 - 10.50
Tin, mg/L (Sn)	ICP	64 ⁹	0.41	0.50 ± 0.45	0.05 - 2.42
Titanium, mg/L (Ti)	ICP	75	1.76	3.26 ± 3.62	0.10 - 19.3
Thallium mg/L (Tl)	ICP	all <0.04			
Vanadium, mg/L (V)	ICP	67 ⁸	0.35	0.58 ± 0.64	0.01 - 2.60
Zinc, mg/L (Zn)	ICP	75	41.5	76.2 ± 90.8	1.2 - 541.0

¹ One extreme outlier was removed

² Remainder of values were <0.10 mg/L

³ Remainder of values were <0.005 mg/L

⁴ Remainder of values were < 0.005 mg/L

⁵ Remainder of values were <0.007 mg/L

⁶ Remainder of values were <0.02 mg/L

⁷ Remainder of values were <0.04 mg/L

⁸ Remainder of values were <0.01 mg/L

⁹ Remainder of values were <0.03 mg/L

Nutrient data from Malley and Vandenbyllaardt (1999)

Table 2. Chemical composition of the samples of hog manure sampled for the ARDI study in 1999 for nutrients (n = 123) and minor elements and metals (n = 67). Data provided by Norwest Labs. Samples with concentrations less than the limits of detection were omitted.

Parameter	Analysis	No. of samples	Value		
			Median	Mean \pm SD	Range
Moisture, %		123	98.3	97.0 \pm 3.1	85.4 - 99.6
Conductivity, mS/cm		123	15.9	15.8 \pm 3.6	8.3 - 23.8
NH ₄ -N, g/L	Nutrients	123	2.02	2.06 \pm 0.86	0.52 - 3.95
Total N, g/L	Nutrients	123	2.4	2.7 \pm 1.3	0.6 - 6.2
Total P, g/L	Nutrients	123	0.50	0.90 \pm 0.99	0.03 - 5.71
Phosphorus, g/L	ICP	67	0.18	0.63 \pm 1.51	0.38 - 10.90
Potassium, g/L	Nutrients	123	1.36	1.34 \pm 0.37	0.66 - 2.22
Potassium, g/L	ICP	67	1.92	1.77 \pm 0.62	0.21 - 3.38
Sodium, g/L	Nutrients	123	0.38	0.45 \pm 0.22	0.14 - 1.18
Sodium, mg/L	ICP	67	0.52	0.54 \pm 0.22	0.19 - 1.22
Calcium, g/L	ICP	67	0.55	1.03 \pm 1.33	0.07 - 8.64
Magnesium, g/L	ICP	67	0.21	0.53 \pm 0.76	0.009 - 4.76
Sulfur, mg/L (S)	ICP	67	157	251 \pm 227	33 - 1220
Aluminum, mg/L (Al)	ICP	67	35.7	99.0 \pm 164.9	1.15 - 825
Antimony, mg/L (Sb)	ICP	most <0.02			
Arsenic, mg/L (As)	ICP	most <0.05			
Barium, mg/L (Ba)	ICP	67	0.72	1.67 \pm 2.32	0.06 - 10.64
Beryllium, mg/L (Be)	ICP	35 ¹	0.012	0.015 \pm 0.012	0.003 - 0.044
Bismuth, mg/L (Bi)	ICP	all <0.04			
Boron, mg/L (B)	ICP	67	1.41	2.04 \pm 1.88	0.32 - 11.2
Cadmium, mg/L (Cd)	ICP	66 ²	0.025	0.042 \pm 0.045	0.003 - 0.193
Chromium, mg/L (Cr)	ICP	67	0.12	0.32 \pm 0.43	0.01 - 2.17
Cobalt, mg/L (Co)	ICP	67	0.046	0.077 \pm 0.081	0.012 - 0.410

Copper, mg/L (Cu)	ICP	67	15.6	31.9 ± 34.9	0.6 - 177.0
Iron, mg/L (Fe)	ICP	67	45.5	130.8 ± 193.8	3.9 - 906.0
Lead, mg/L (Pb)	ICP	67	0.09	0.12 ± 0.11	0.01 - 0.47
Lithium, mg/L (Li)	ICP	67	0.29	0.36 ± 0.26	0.05 - 1.41
Manganese, mg/L (Mn)	ICP	67	6.8	16.7 ± 22.1	0.4 - 134.0
Molybdenum, mg/L (Mo)	ICP	67	0.16	0.33 ± 0.34	0.02 - 1.59
Nickel, mg/L (Ni)	ICP	67	0.26	0.41 ± 0.38	0.04 - 1.42
Selenium, mg/L (Se)	ICP	66 ³	0.15	0.19 ± 0.16	0.01 - 0.97
Silicon, mg/L (Si)	ICP	67	29.3	30.2 ± 12.04	9.5 - 64.0
Silver, mg/L (Ag)	ICP	all <0.005			
Strontium, mg/L (Sr)	ICP	67	1.71	2.41 ± 2.63	0.13 - 15.80
Tin, mg/L (Sn)	ICP	49 ⁴	0.091	0.121 ± 0.007	0.016 - 0.382
Titanium, mg/L (Ti)	ICP	67	0.96	2.31 ± 2.83	0.05 - 10.9
Thallium, mg/L (Tl)	ICP	all <0.02			
Vanadium, mg/L (V)	ICP	67	0.18	0.45 ± 0.61	0.02 - 2.80
Zinc, mg/L (Zn)	ICP	67	21.5	40.2 ± 45.8	1.5 - 239.0

¹ Remainder of values were <0.003 mg/L

² One value was <0.003 mg/L

³ One value was <0.02 mg/L

⁴ Remainder of values were <0.02 mg/L

Table 3. Composition of the 121 hog manure samples collected in fall 2000 for nutrients (n = 121) and minor elements and metals (n = 80)

Parameter	Analysis	No. of samples	Value					
			Mean \pm SD	Range	Median	CV	Median lb/ton	Median lb/1000 gal
Moisture, %	NWL	80	97.6 \pm 2.8	88.5 - 99.7	98.8	2.9	N/A	N/A
pH	FWI	121		6.66 - 8.1	7.71	4.7	N/A	N/A
Conductivity, mS/cm	FWI	121	15.14 \pm 4.73	6.84 - 27.20	15.28	31.3	N/A	N/A
Density, g/mL	FWI	121	1.023 \pm 0.010	1.002 - 1.049	1.022	1.0	N/A	N/A
NH ₄ -N, g/L	FWI	121	2.18 \pm 1.11	0.56 - 5.54	1.95	51.0	3.82	16.25
Total Dissolved N, g/L	FWI	121	2.40 \pm 1.21	0.59 - 6.11	2.11	50.6	4.14	17.61
Suspended N, g/L	FWI	121	0.602 \pm 0.798	0.014 - 4.083	0.306	132.7	0.597	2.55
Total N, g/L	FWI	121	3.00 \pm 1.89	0.61 - 10.14	2.46	62.9	4.83	20.54
Soluble Reactive P, g/L	FWI	121	0.562 \pm 0.703	0.047 - 3.813	0.363	125.1	0.702	3.03
Total Dissolved P, g/L	FWI	121	0.580 \pm 0.716	0.055 - 3.86	0.378	123.3	0.734	3.15
Suspended P, g/L	FWI	121	0.380 \pm 0.573	0.003 - 2.650	0.125	150.9	0.245	1.04
Total P, g/L	FWI	121	0.960 \pm 1.268	0.055 - 6.512	0.579	132.0	1.13	4.83
Phosphorus, g/L	NWL-ICP	80	1.10 \pm 1.46	0.053 - 6.03	0.54	132.4	1.06	4.50
Suspended C, g/L	FWI	121	6.10 \pm 10.007	0.092 - 54.602	2.4	164.0	4.67	20.03

Potassium, g/L	NWL-ICP	80	1.44 ± 0.53	0.71 - 2.81	1.38	36.8	2.66	11.53
Sulfur, mg/L	NWL-ICP	80	88.3 ± 54.4	15 - 235	77.5	61.6	0.150	0.647
Sodium, mg/L	NWL-ICP	80	419 ± 84	221 - 573	394	20.0	0.772	3.28
Calcium, g/L	NWL-ICP	80	0.82 ± 1.21	0.06 - 5.37	0.31	147.5	0.603	2.56
Magnesium, g/L	NWL-ICP	80	0.48 ± 0.71	0.01 - 38.75	0.15	146.3	0.298	1.27
Aluminum, mg/L	NWL-ICP	80	43.75 ± 51.15	1.20 - 199.03	19.12	116.9	0.038	0.160
Boron, mg/L	NWL-ICP	80	6.89 ± 2.42	2.85 - 15.43	6.4	35.2	0.013	0.054
Barium, mg/L	NWL-ICP	80	1.53 ± 1.81	0.20 - 6.92	0.63	118.3	0.001	0.005
Beryllium, mg/L	NWL-ICP	80	0.023 ± 0.016	0.010 - 0.090	0.02	69.5	3.93	0.0002
Cadmium, mg/L	NWL-ICP	79	0.047 ± 0.057	0.010 - 0.270	0.03	121.7	5.86	0.0003
Cobalt, mg/L	NWL-ICP	71	0.118 ± 0.088	0.050 - 0.430	0.08	75.1	0.0002	0.0007
Chromium, mg/L	NWL-ICP	80	0.303 ± 0.473	0.010 - 2.100	0.105	156.0	0.0002	0.0009
Copper, mg/L	NWL-ICP	80	23.84 ± 39.49	0.65 - 175.47	10.91	165.7	0.021	0.091
Iron, mg/L	NWL-ICP	80	103.09 ± 125.01	4.17 - 513.60	46.53	121.3	0.091	0.388
Lithium, mg/L	NWL-ICP	80	0.137 ± 0.073	0.040 - 0.330	0.11	53.7	0.0002	0.0009
Manganese, mg/L	NWL-ICP	80	16.72 ± 26.80	0.22 - 118.00	6.21	160.3	0.012	0.052
Molybdenum, mg/L	NWL-ICP	80	0.236 ± 0.267	0.010 - 1.230	0.17	113.0	0.0003	0.001

Nickel, mg/L	NWL-ICP	80	0.534 ± 0.667	0.090 - 3.190	0.36	124.9	0.0007	0.003
Lead, mg/L	NWL-ICP	31	0.214 ± 0.063	0.040 - 0.350	0.2	29.6	0.0004	0.002
Silicon, mg/L	NWL-ICP	80	146.2 ± 92.9	33.4 - 442.3	120.2	63.5	0.235	1.00
Tin, mg/L	NWL-ICP	23	0.574 ± 0.364	0.210 - 1.360	0.42	63.3	0.0008	0.004
Strontium, mg/L	NWL-ICP	80	1.845 ± 2.525	0.160 - 11.560	0.89	136.9	0.002	0.007
Vanadium, mg/L	NWL-ICP	49	0.684 ± 0.745	0.030 - 2.910	0.5	108.8	0.0010	0.004
Zinc, mg/L	NWL-ICP	80	75.48 ± 129.43	2.300 - 590.3	27.85	171.5	0.055	0.232
Zirconium, mg/L	NWL-ICP	80	0.086 ± 0.083	0.010 - 0.360	0.05	96.5	9.84	0.0004

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

Moisture, conductivity and nutrient data from Malley, Martin, and Woods (2001)

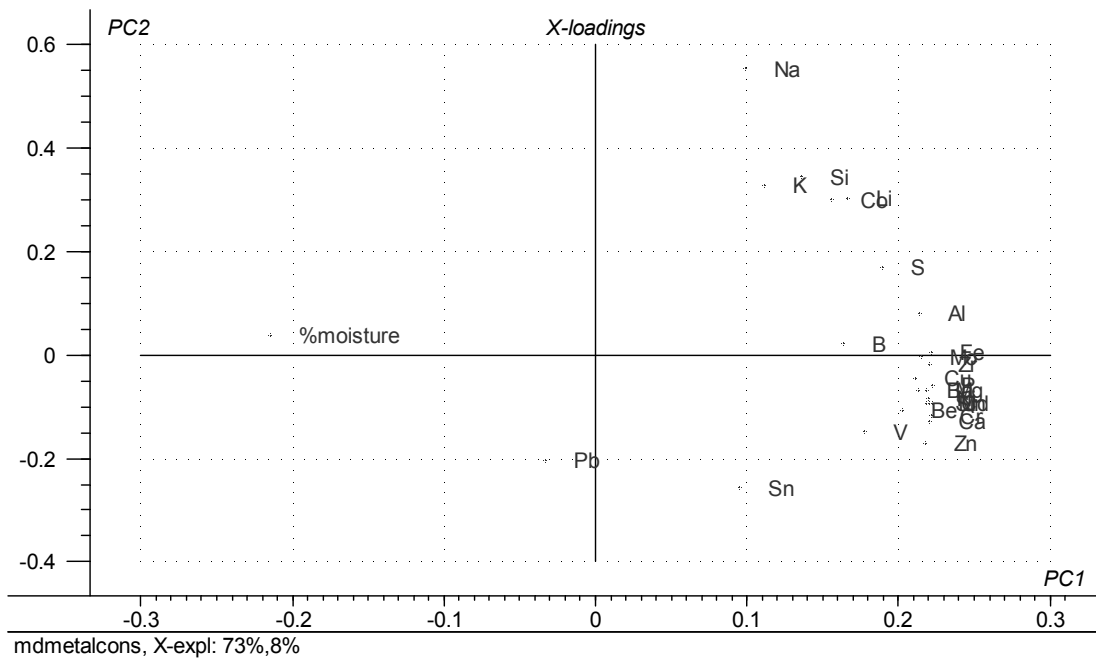


Fig. 2. Loadings plot for moisture, metals and minor nutrients in 80 samples of hog manure collected in fall 2000 on the first two principal components explaining the variance in constituent concentrations.

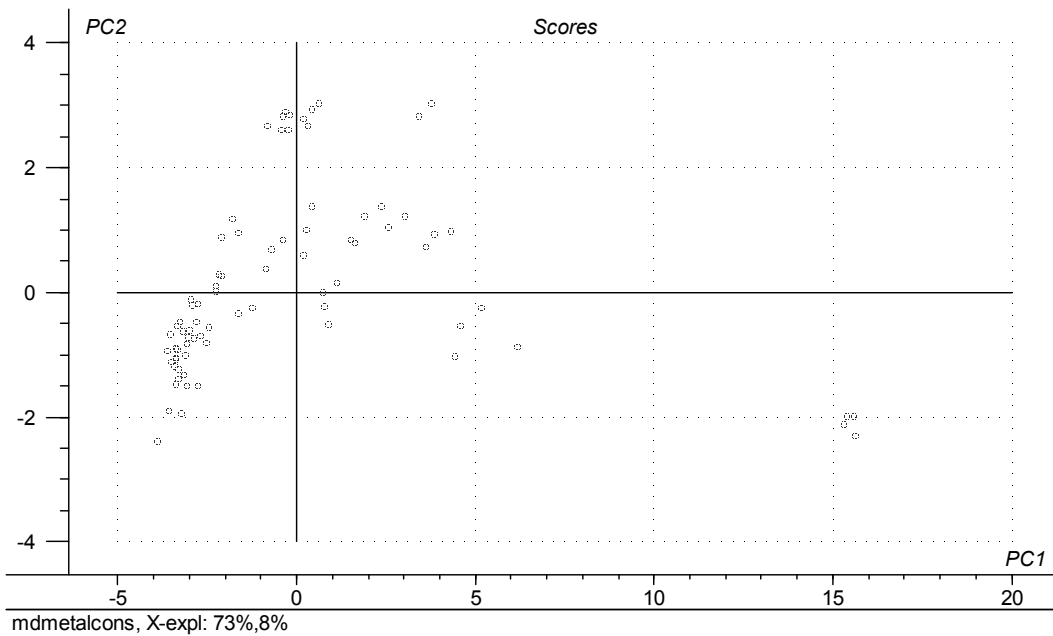


Fig. 3. Scores plot for the 80 samples of hog manure collected in fall 2000 on the first two principal components explaining the variance in constituent concentrations.

Table 4. Correlation, r, matrix among the nutrients, minor elements, and metals in 80 of the 121 samples of hog manure collected in fall 2000.

	Moisture	Dry matter	pH	Cond	Density	NH₄-N	TDN	Susp N	Total N
Moisture	1.000								
Dry matter	-1.000	1.000							
pH	0.760	-0.760	1.000						
Cond	-0.164	0.164	-0.028	1.000					
Density	-0.284	0.284	-0.384	0.384	1.000				
NH₄-N	-0.791	0.791	-0.488	0.749	0.411	1.000			
TDN	-0.781	0.781	-0.478	0.759	0.397	0.998	1.000		
Susp N	-0.960	0.960	-0.690	0.158	0.296	0.763	0.746	1.000	
Total N	-0.904	0.904	-0.600	0.555	0.381	0.965	0.960	0.904	1.000
SRP	-0.949	0.949	-0.643	0.236	0.249	0.811	0.798	0.980	0.928
TDP	-0.950	0.950	-0.643	0.243	0.258	0.814	0.803	0.978	0.930
Susp P	-0.939	0.939	-0.608	0.109	0.342	0.705	0.685	0.973	0.853
Total P	-0.955	0.955	-0.638	0.187	0.300	0.778	0.763	0.992	0.911
Susp C	-0.951	0.951	-0.701	0.105	0.175	0.728	0.714	0.984	0.876
Al	-0.854	0.854	-0.575	0.145	0.287	0.705	0.687	0.900	0.819
B	-0.705	0.705	-0.550	0.203	0.157	0.621	0.621	0.689	0.686
Ba	-0.892	0.892	-0.550	0.135	0.304	0.725	0.705	0.922	0.840
Be	-0.784	0.784	-0.413	0.136	-0.002	0.702	0.692	0.874	0.811
Ca	-0.958	0.958	-0.661	0.101	0.102	0.768	0.755	0.984	0.898
Cd	-0.923	0.923	-0.601	0.139	0.076	0.780	0.765	0.981	0.903
Co	-0.165	0.165	0.013	0.567	0.275	0.526	0.526	0.252	0.484
Cr	-0.903	0.903	-0.549	0.121	0.058	0.764	0.749	0.972	0.889
Cu	-0.916	0.916	-0.725	0.164	0.009	0.786	0.777	0.943	0.894
Fe	-0.900	0.900	-0.581	0.157	0.245	0.756	0.738	0.950	0.873
K	-0.426	0.426	-0.214	0.878	0.159	0.851	0.864	0.417	0.719
Li	-0.721	0.721	-0.670	0.242	0.485	0.621	0.610	0.682	0.677
Mg	-0.988	0.988	-0.738	0.109	0.279	0.761	0.747	0.973	0.888
Mn	-0.939	0.939	-0.656	0.151	0.057	0.788	0.778	0.973	0.908
Mo	-0.837	0.837	-0.538	0.269	0.082	0.814	0.803	0.925	0.902
Na	-0.378	0.378	-0.366	0.673	0.505	0.639	0.636	0.337	0.543
Ni	-0.897	0.897	-0.578	0.171	-0.002	0.793	0.782	0.961	0.905
P	-0.975	0.975	-0.665	0.188	0.250	0.814	0.801	0.980	0.925
Pb	0.262	-0.262	0.254	-0.147	-0.221	-0.173	-0.180	-0.333	-0.215
S	-0.805	0.805	-0.695	0.479	0.348	0.859	0.855	0.802	0.881
Si	-0.530	0.530	-0.405	0.196	0.668	0.439	0.421	0.517	0.487
Sn	-0.765	0.765	-0.505	0.051	-0.630	0.868	0.856	0.929	0.901
Sr	-0.974	0.974	-0.751	0.120	0.114	0.780	0.769	0.978	0.904
V	-0.849	0.849	-0.464	-0.063	-0.270	0.735	0.717	0.948	0.873
Zn	-0.912	0.912	-0.587	0.085	-0.011	0.750	0.737	0.972	0.882
Zr	-0.925	0.925	-0.657	0.152	0.278	0.760	0.743	0.960	0.880

Table 4. cont'd.

	SRP	TDP	Susp P	Total P	Susp C	Al	B	Ba	Be
SRP	1.000								
TDP	0.999	1.000							
Susp P	0.938	0.935	1.000						
Total P	0.988	0.987	0.980	1.000					
Susp C	0.978	0.976	0.935	0.973	1.000				
Al	0.875	0.875	0.904	0.897	0.861	1.000			
B	0.685	0.684	0.679	0.689	0.684	0.652	1.000		
Ba	0.883	0.883	0.961	0.926	0.871	0.912	0.664	1.000	
Be	0.871	0.870	0.892	0.889	0.856	0.830	0.586	0.853	1.000
Ca	0.972	0.971	0.981	0.986	0.979	0.876	0.688	0.933	0.872
Cd	0.975	0.974	0.973	0.984	0.970	0.908	0.668	0.929	0.897
Co	0.351	0.340	0.199	0.282	0.192	0.413	0.203	0.252	0.356
Cr	0.960	0.959	0.978	0.978	0.956	0.909	0.671	0.945	0.924
Cu	0.958	0.956	0.880	0.933	0.965	0.832	0.679	0.783	0.797
Fe	0.928	0.927	0.961	0.952	0.913	0.981	0.666	0.962	0.884
K	0.498	0.501	0.357	0.444	0.409	0.355	0.416	0.330	0.410
Li	0.672	0.676	0.648	0.671	0.656	0.795	0.503	0.641	0.520
Mg	0.951	0.951	0.965	0.967	0.955	0.886	0.701	0.935	0.812
Mn	0.974	0.971	0.951	0.973	0.975	0.873	0.706	0.892	0.873
Mo	0.929	0.928	0.910	0.930	0.906	0.881	0.612	0.861	0.895
Na	0.366	0.371	0.280	0.336	0.297	0.488	0.324	0.313	0.260
Ni	0.970	0.968	0.947	0.969	0.961	0.890	0.687	0.893	0.896
P	0.970	0.970	0.978	0.984	0.958	0.890	0.699	0.952	0.858
Pb	-0.151	-0.152	-0.230	-0.199	-0.305	-0.298	-0.087	-0.187	-0.019
S	0.817	0.817	0.765	0.803	0.780	0.708	0.575	0.713	0.684
Si	0.473	0.476	0.542	0.510	0.432	0.799	0.416	0.634	0.441
Sn	0.898	0.897	0.947	0.928	0.900	0.934	0.646	0.870	0.926
Sr	0.969	0.969	0.951	0.971	0.985	0.856	0.705	0.884	0.824
V	0.925	0.922	0.952	0.948	0.921	0.929	0.769	0.930	0.915
Zn	0.968	0.966	0.968	0.977	0.973	0.851	0.654	0.905	0.905
Zr	0.929	0.928	0.968	0.955	0.922	0.939	0.658	0.958	0.869

Table 4. cont'd.

	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg
Ca	1.000								
Cd	0.978	1.000							
Co	0.129	0.381	1.000						
Cr	0.975	0.989	0.335	1.000					
Cu	0.917	0.923	0.381	0.893	1.000				
Fe	0.940	0.961	0.372	0.965	0.862	1.000			
K	0.401	0.419	0.472	0.412	0.462	0.390	1.000		
Li	0.654	0.645	0.237	0.610	0.674	0.742	0.378	1.000	
Mg	0.972	0.943	0.156	0.930	0.908	0.933	0.360	0.721	1.000
Mn	0.967	0.973	0.522	0.961	0.956	0.923	0.434	0.625	0.948
Mo	0.895	0.953	0.625	0.945	0.884	0.925	0.510	0.600	0.852
Na	0.286	0.311	0.405	0.279	0.383	0.423	0.644	0.724	0.342
Ni	0.968	0.977	0.388	0.979	0.926	0.939	0.490	0.637	0.911
P	0.983	0.966	0.245	0.960	0.903	0.949	0.444	0.692	0.988
Pb	-0.395	-0.320	-0.178	-0.142	-0.291	-0.310	-0.124	-0.216	-0.242
S	0.772	0.786	0.458	0.748	0.776	0.755	0.631	0.657	0.786
Si	0.467	0.505	0.379	0.503	0.421	0.705	0.188	0.796	0.566
Sn	0.924	0.945	-0.294	0.960	0.826	0.970	0.836	0.571	0.835
Sr	0.985	0.953	0.134	0.938	0.952	0.909	0.421	0.696	0.975
V	0.936	0.968	0.255	0.984	0.867	0.978	0.329	0.504	0.892
Zn	0.985	0.983	0.167	0.985	0.910	0.925	0.405	0.574	0.930
Zr	0.943	0.956	0.398	0.949	0.871	0.971	0.364	0.714	0.956

Table 4. cont'd.

	Mn	Mo	Na	Ni	P	Pb	S	Si	Sn
Mn	1.000								
Mo	0.929	1.000							
Na	0.293	0.376	1.000						
Ni	0.959	0.930	0.336	1.000					
P	0.959	0.895	0.358	0.940	1.000				
Pb	-0.316	-0.382	-0.086	-0.262	-0.212	1.000			
S	0.797	0.837	0.535	0.761	0.813	-0.281	1.000		
Si	0.450	0.517	0.632	0.462	0.547	-0.285	0.485	1.000	
Sn	0.864	0.888	0.387	0.942	0.884	ERR	0.721	0.062	1.000
Sr	0.967	0.867	0.336	0.947	0.969	-0.328	0.794	0.455	0.877
V	0.940	0.938	0.073	0.958	0.926	-0.459	0.666	0.387	0.954
Zn	0.963	0.923	0.225	0.979	0.955	-0.287	0.757	0.395	0.934
Zr	0.942	0.919	0.366	0.913	0.962	-0.289	0.810	0.650	0.941

Table 4. cont'd.

	Sr	V	Zn	Zr
Sr	1.000			
V	0.895	1.000		
Zn	0.958	0.945	1.000	
Zr	0.924	0.955	0.920	1.000

NIR Prediction of Minor Elements and Metals in Hog Manure

An excellent calibration was developed for moisture in the fall 2000 samples. It predicted moisture to within 0.5 % with $r^2 = 0.97$ and RPD = 5.6 (Table 6; Fig. 4).

Cadmium and Cu were predicted successfully across the three sets of samples, ARDI 1998, ARDI 1999, and fall 2000, with r^2 generally >0.9 and RPD >3.0 (Tables 5,6). Moderately successful calibrations (r^2 generally >0.8 and RPD >2.25) were achieved across the three sets for Ca, Fe, Mg, Mn, Mo, S, and Sn (Tables 5,6). The following elements were predicted successfully or moderately successfully in two of the three years, or only had two years of data, Al, Ba, Be, Cr, Ni, Se, Sr and Ti. Several elements showed inconsistent response across the sets, including Co, K, Na, Pb, Si, V, and Zn. Several elements were not predictable in any of the three sets, including B and Li. There was only one year of data for As (not successful), Zr (successful).

Figure 4 shows the calibration results for the year 2000 samples graphically. The distribution of concentrations for a number of constituents is not continuous, due to the several samples with high particulate content, producing a "dumbbell". Nevertheless, the figures show that for the successful calibrations the medium and low values fit the line; statistical success was not due primarily to the large range.

Table 5. Accuracy of prediction for NIR calibrations for metals and minor elements in samples of hog manure from 1998 (ARDI Year 1 samples) and 1999 (ARDI Year 2 samples). A/B and B/A are reciprocal calibrations using half the samples, A, to predict the other half, B, and vice versa. In 1998, all calibrations were A/B. "bdl" below the limits of detection. The statistics are described in the Methods. "n/d" is no data.

Statistic	Al			As			B			Ba		
	1998	1999		1998	1999		1998	1999		1998	1999	
		A/B	B/A		A/B	B/A		A/B	B/A		A/B	B/A
r²	0.58	0.81	0.79	0.57	bdl	bdl	0.68	0.62	0.53	0.89	0.63	0.79
SEP	65.0	67.8	58.5	0.05	bdl	bdl	0.81	0.865	1.09	0.68	1.37	1.08
RPD	1.54	2.28	2.17	1.52	bdl	bdl	1.75	1.63	1.47	2.97	1.64	2.19
RER	6.48	9.38	8.50	5.69	bdl	bdl	7.36	6.51	6.40	10.7	7.73	9.86

Statistic	Be			Ca			Cd			Co		
	1998	1999		1998	1999		1998	1999		1998	1999	
		A/B	B/A		A/B	B/A		A/B	B/A		A/B	B/A
r²	0.93	bdl	bdl	0.85	0.89	0.74	0.90	0.97	0.87	0.51	0.61	0.73
SEP	0.005	bdl	bdl	0.40	292	516	0.01	0.007	0.02	0.04	0.05	0.03
RPD	3.77	bdl	bdl	2.62	2.99	1.96	3.10	5.66	2.76	1.42	1.58	1.94
RER	13.5	bdl	bdl	11.1	12.8	8.95	11.4	22.5	10.8	6.53	6.89	7.46

Statistic	Cr			Cu			Fe			K		
	1998	1999		1998	1999		1998	1999		1998	1999	
		A/B	B/A		A/B	B/A		A/B	B/A		A/B	B/A
r²	0.88	0.70	0.75	0.93	0.92	0.89	0.84	0.82	0.70	0.4	0.26	0.29
SEP	0.14	0.206	0.174	8.97	8.48	9.65	57.8	75.6	87.4	0.38	509	535
RPD	2.92	1.82	1.99	3.87	3.61	3.02	2.48	2.36	1.81	1.28	1.18	1.19
RER	11.8	7.85	8.68	16.8	12.7	10.0	8.82	10.5	8.02	4.64	4.62	5.36

Statistic	Li			Mg			Mn			Mo		
	1998	1999		1998	1999		1998	1999		1998	1999	
		A/B	B/A		A/B	B/A		A/B	B/A		A/B	B/A
r²	0.54	0.63	0.59	0.82	0.74	0.86	0.83	0.83	0.61	0.84	0.85	0.87
SEP	0.09	0.14	0.141	0.26	271	216	8.73	7.30	16.1	0.12	0.116	0.117
RPD	1.48	1.64	1.57	2.33	1.95	2.68	2.40	2.42	1.60	2.49	2.54	2.73
RER	5.92	6.91	6.48	9.83	7.04	10.8	10.1	9.90	8.30	9.27	8.64	10.6

Statistic	Na			Ni			Pb			S		
	1998	1999		1998	1999		1998	1999		1998	1999	
		A/B	B/A		A/B	B/A		A/B	B/A		A/B	B/A
r²	0.33	0.40	0.41	0.84	0.55	0.66	0.73	0.92	0.74	0.86	0.77	0.87
SEP	0.21	159	163	0.15	0.24	0.225	0.06	0.03	0.05	69.7	91.4	70.9
RPD	1.22	1.29	1.3	2.48	1.49	1.72	1.93	3.44	1.97	2.63	2.08	2.8
RER	5.87	5.39	5.44	11.6	5.72	6.13	6.72	14.4	8.72	9.79	8.08	10.7

Statistic	Se			Si			Sn			Sr		
	1998	1999		1998	1999		1998	1999		1998	1999	
		A/B	B/A		A/B	B/A		A/B	B/A		A/B	B/A
r²	0.80	0.73	0.81	0.67	0.13	0.109	0.92	0.82	0.85	0.83	0.78	0.73
SEP	0.08	0.06	0.06	136	10.2	11.2	0.11	0.03	0.03	0.80	0.85	1.15
RPD	2.18	1.93	2.29	1.75	1.07	1.06	3.52	2.35	2.55	2.43	2.15	1.95
RER	8.94	7.63	9.02	7.45	3.95	4.55	11.7	7.28	7.84	10.4	7.44	9.10

Statistic	Ti			V			Zn		
	1998	1999		1998	1999		1998	1999	
		A/B	B/A		A/B	B/A		A/B	B/A
r²	0.84	0.77	0.84	0.84	0.76	n/d	0.80	0.68	n/d
SEP	1.28	1.18	1.11	0.26	0.31	n/d	34.6	28.7	n/d
RPD	2.5	2.08	2.50	2.48	2.04	n/d	2.25	1.77	n/d
RER	6.72	7.53	9.69	7.33	8.86	n/d	9.73	8.27	n/d

Table 6. Accuracy of prediction for NIR calibrations for metals and minor elements in 80 samples of hog manure from fall 2000. In 2000, all calibrations were A/B. “bdl” below the limits of detection

Statistic	H₂O	Al	B	Ba	Be	Ca	Cd	Co	Cr
r²	0.97	0.92	0.62	0.94	0.88	0.97	0.99	0.76	0.97
SEP	0.49	14.6	1.56	0.44	0.006	0.208	0.007	0.043	0.084
RPD	5.60	3.57	0.92	4.21	2.89	5.96	8.29	2.04	5.75
RER	22.7	13.5	7.90	15.2	14.1	25.5	36.6	8.39	25.0

Statistic	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni
r²	0.99	0.96	0.92	0.64	0.98	0.96	0.94	0.85	0.96
SEP	4.91	25.4	0.16	0.046	0.102	5.27	0.071	32.3	0.13
RPD	8.18	5.01	3.45	1.66	7.09	5.14	3.91	2.61	5.37
RER	35.6	20.0	13.1	6.35	27.2	22.3	17.3	10.3	24.5

Statistic	P	Pb	S	Si	Sn	Sr	V	Zn	Zr
r²	0.98	0.28	0.95	0.80	0.97	0.98	0.96	0.98	0.96
SEP	0.21	0.046	12.3	41.9	0.064	0.35	0.14	17.0	0.017
RPD	7.08	1.18	4.48	2.25	5.69	7.47	5.13	7.68	4.90
RER	28.3	3.89	17.6	9.53	15.7	32.9	19.6	34.6	20.4

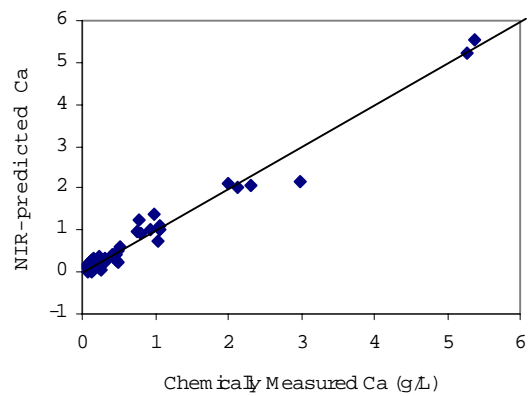
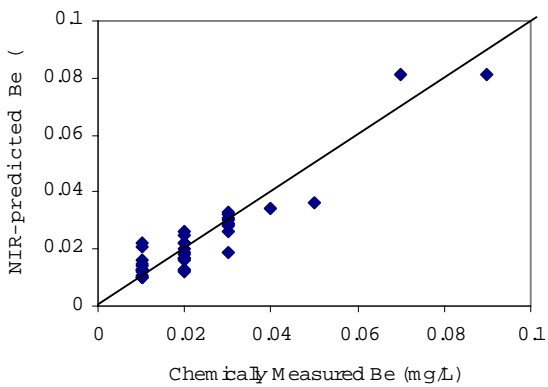
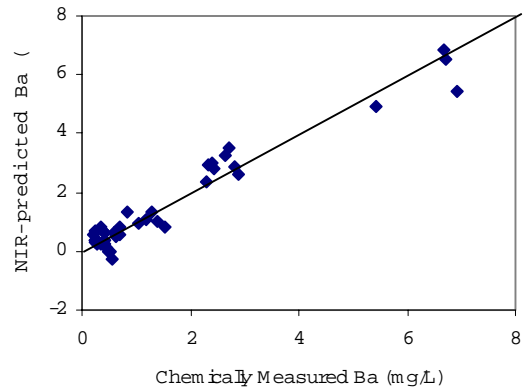
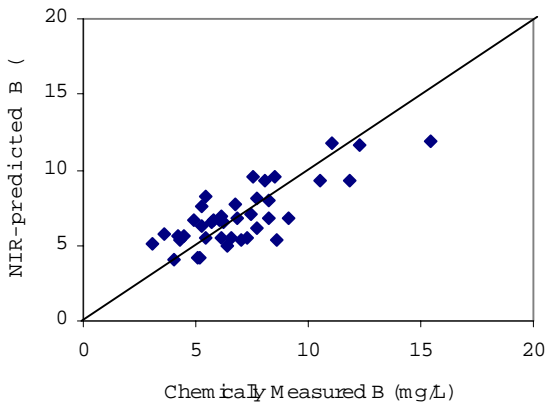
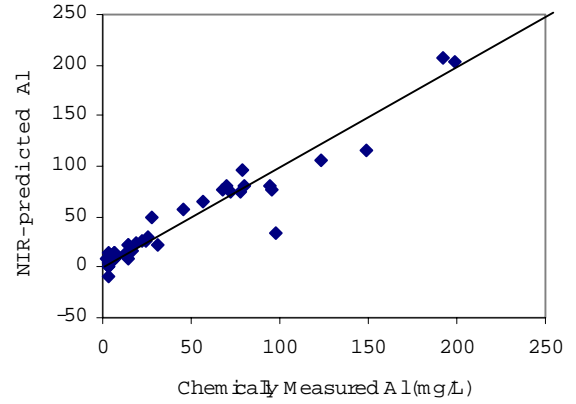
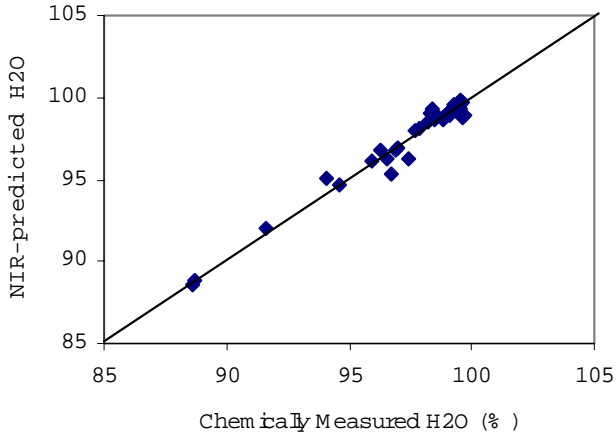


Figure 4. Linear regression relationships between the NIR-predicted and the chemically-determined values for each constituent in the manure samples collected in fall 2000. The line is 1:1 and goes through the origin. R^2 and other statistics are given in Table 6.

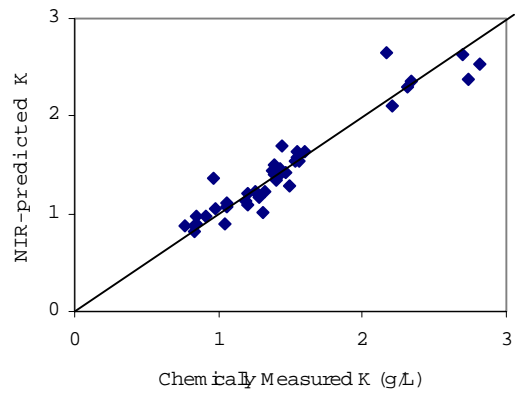
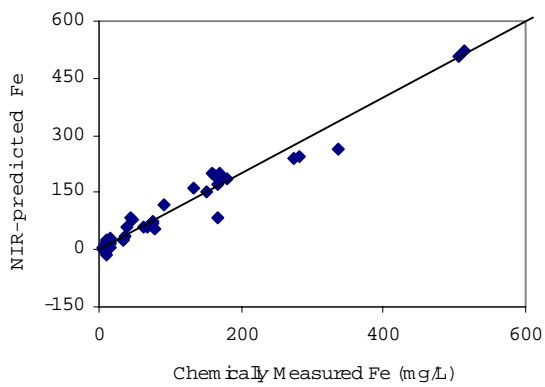
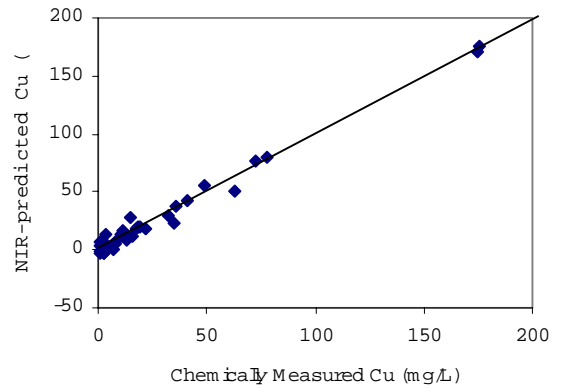
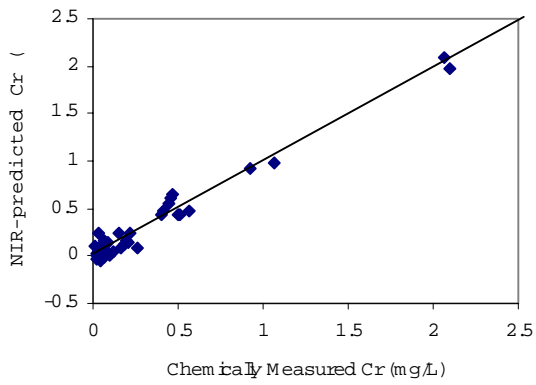
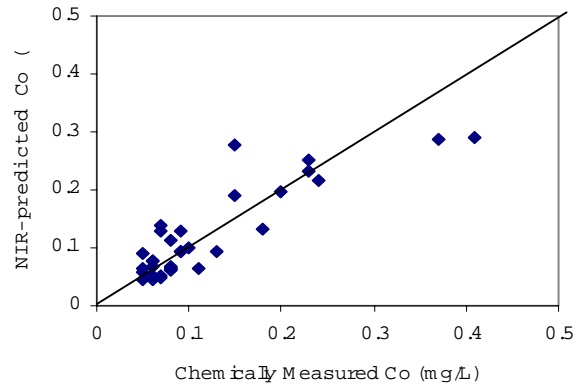
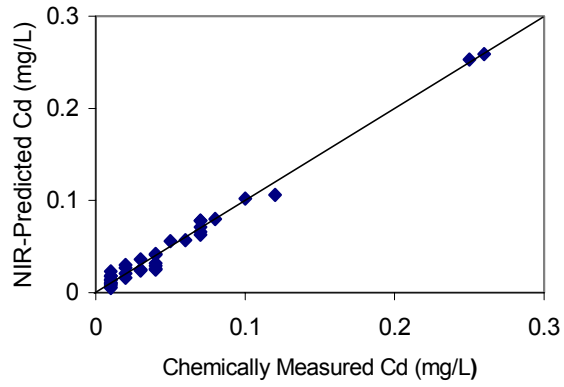


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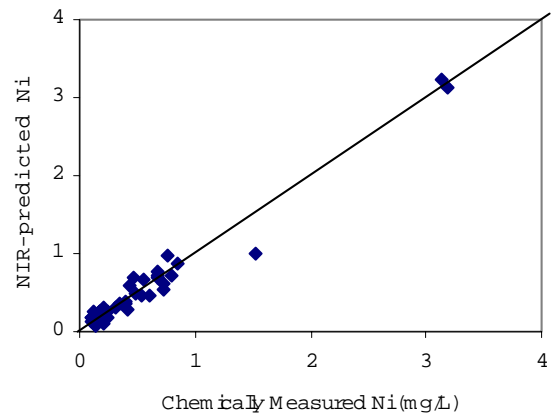
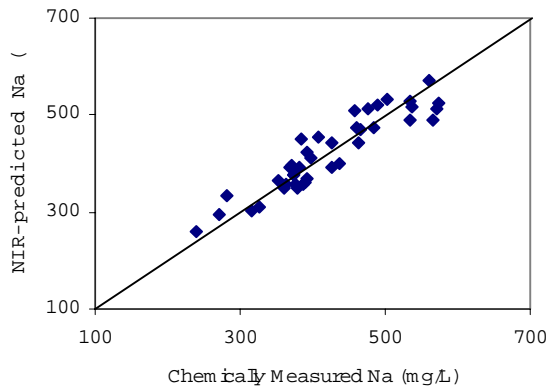
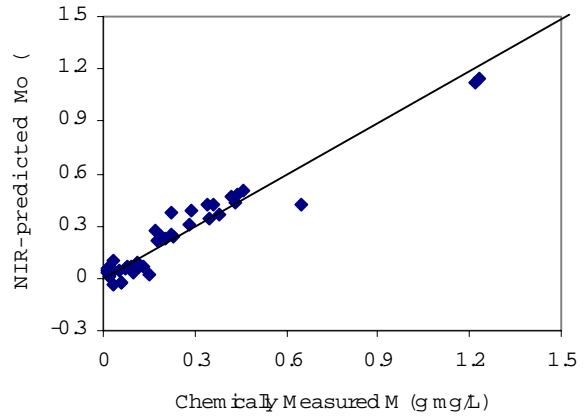
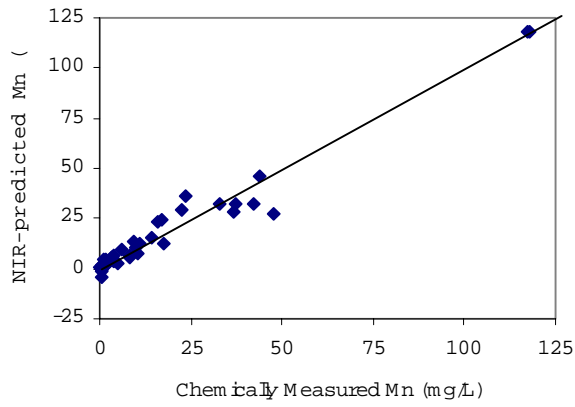
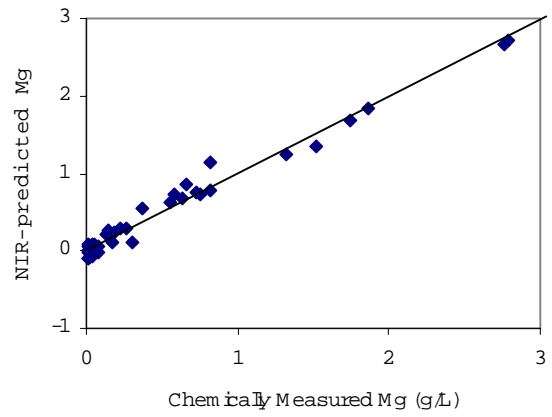
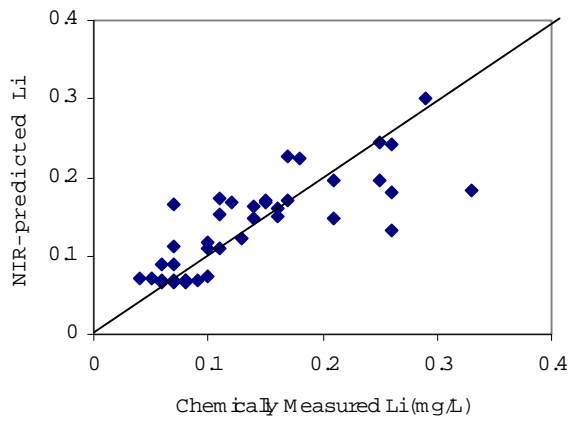


Fig. 4. con't

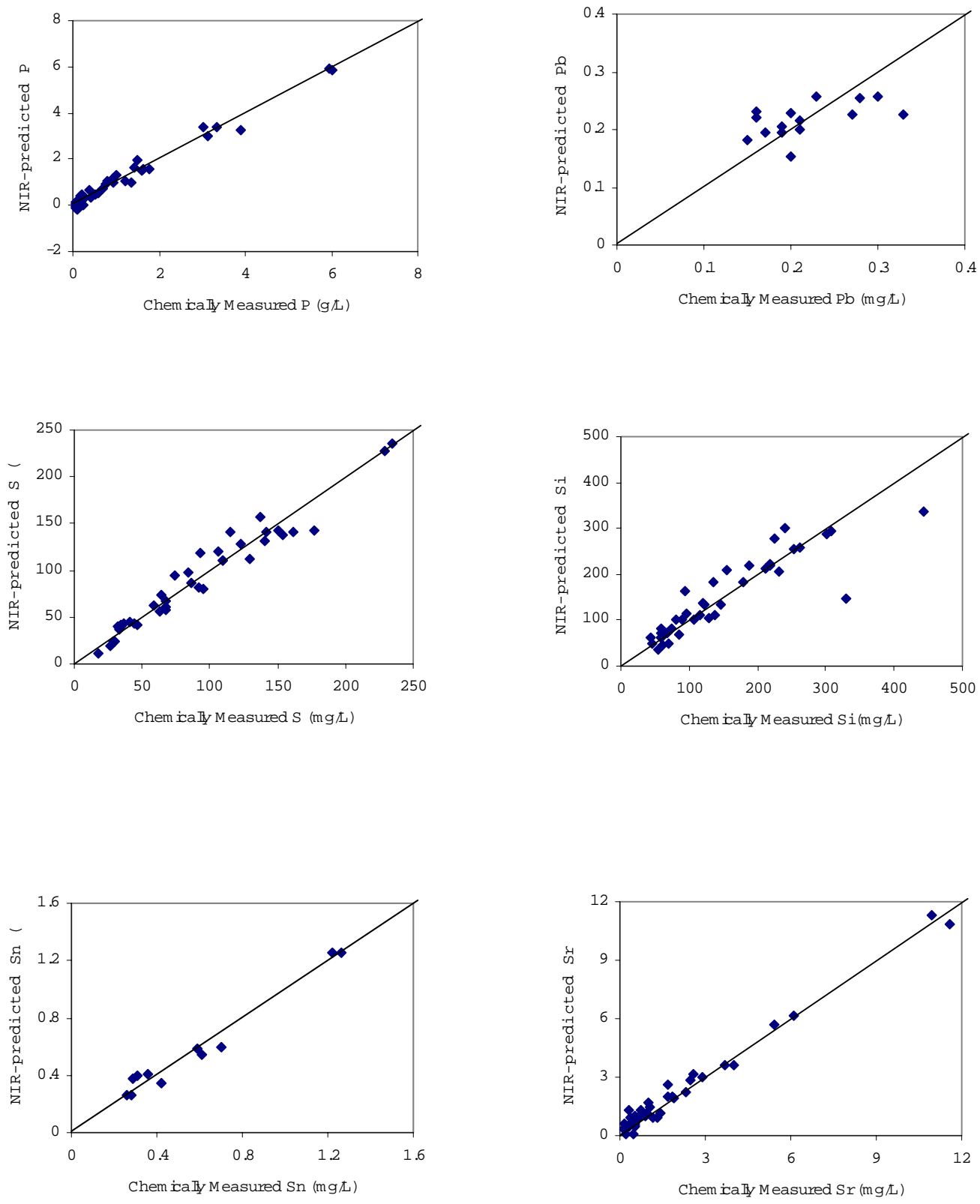


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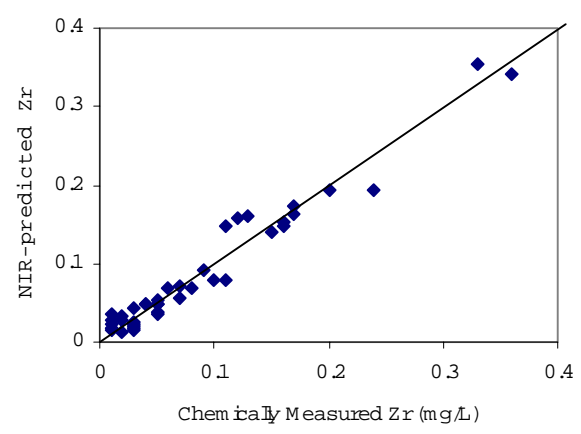
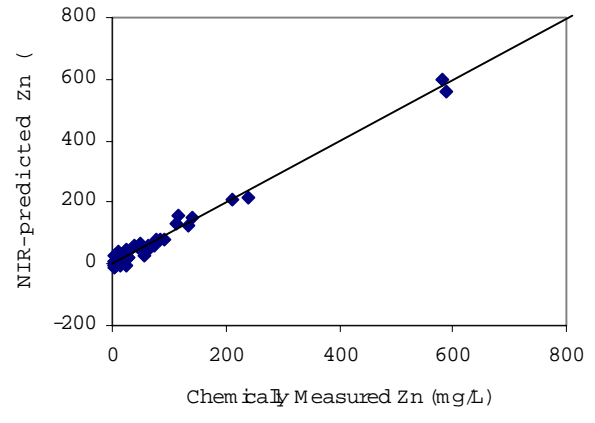
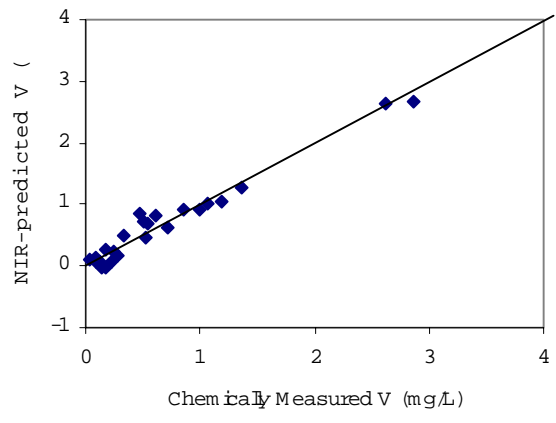


Figure 4 con't.

Discussion

In the context of this study that evaluated the performance of two field-portable NIR instruments for the analysis of metals and minor elements in hog manure, the use of the NIRSystems model 6500 provided a baseline instrument of wide wavelength range (400 - 2500 nm), and well-known performance history. The 6500 is the most commonly used bench-top NIR instrument and has been in use for about 15 years. Calibrations produced using the 6500 can be used for the rapid, low-cost analysis of hog manure samples in the laboratory.

Based on repeatable results for the 6500 across three independent sets of samples, this study demonstrated the feasibility of estimating a number metals and minor elements in hog manure with NIRS. Once suitable calibrations have been developed, these elements in manure samples can be predicted in the laboratory simultaneously with the macro-nutrients with little additional cost.

Moisture was predicted very successfully. Based on calibrations for the three years of data, successful calibrations were developed for Cu and Cd. Moderately successful calibrations were developed for Ca, Fe, Mg, Mn, Mo, S, and Sn. Based on two of three sets, the elements Al, Ba, Be, Cr, Ni, Se, Sr and Ti were predicted successfully or moderately successfully. Calibrations were inconsistent for Co, K, Na, Pb, Si, V, and Zn. Of these elements, S is the most important as a nutrient. The metals Cu, Cr, and Zn are important as micro-nutrients. When they are in high concentrations in the manure and at risk of accumulating in soil, Cd, Cu, Cr, Pb, and Zn are important as potentially-toxic metals. The most important elements that were found not reliably predicable by NIRS were K and B.

Calibrations developed for the year 2000 samples tended to be more successful than those for the two ARDI sets. This may be related to the lesser heterogeneity among samples in year 2000. The 80 samples in 2000 represented 13 manure stores, in contrast to 25 stores represented in ARDI 1998 samples and at least that many in the ARDI 1999 samples. Experience with the determination of nutrients in hog manure by NIRS suggests that calibration success appears to vary inversely with sample heterogeneity (Malley and Vandenbyllaardt 1999).

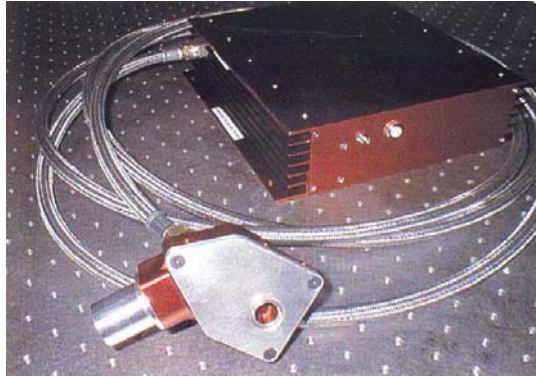
Further analysis of the data is required to test the robustness of calibrations by predicting constituents in each set of samples with calibrations developed on the other sets of samples. It is expected that the calibrations based on more heterogeneous sample sets may be more robust, i.e., better predict new sample sets. Ultimately, the sample sets from the three years will be pooled and the calibrations updated. With a set of over 300 samples, it will be possible to explore if there is an improvement in calibration performance if calibrations are developed separately for different types of hog operations or manure stores. Possibly future unknown samples will be more successfully predicted if calibrations are tailored for specific groups of samples.

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Analysis of Minor Elements and Metals in Hog Manure by Field-portable Near-infrared Spectroscopy: Results for the Textron/Case NH ProSpectra™ Spectrometer



Final Report 2 of 3 to Manitoba Livestock Manure Management Initiative on Project 00-02-03

July 2001 (Revised November 2001)

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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 is 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 a prototype of 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 laptop 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 at 13 application operations during September to November 2000. A total of 121 manure samples were collected. Using conventional physical and chemical methods, the samples were analyzed for moisture, pH, density, conductivity, nutrients, metals and minor elements.

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 to predict composition of future manure samples.

This is the fourth of six reports describing the results from the overall project. It reports the results from developing calibrations for the minor elements and metals from the spectra obtained with the prototype ProSpectra™ spectrometer.

The ProSpectra™ is a solid state spectrometer using a Charge Coupled Device (CCD) Linear Array to detect the light and is equipped with a diffuse reflectance probe. The instrument records absorbance of the sample every 0.5 nm in the wavelength range 600 to 1075 nm. The instrument is sufficiently fast to acquire spectra in a process stream in real time.

Samples were presented to the instrument in two main ways. In order to have the sample come in direct contact with the window of the sensor in the fibre optic probe, we designed and custom-built a circulating cell. This provided an infinite path length allowing all of the light to be scattered within the sample and did not allow the particulates in the manure to settle. The sample inside the circulating cell was moved at a fast speed or a slow speed controlled by changing the speed of the internal propeller. Secondly, samples were presented in a static cell with 2-mm path length in which the sample came in direct contact with the sensor window and light passing through the sample was reflected back to the detector by a non-absorbing ceramic.

The calibration results for the 2-mm path length cell were better than for the circulating cell. An excellent calibration was developed for moisture and successful calibrations were obtained for Cu and Sr. Moderately successful calibrations were obtained for Al, Ba, Cd, Mg, Ni, P and S and useful calibrations for Be, Ca, Cr, Fe, Mn, Mo, V, Zn, and Zr. Calibrations were not successful for B, Co, K, Li, Na, and Si.

This study demonstrated the importance of sample presentation in evaluating the capability of an NIR instrument. It is hypothesized that the sub-optimal performance of the circulating cell was related to the infinite path length and not primarily to the motion of the manure. The ProSpectra shows promise to serve as a free-standing NIR instrument for on-site analysis of hog manure in the field. More work is required to explore its role as an in-stream nutrient sensor as manure is applied to land.

Acknowledgments

This hog manure field demonstration project received funding from the Manitoba Livestock Manure Management Initiative Inc. as project 00-02-03 for the purpose of exploring the application of field-portable near-infrared (NIR) spectrometers for the analysis of minor elements and metals in hog manure.

The development of the mobile near-infrared spectroscopy (NIRS) laboratory and the analysis of nutrients using the field-portable NIR instruments was funded by the TEAM (Technology Early Action Measures) component of the Climate Change Action Fund) and Western Economic Diversification through the Hog Manure Management Strategic Initiative of CETAC-West, Calgary.

We gratefully acknowledge the in-kind support from Textron Systems Corp, Wilmington MA, including that from Sean Dempsey, and from Case NH, Burr Ridge IL, including that from Monte Weller, in making a prototype model of the ProSpectra™ available for this study. We thank David Mays of D Squared Technologies for technical assistance and advice.

The photo on the cover shows the prototype model of the ProSpectra™. Photo is property of Textron Systems Corporation.

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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 variable nutrient content (Malley, Martin and Woods 2001) and variability in concentrations of minor elements and metals (Fitzgerald and Racz 2001).

A method of analytical testing that is rapid, cost effective, and, if possible, field-portable and in-stream that has the capability to analyze nutrients and minor constituents in liquids and slurries would have wide use. Near-infrared spectroscopy is a 30-year old rapid, analytical technology that has the capability of determining quantities of organic constituents in liquids, slurries, and solids. It is described in more detail by Malley, Martin, Woods and Dettman (2001). PDK Projects, Inc. has demonstrated that near-infrared spectroscopy (NIRS), a rapid, non-destructive analytical technology based on the measurement of the absorption of near-infrared light, is useful in the laboratory for the analysis of nutrients and minor elements in hog manure (Malley 1999; Malley and Currie 1999; Malley and Vandenbyllaardt 1999; Malley et al. 1999; Malley et al. submitted for publication).

The development of field portable NIR instruments for field and on-the-go analysis of agricultural crops provides instruments that have the potential for analyzing manure composition as it is applied to agricultural land. The ProSpectra™ Near Infrared (NIR) Spectrometer (Textron Systems, Wilmington, MA) measures constituents and process ingredients in real-time. It has no moving parts and is suitable for real-time measurements in process control applications. Designed for continuous-flow measurement and real-time analysis, the ProSpectra™ Spectrometer is suitable for pharmaceutical, chemical, petrochemical, food processing and agricultural applications. Already in use for grain quality analysis, the NIR spectrometer measures moisture, protein and oil levels as cereal grain flows past the sensor probe.

In a field demonstration study, a prototype of the ProSpectra™ was mounted and operated on a truck lab to evaluate its performance for the analysis of hog manure. Six reports describe the overall results. The overall goals of the study, the design and construction of the truck lab, sampling of hog manure and results for nutrients from the use of a laboratory visible/near-infrared spectrophotometer, the Foss NIRSystems Model 6500 are described by Malley, Martin and Woods (2001). The second report describes the results for the ProSpectra™ for nutrients (Malley, Martin and Moffatt 2001a). The third report describes the results for the nutrients from the operation of the Zeiss Corona® spectrometer (Malley, Martin, and Dettman 2001a). The fourth report by Malley, Martin, Woods and Dettman (2001) describes the results with the 6500 for metals and minor nutrients. This is the fifth report. The sixth report is a companion

report to Malley, Martin and Dettman (2001a) and describes the results with the Corona for metals and minor elements (Malley, Martin and Dettman 2001b).

This report describes the calibrations developed for metals and minor elements from spectra obtained with the ProSpectra™ on 80 samples of hog manure collected in fall 2000.

Methods

Development of the Truck Lab and Sampling of Manure in Fall 2000

The design and construction of the truck lab are described by Malley, Martin and Woods (2001).

The sampling of hog manure samples from 13 hog operations in the vicinity of Winnipeg from September to November 2000 is described by Malley, Martin and Woods (2001).

Analysis of Hog Manure Samples

The analysis of metals and minor elements in 80 of the 121 hog manure samples in this study is described by Malley, Martin, Woods, and Dettman (2001). The following elements were analyzed by inductively-coupled plasma spectroscopy: Al, Ba, B, Be, Ca, Cd, Cr, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Sr, V, Zn, and Zr. For Pb and Sn, the number of samples with analytical values above the limits of detection was too low. Calibrations were not developed for these elements.

The compositional data for pH, conductivity and nutrients are given in Malley, Martin and Woods (2001).

Features of the ProSpectra™ Near Infrared Spectrometer

The specifications and environmental features of the ProSpectra™ are described by Malley, Martin and Moffatt (2001a).

Presentation of Samples to the ProSpectra™ Prototype Spectrometer

The instrument used in this study (Fig. 1). was a fully-functioning prototype of the present version described in Tables 1 and 2. The fibre optic probe was immobilized by mounting on an aluminum table for better access (Fig. 2).

Three sample presentation methods were explored in this study. The initial trials were conducted with a 7.3-cm diameter cell with a 5-cm diameter quartz window and a 1-cm path length. The back side of the cell was a ceramic. The cell was placed on the sapphire window of the instrument's fibre optic probe. The sample thus was 2-3 mm above the sapphire window. This presentation method was not used further following information from the design engineer that the light beam focussed just at the upper

surface of the sapphire window. The sample should come in direct contact with the window.

Therefore, PDK designed and constructed in-house a new, re-circulating cell (Fig. 3) that allowed the sample to come directly into contact with the sapphire window above the sensor head. This cell met the following requirements:

- unobstructed view by the sensor, i.e., propulsion system outside of the viewing area
- path length of at least 10 cm to ensure all the light is scattered within the sample
- continual movement of sample past the sensor head to prevent settling of particles
- sample volume of no more than 700 mL to fill the cell (most samples collected were about 1 L)
- built of opaque materials to remove any possibility of ambient light penetration to the system
- uniform and reproducible rates of movement (flow rate) of manure past sensor head
- easy to fill and easy to clean between loadings, to make the process reliable, reproducible, and time-efficient
- allows for reclamation of the sample once scanned.
- watertight and closed to any possibility of air entry to avoid entraining bubbles of air
- easily attached/detached from the sensor head assembly.

This cell was designed to be a continuous-flow intermediate step between free-standing use of the instrument and its use in the manure stream in a pipe or hose. The circulating cell was the sample presentation used when the ProSpectra was operated on the truck lab.

The third sample presentation method was developed late in the study as a way of scanning individual samples that was simpler and required less sample volume. A rubber ring, 5 cm in outer diameter, 4.5 cm in inner diameter, and 2 mm in height was fastened around the sapphire window with rubber cement. This was filled with about 4 mL of sample and an opaque ceramic disc was placed on top of ring. Path length was 2 mm. Scanning with this sample presentation method was conducted in the laboratory.

Recording Spectra with the ProSpectra™ Prototype Spectrometer

The ProSpectra operates using Delight D Squared custom software. This records absorbance data from 603 to 1103 nm (620 - 1050 nm useful range) every 0.5 nm. The instrument automatically records internal light and dark references every 15 min.

Calibration Procedure using Near-infrared Spectral Analysis Software

The general calibration procedure using NSAS and statistical evaluation of calibrations are described by Malley, Martin, Woods and Dettman (2001).

The development of calibrations from the spectra produced by the ProSpectra is described by Malley, Martin, and Moffatt (2001).

Results

NIR Prediction of Minor Elements and Metals in Hog Manure

Table 1 and Fig. 1 show that calibrations achieved with the ProSpectra using the circulating cell at the fast speed were generally not very successful. The most successful calibration was for V with r^2 about 0.9 and RPD of 3. The calibration for S was moderately successful with r^2 about 0.8 and RPD about 2.25). Some of the calibrations, including Al, Ba, Cu, Fe, Mo, and Zr were moderately useful ($r^2 = 0.7 - 0.8$, RPD = 1.75 - 2.25). Those for Ca, Cd, Cr, Mn, Na, Ni, P, Si, Sr and Zn may be useful for distinguishing high from low samples. Those for B, Be, K, and Li were not successful.

Figure 1 shows that for most of the constituents the predicted values were curvilinear as a function of the chemically-measured values. In most cases, the lowest values were negative and the highest values were predicted too low. The exceptions to this were for V and S, for which calibrations were most successful. The shape of the curve was opposite for moisture where the lowest and the highest values tended to be above the 1:1 line.

The calibration results for the 2-mm path length cell were better than for the circulating cell, with an excellent calibration achieved for moisture with $r^2 > 0.95$ and RPD of >5 (Table 2). Successful calibrations were obtained for Cu and Sr with $r^2 > 0.90$ and RPD of >3 . Moderately successful calibrations were obtained for Al, Ba, Cd, Mg, Ni, P and S with $r^2 > 0.8$ and RPD of >2.25 . Useful calibrations were obtained for Be, Ca, Cr, Fe, Mn, Mo, V, Zn, and Zr ($r^2 > 0.7$ and RPD of $>1.75 - 2.25$)(Table 2). Calibrations were not successful for B, Co, K, Li, Na, and Si.

A number of the calibrations developed from spectra recorded using the circulating cell tended to be non-linear (Fig. 1). Low values were over-estimated by the NIR calibrations, and high values were under-estimated. For calibrations developed from the static cell spectra, the relationships between the chemically-determined values and the NIR-predicted were closer to the 1:1 line (figure not shown).

Table 1. Accuracy of prediction for NIR calibrations for metals and minor elements in 80 samples of hog manure collected in fall 2000 and scanned using the ProSpectra™ in the circulating cell at the fast speed. Wavelength range was 600 - 1075 nm. Calibrations were developed using NSAS.

Statistic	H₂O mg/L	Al mg/L	B mg/L	Ba mg/L	Be mg/L	Ca g/L	Cd mg/L
r²	0.637	0.712	0.456	0.714	0.466	0.608	0.615
SEP	1.65	28.0	1.88	1.00	0.014	0.78	0.035
RPD	1.66	1.86	1.36	1.87	1.32	1.60	1.62
RER	6.72	7.04	6.55	6.74	5.71	6.84	7.14

Statistic	Co mg/L	Cr mg/L	Cu mg/L	Fe mg/L	K mg/L	Li mg/L
r²		0.661	0.709	0.717	0.464	0.578
SEP		0.28	21.7	67.5	0.40	0.05
RPD		1.72	1.85	1.88	1.37	1.52
RER		7.46	8.05	7.53	5.15	5.83

Statistic	Mg g/L	Mn mg/L	Mo mg/L	Na mg/L	Ni mg/L	P g/L
r²		0.686	0.707	0.615	0.679	0.651
SEP		15.2	0.15	52.3	0.38	0.87
RPD		1.78	1.85	1.61	1.76	1.69
RER		7.75	8.19	5.35	8.07	6.84

Statistic	S Mg/L	Si mg/L	Sr mg/L	V Mg/L	Zn mg/L	Zr mg/L
r²	0.799	0.692	0.696	0.893	0.654	0.792
SEP	24.7	52.2	1.43	0.24	76.9	0.039
RPD	2.24	1.80	1.81	3.07	1.70	2.19
RER	8.79	7.65	7.97	11.70	7.64	9.76

Table 2. Accuracy of prediction for NIR calibrations for metals and minor elements in 80 samples of hog manure collected in fall 2000 and scanned using the ProSpectra™ with the 2-mm static cell. Wavelength range was 600 - 1075 nm. Calibrations were developed using NSAS.

Statistic	H₂O mg/L	Al mg/L	B mg/L	Ba mg/L	Be mg/L	Ca g/L	Cd mg/L
r²	0.962	0.805	0.462	0.834	0.764	0.738	0.843
SEP	0.567	23.1	1.87	0.758	0.008	0.634	0.023
RPD	5.16	2.26	1.36	2.46	2.06	1.95	2.52
RER	19.4	8.53	6.59	8.85	10.05	8.37	11.21

Statistic	Co Mg/L	Cr mg/L	Cu mg/L	Fe Mg/L	K mg/L	Li mg/L
r²	0.588	0.778	0.918	0.771	0.623	0.426
SEP	0.058	0.227	11.60	60.8	0.32	0.056
RPD	1.56	2.12	3.46	2.09	1.63	1.32
RER	6.56	12.78	15.06	8.36	6.17	5.19

Statistic	Mg g/L	Mn mg/L	Mo mg/L	Na Mg/L	Ni mg/L	P g/L
r²	0.857	0.780	0.783	0.612	0.834	0.854
SEP	0.272	12.7	0.129	52.5	0.273	0.571
RPD	2.65	2.13	2.14	1.60	2.45	2.52
RER	10.19	9.26	9.46	6.40	11.32	10.35

Statistic	S mg/L	Si mg/L	Sr mg/L	V Mg/L	Zn mg/L	Zr mg/L
r²	0.837	0.643	0.895	0.741	0.789	0.769
SEP	22.2	56.4	0.835	34.2	60.1	0.040
RPD	2.48	1.67	3.09	1.97	2.17	2.08
RER	9.78	7.08	13.64	7.06	9.78	8.66

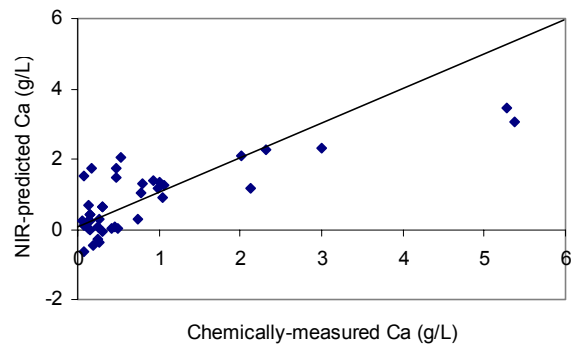
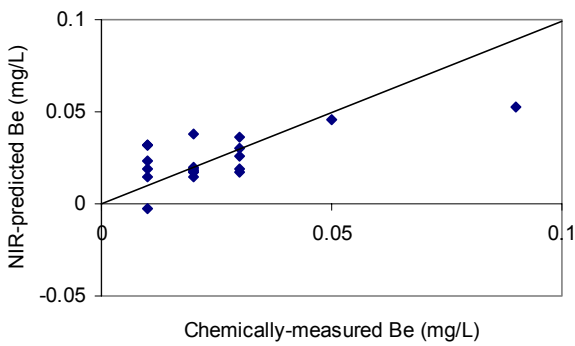
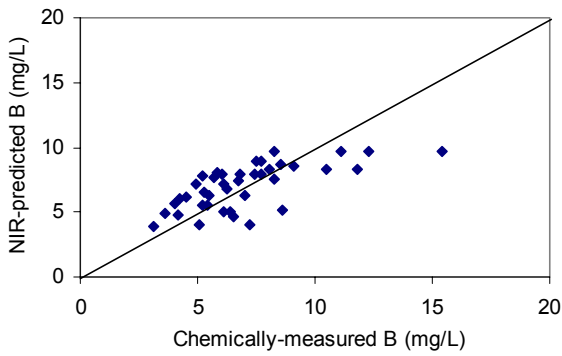
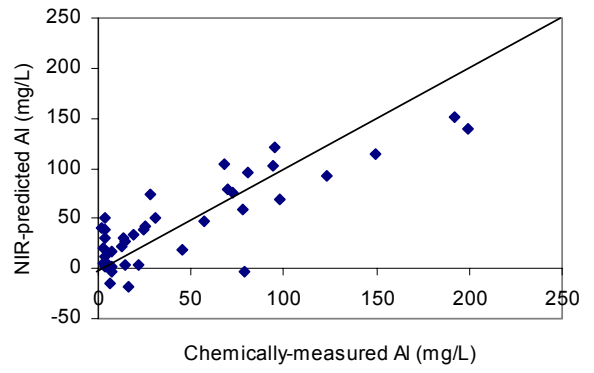
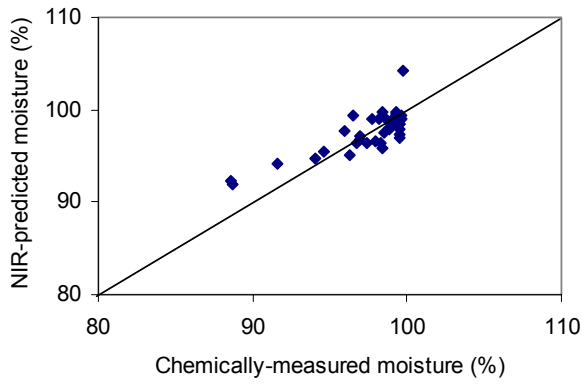


Fig. 1. Linear regression relationships between the NIR-predicted and the chemically-measured values for each constituent in manure. Samples were scanned in the circulating cell at the fast speed. The line is 1:1 and passes through the origin. R^2 and other statistics are given in Table 1.

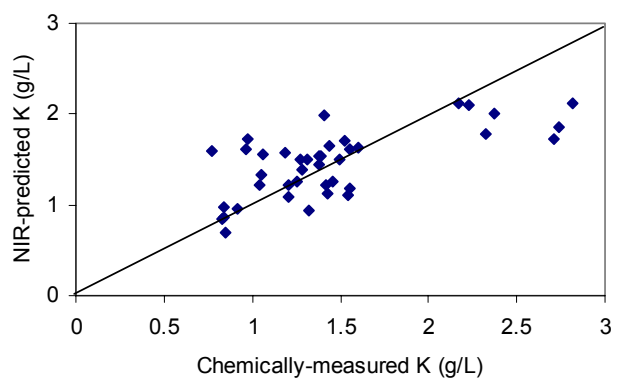
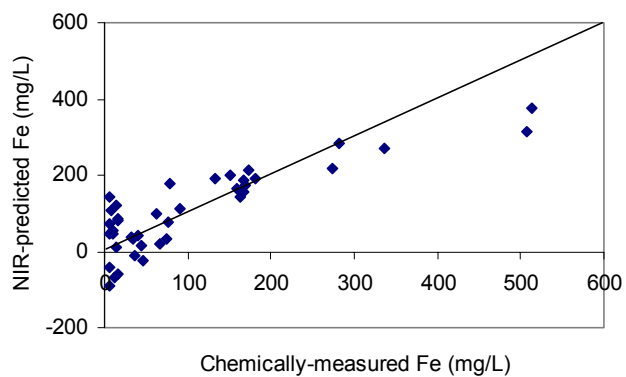
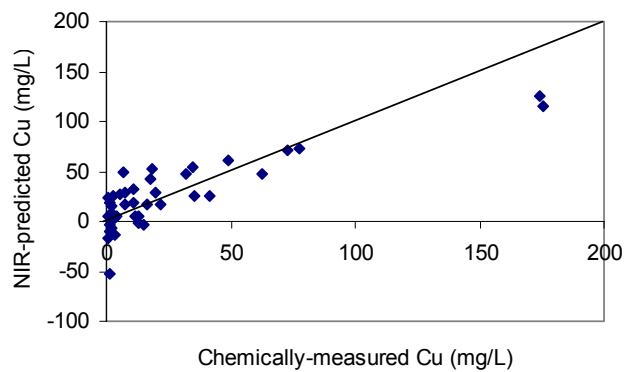
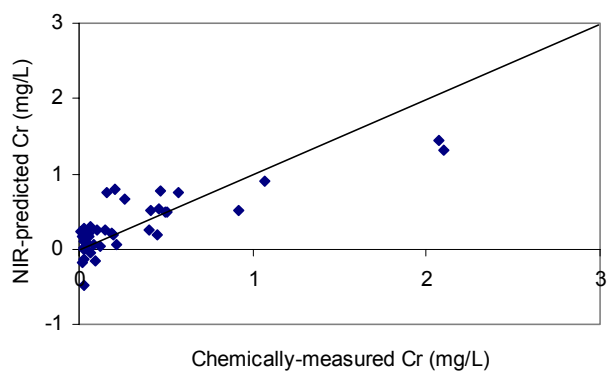
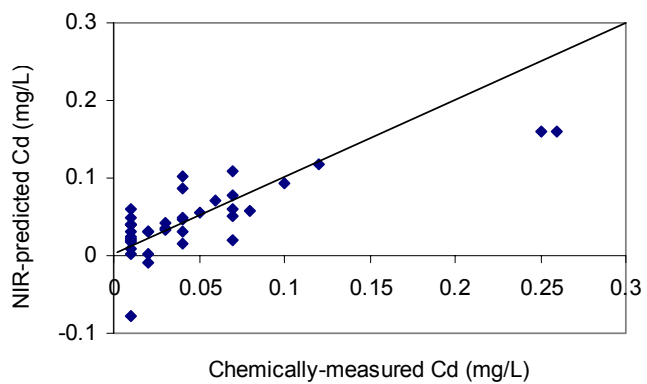
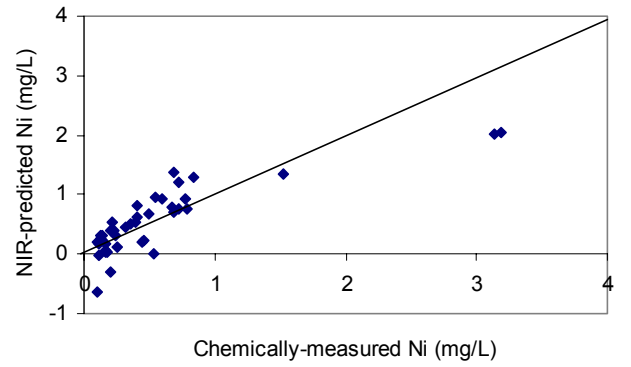
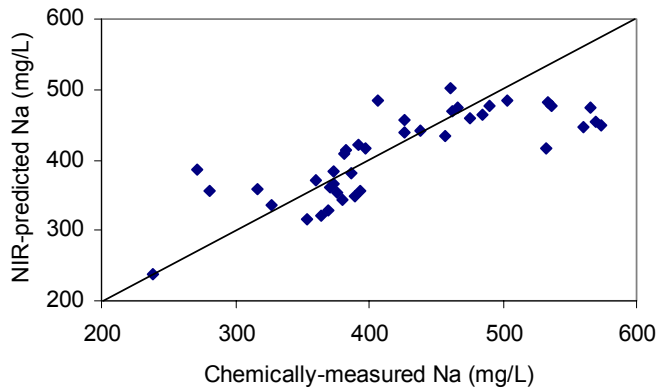
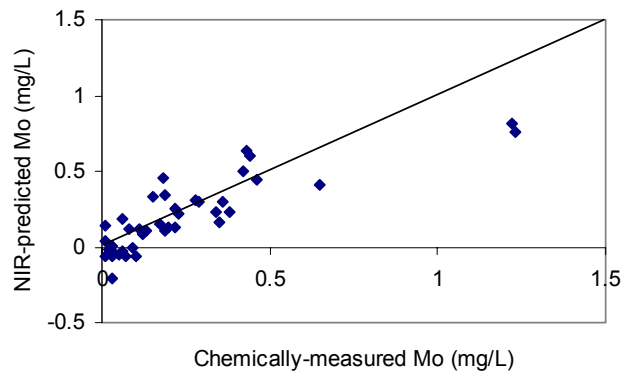
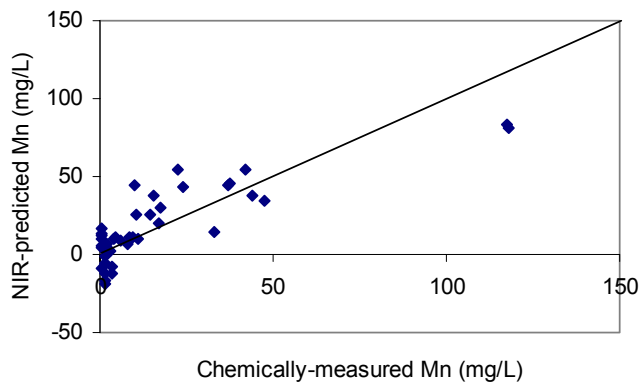
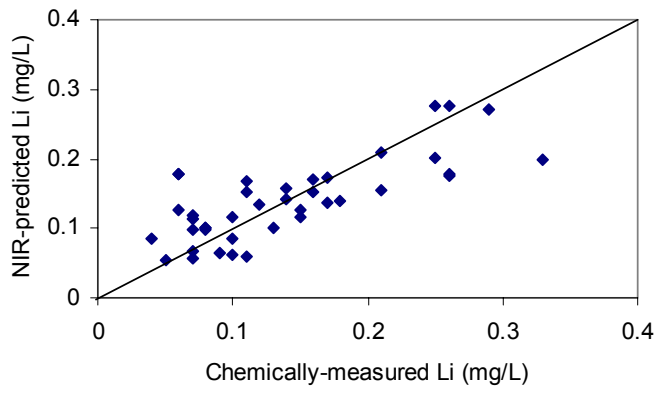


Fig. 1 cont'd



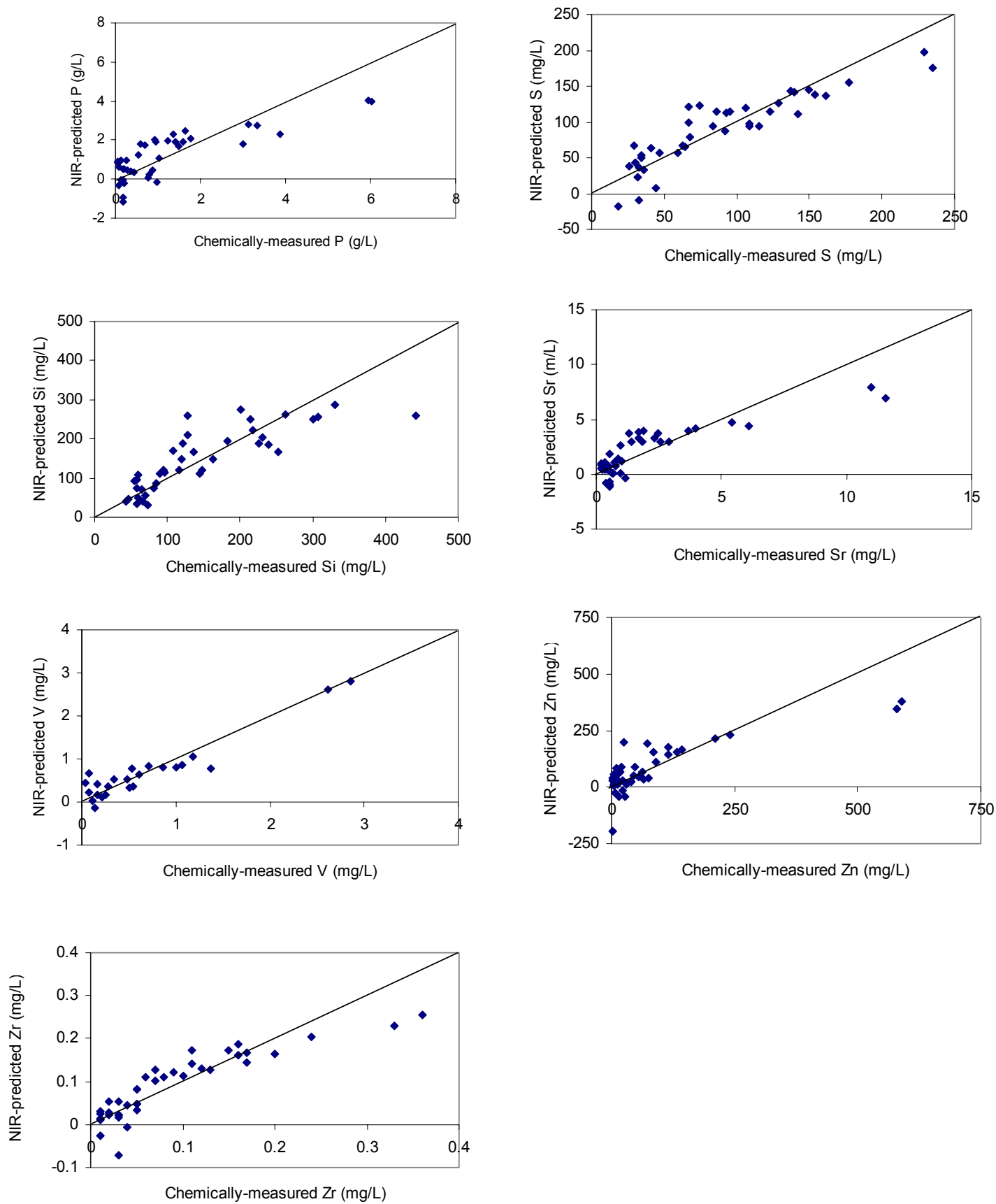


Fig. 1. cont'd

Discussion

Better calibration results were achieved with the static 2-mm path length cell than with the circulating cell for minor elements in this report and for nutrients as described by Malley, Martin, and Moffat (2001). The two presentation systems varied by two factors, movement and path length. In designing an in-stream sample presentation, it is critical to understand whether the non-linearity in the calibrations developed from scans with the circulating cell was due to the movement of the manure or to the infinite path length. In the circulating cell, the manure was flowing and in the other it was static. Secondly, in the circulating cell the path length was infinite, meaning that unless light interacted with particles and was reflected back to the detector, it was “lost”. In the 2-mm cell, the path length was finite and light not reflected back to the detector after interacting with particles was reflected back from the ceramic. The fact that spectra recorded with the circulating cell from thin samples, i.e., those with low particulate content to reflect light back to the detector, had higher absorbances than thick samples (Malley, Martin, and Moffat 2001) is interpreted to indicate that “loss” of light was recorded as absorbance. Thus, future work will utilize a finite path length presentation. There was, nevertheless, an effect of motion on the spectra and on the calibration success (Malley, Martin, and Moffat 2001). Spectra recorded at the slower speed resulted in better calibrations. Therefore, movement of the manure past the sensor will be a variable to be tested in an in-stream system. NIRS is used effectively to monitor liquids and slurries in motion in numerous industrial process applications. It is expected that moving manure will be amenable to measurement by NIRS.

Numerous ionic metals and non-metals were reported in this study to be predictable by NIRS using spectra obtained with the model 6500 instrument (Malley, Martin, Woods and Dettman, 2001). Metals and ionic species do not absorb NIR light and are not directly measurable by NIRS. Nevertheless, these chemical species may be predictable 1.) if they are bound to organic components such as organic matter, ammonium-N, inorganic clays, or carbonates; 2.) if they are correlated with spectrally-active forms, or 3.) if they reproducibly change the spectrum of water.

It is expected that metals such as Ca, Zn, and Cu and non-metal, P, are present in the manure because of the addition of mineral supplements to animal feed (Fitzgerald and Racz 2001). Cadmium, Pb, and Ni are probably in the manure because they are contaminants in the mineral supplements (Fitzgerald and Racz 2001). Some metals are present because of inclusion of minerals from clay-lined earthen manure stores, such as Al, Fe, and Si, perhaps as a result of agitation. Many of these constituents that are in the feed are highly correlated with one another. For example, Al, Fe, Zn, Ca, P (ICP), Cd, suspended P, suspended N, and suspended C and some others are highly intercorrelated (Malley, Martin, Woods, and Dettman 2001). It is not a straightforward process to determine which constituents are the spectrally-active substances responsible for the prediction of a group of intercorrelated constituents. Only spectrally-active substances, such as suspended C, N, and P in organic matter, will be measured dependably. The predictability of non-spectrally-active constituents will depend upon the reliability of the

chemical absorption or correlation relationships. Considerable testing of the manure to be predicted by NIRS is required to determine the reliability with which non-spectrally-active constituents can be measured. Any change in the feed or method of handling and storing manure are more likely to impact the predictability of the non-spectrally-active constituents than the organic, spectrally-active constituents.

The results reported here for the ProSpectra indicate that the calibrations developed from spectra recorded with 2-mm path length cell presentation were successful for moisture Al, Ba, Cd Cu Mg, Ni, P, S, and Sr.

Ultimately, the decision to utilize NIRS for rapid, on-site analysis of hog manure, and the choice of instrument, will depend on the expectation of achieving economic, environmental, and/or regulatory benefits that exceed the cost of employing the technology. The choice among instruments and presentation methods will be guided in part by the accuracy that is required for various nutrients in various application situations.

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Analysis of Minor Elements and Metals in Hog Manure by Field-portable Near-infrared Spectroscopy: Results for the Zeiss Corona® Spectrometer



Final Report 3 of 3 to Manitoba Livestock Manure Management Initiative on Project 00-02-03

July 2001 (Revised November 2001)

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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 is 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 laptop 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 at 13 application operations during September to November 2000. A total of 121 manure samples were collected. Using conventional physical and chemical methods, the samples were analyzed for moisture, pH, density, conductivity, nutrients, metals and minor elements.

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 to predict composition of future manure samples.

This is the sixth of six reports describing the results from the overall project. It reports the results from developing calibrations for the minor elements and metals from the spectra obtained with the Zeiss Corona® 45 NIR spectrometer.

The Corona® is a diode array instrument with rapid scanning times. The instrument used had a polychromator head containing a light source and a number of diode array detectors. It collected spectral data from 938 to 1700 nm wavelengths.

Calibrations were developed using The Unscrambler® multivariate analysis software using Principal Component Analysis/Partial Least Squares regression. Calibrations were developed on two-thirds of the samples and validated using the test set method on the remaining third.

Using statistical criteria defined in this study for evaluating calibrations, calibrations developed with the Corona® for Al, Ba, Cd, Cu, Fe, Mg and V were excellent. Those developed for Ca, Cr, Ni, P, Sr, Zn, and Zr were successful and those for Li, Mn, Mo, Na, S and Si, moderately successful. Calibrations for Be, B, and K were marginal and that for Co was not successful.

For some constituents, the performance of the Corona® compared favourably with the Foss NIRSystems Inc. model 6500 that has a considerably larger wavelength range. The Corona® shows potential to be an effective instrument for the on-site analysis of individual samples of hog manure for a number of minor elements and metals.

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The photo on the cover shows the Zeiss Corona® mounted on the PDK Projects Inc. truck lab and operated by a bank of batteries. 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 the contents of nutrients (Malley, Martin and Woods 2001) and metal and minor elements (Malley, Martin, Woods and Dettman 2001) can vary widely. Metals are of interest in low concentrations as essential trace elements or as contaminants that may accumulate to potentially-toxic levels through repeated application (Fitzgerald and Racz 2001).

A method of analytical testing that is rapid, cost effective, and, if possible, field-portable and in-stream that has the capability to analyze not only nutrients but also minor constituents in liquids and slurries would have wide use. Near-infrared spectroscopy is a 30-year old rapid, analytical technology that has the capability of determining quantities of organic constituents in liquids, slurries, and solids. It is described in more detail by Malley, Martin and Woods (2001). PDK Projects, Inc. has demonstrated that near-infrared spectroscopy (NIRS), a rapid, non-destructive analytical technology based on the measurement of the absorption of near-infrared light, is useful in the laboratory for the analysis of nutrients and minor elements in hog manure (Malley 1999; Malley and Currie 1999; Malley and Vandenbyllaardt 1999; Malley et al. 1999; Malley et al. submitted for publication).

The development of field portable NIR instruments for field and on-the-go analysis of agricultural crops provides instruments that have the potential for analyzing manure composition as it is applied to agricultural land. One such instrument is the Corona® manufactured by Carl Zeiss, Germany. The Corona® is an industrial reflection/transmission head for measuring applications in the UV/VIS/NIR range in which the spectral sensor and micro-computer are already integrated. Using a combination of modern diode array technology, high-precision optics, fast and high-resolution electronics, the Corona® is employed in process monitoring, quality control and in the laboratory in food, agricultural, plastics and pharmaceutical industries. There are no moving mechanical components resulting in a high degree of reliability and accuracy of spectral wavelengths. Scanning time is in the milliseconds range with simultaneous detection of a wavelength range from as low as 200 nm to over 2000 nm. The Corona® has been tested in Europe on a Haldrup harvester for the analysis of grain and forage quality during the harvesting process (Rode 2001).

In a field demonstration study, the Corona® was mounted and operated on a truck lab to evaluate its performance for the analysis of hog manure. Six reports describe the overall results. The overall goals of the study, the design and construction of the truck lab, sampling of hog manure and results for nutrients from the use of a laboratory visible/near-infrared spectrophotometer, the Foss NIRSystems Model 6500, are described

by Malley, Martin and Woods (2001). The second report describes the results for the nutrients from the operation of the Textron/Case NH ProSpectra™ spectrometer (Malley, Martin, and Moffatt 2001a). The third report describes the results for the nutrients from the operation of the Zeiss Corona® spectrometer (Malley, Martin, and Dettman 2001). The fourth report by Malley, Martin, Woods and Dettman (2001) describes the results with the 6500 for metals and minor nutrients. The fifth report is a companion report to Malley, Martin and Moffatt (2001a) and describes the results for the ProSpectra™ for metals and minor elements (Malley, Martin and Moffatt 2001b). This is the sixth report.

This report describes the success of calibrations developed for metals and minor elements using spectra obtained with the Corona® spectrometer.

Methods

Development of the Truck Lab and Sampling of Manure in Fall 2000

The design and construction of the truck lab, and the sampling and analysis of the hog manure are described by Malley, Martin and Woods (2001).

The collection of hog manure samples for this study from 13 hog operations in the vicinity of Winnipeg from September to November 2000 is described in Malley, Martin and Woods (2001).

Analysis of Hog Manure Samples

The analysis of metals and minor elements in 80 of the 121 hog manure samples in this study is described by Malley, Martin, Woods, and Dettman (2001). The following elements were analyzed by inductively-coupled plasma spectroscopy: Al, Ba, B, Be, Ca, Cd, Cr, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Sr, V, Zn, and Zr. For Pb and Sn, the number of samples with analytical values above the limits of detection was too low. Calibrations were not developed for these elements.

Recording Spectra with the Zeiss Corona® 45 NIR

The Zeiss Corona® 45 NIR and the methods used for scanning hog manure samples are described by Malley, Martin and Dettman (2001).

Representative spectra recorded on the manure samples are shown in Malley, Martin and Dettman (2001).

Calibration Procedure using The Unscrambler®

The procedure used for developing calibrations from the spectral data recorded with the Corona is described by Malley, Martin and Dettman (2001). Statistical criteria

for evaluating the success of calibrations are defined by Malley, Martin, Woods and Dettman (2001).

Results

NIR Prediction of Minor Elements and Metals in Hog Manure

Calibrations developed for 24 of the 26 elements determined in this study are shown in Table 1 and Fig. 1. Calibrations developed for Al, Ba, Cd, Cu, Fe, Mg and V were excellent with $r^2 \sim 0.95$, RPD ~ 4.0 (Table 1). Those developed for Ca, Cr, Ni, P, Sr, Zn, and Zr were successful ($r^2 \sim 0.9$, RPD ~ 3.0). Those for Li, Mn, Mo, Na, S and Si were moderately successful (with $r^2 \sim 0.8$, RPD ~ 2.25), and those for Be, B, and K may be useful ($r^2 \sim 0.70$, RPD ~ 1.75). The calibration for Co was not successful (Table 1).

Of these calibrations, the most important ones were for P, S, and the essential trace metals, Cu, Fe, and Zn. Other metals, such as Co, Cr (trivalent), and Ni, are of physiological importance in small quantities and may be toxic in large quantities. Several metals, such as Al, Cd, Pb, Sn, have no physiological role and can be toxic in large quantities.

The calibration for P by ICP reported here ($r^2 = 0.94$, RPD = 4.2) was better than those for SRP, TDP or suspended P ($r^2 = 0.74 - 0.92$, RPD = 1.7 - 3.6) reported for the Corona by Malley, Martin and Dettman (2001).

Table 1. Accuracy of prediction for NIR calibrations for metals and minor elements in 80 samples of hog manure collected in fall 2000 and scanned using the Zeiss Corona®. Wavelength range was 938 - 1700 nm. Calibrations were developed with The Unscrambler® multivariate analysis software.

Statistic	Al mg/L	B mg/L	Ba mg/L	Be mg/L	Ca g/L	Cd mg/L
r^2	0.956	0.736	0.943	0.729	0.901	0.937
RMSEP	10.75	1.23	0.40	0.01	0.35	0.01
RPD	4.80	1.99	4.55	1.60	3.49	5.80
RER	187.08	10.23	16.80	8.00	15.71	26.00

Statistic	Co mg/L	Cr mg/L	Cu mg/L	Fe mg/L	K mg/L	Li mg/L
r²	0.634	0.880	0.945	0.972	0.750	0.865
RMSEP	0.06	0.16	8.71	21.67	0.24	0.03
RPD	1.47	2.99	4.59	5.82	2.13	2.47
RER	6.33	13.06	20.07	23.51	8.75	9.67

Statistic	Mg g/L	Mn mg/L	Mo mg/L	Na mg/L	Ni mg/L	P g/L
r²	0.960	0.876	0.876	0.799	0.914	0.935
RMSEP	0.14	9.06	0.09	38.67	0.18	0.35
RPD	5.07	2.99	2.99	2.16	3.75	4.17
RER	9.81	13.00	13.56	9.10	17.22	17.08

Statistic	S mg/L	Si mg/L	Sr mg/L	V mg/L	Zn mg/L	Zr mg/L
r²	0.843	0.841	0.908	0.935	0.931	0.922
RMSEP	21.72	36.75	0.74	0.18	0.96	0.02
RPD	2.53	2.55	3.45	4.17	4.18	4.20
RER	10.13	11.13	15.41	16.00	18.77	17.5

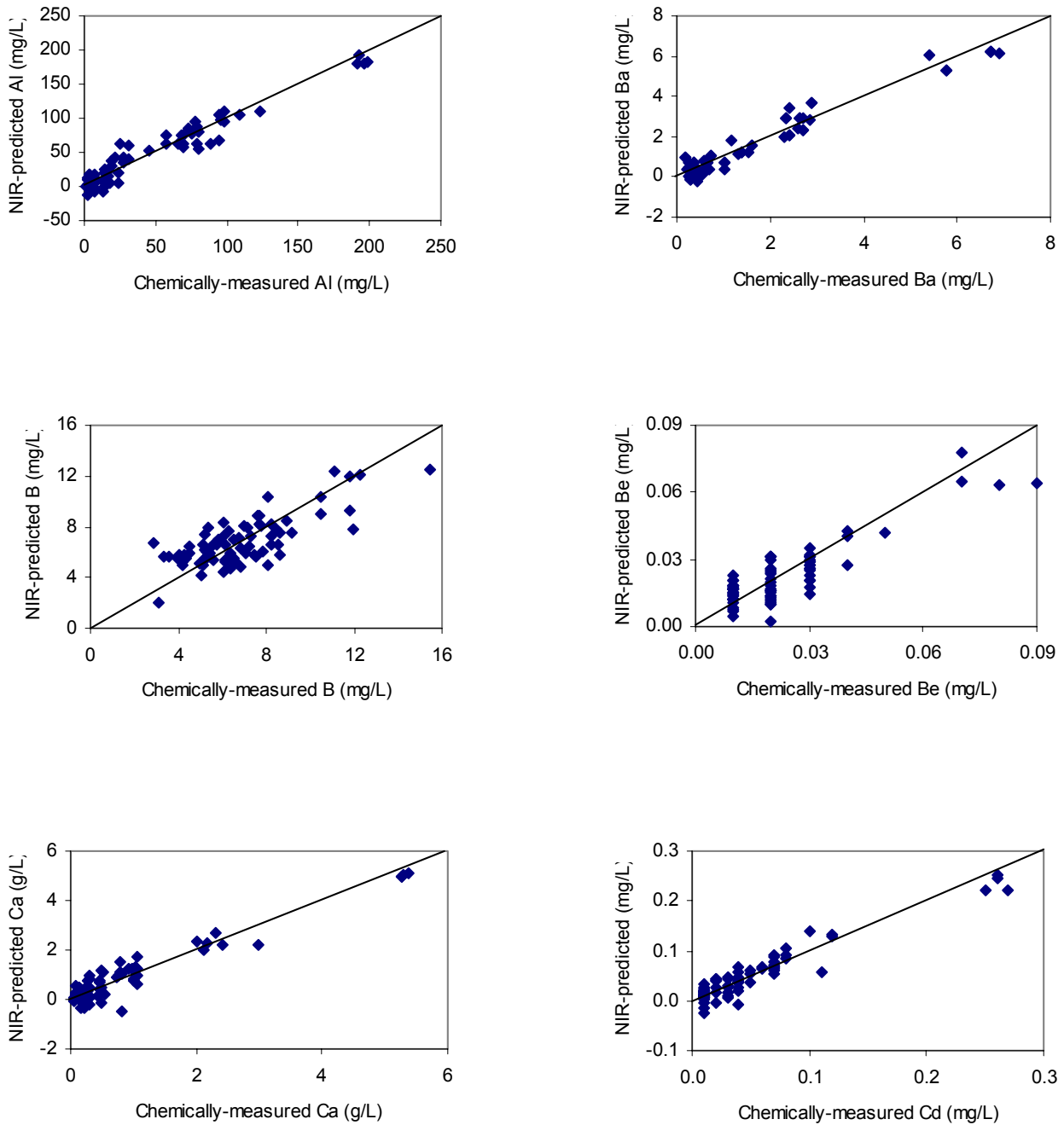


Figure 1. Linear regression relationships between the NIR-predicted and the chemically-determined values for each constituent in manure. The line is 1:1 and passes through the origin. R^2 and other statistics are given in Table 1.

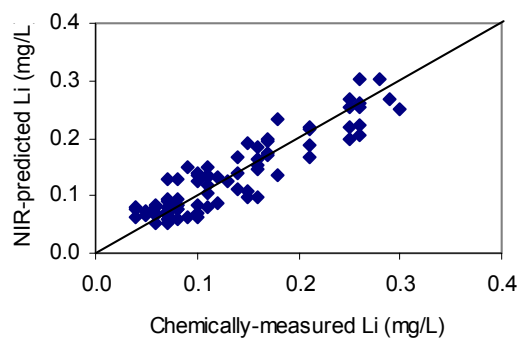
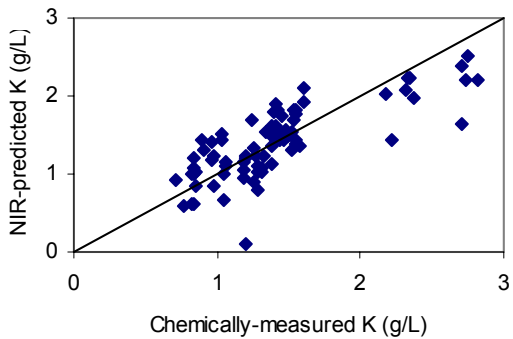
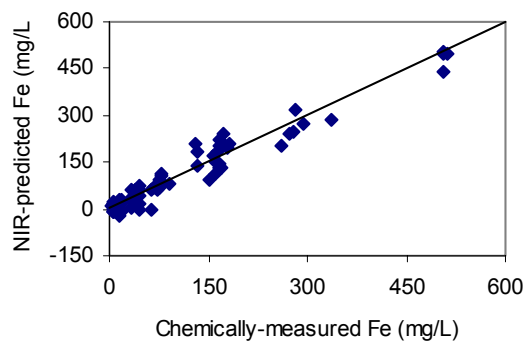
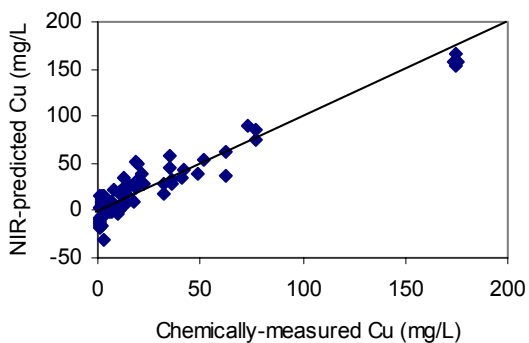
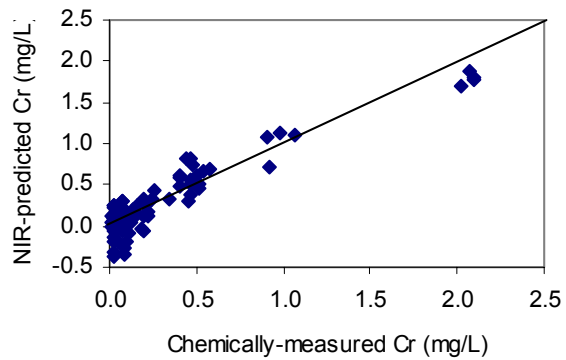
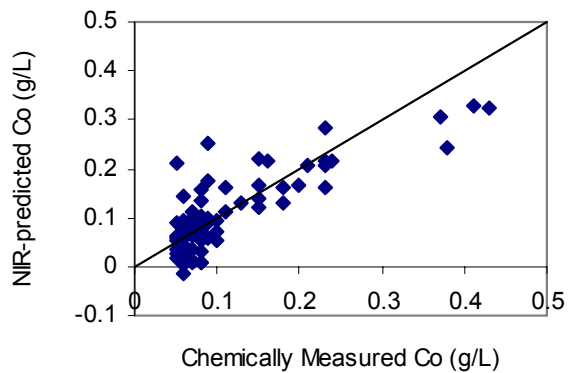


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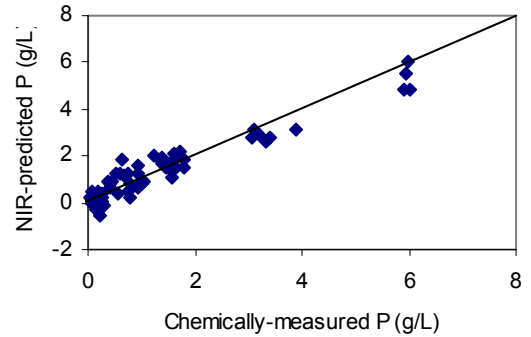
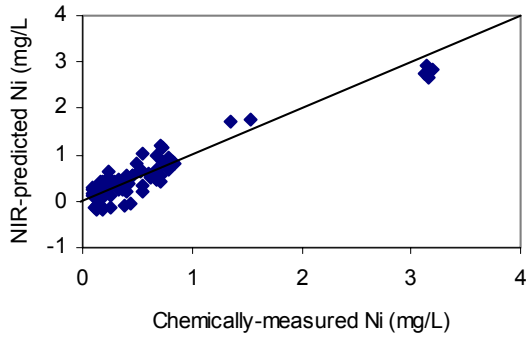
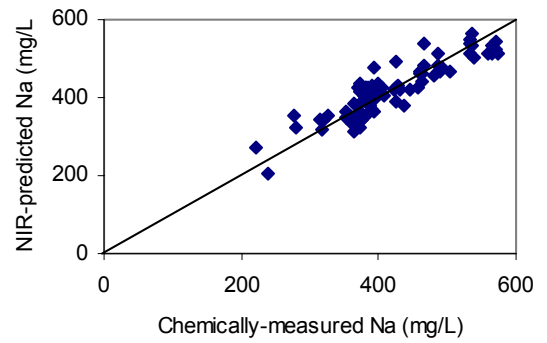
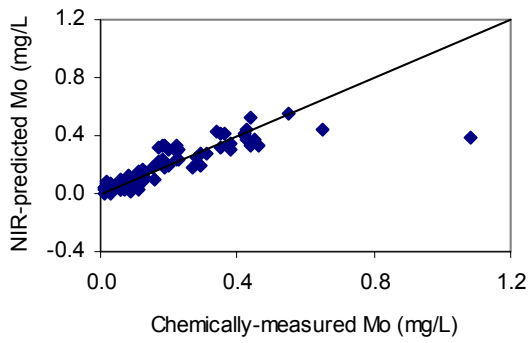
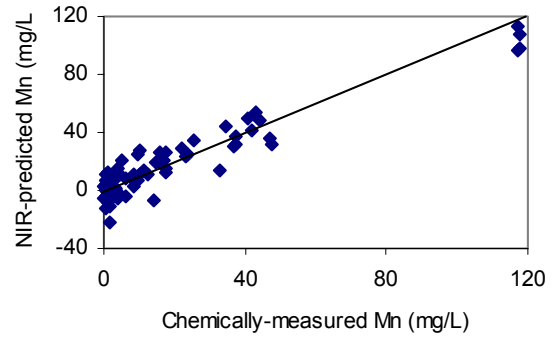
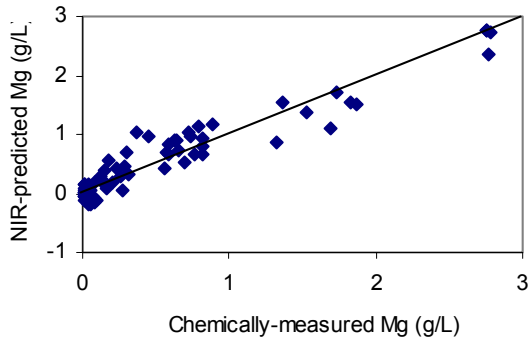


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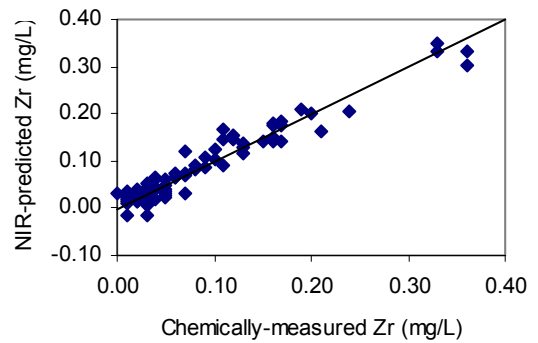
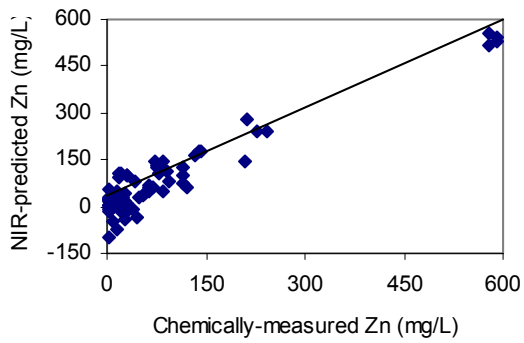
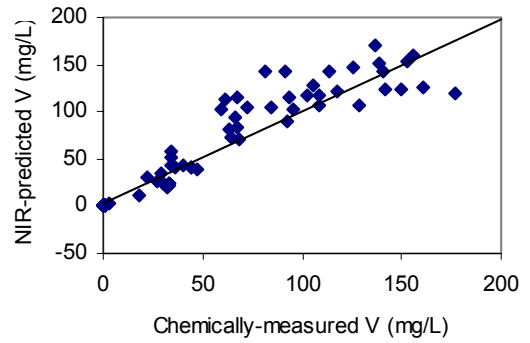
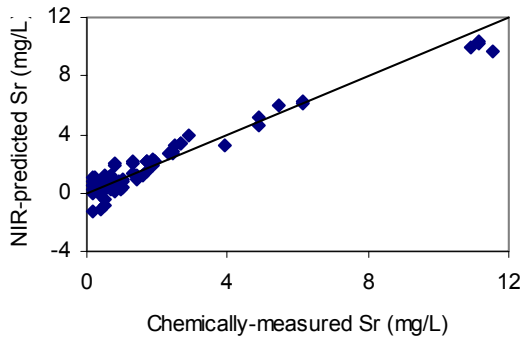
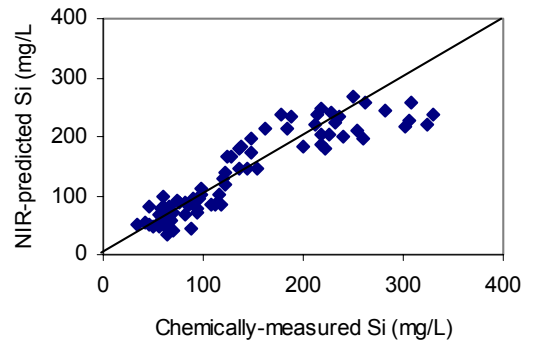
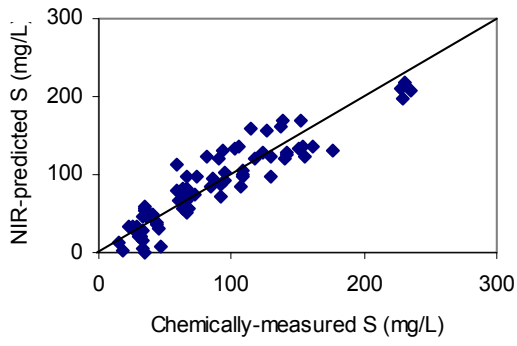


Fig. 1. cont'd

Discussion

The calibrations developed for a number of metals and minor from spectra recorded by the Corona® on hog manure indicate that the instrument has promise for the rapid, on-site measurement of a number of these constituents. Calibrations developed from the Corona spectral data for Al, Ba, Cd, Cu, Fe, Mg and V were excellent. Compared with the calibrations developed using spectra on the same samples obtained with the 6500 (Table 2 from Malley, Martin, Woods, and Dettman 2001), the calibrations developed with the Corona were superior for Al, B, Fe, Li, and Si and the same as that for the 6500 for Ba. For the other constituents, the performance of the 6500 was superior, nevertheless, the instruments were comparable in performance despite a large difference in wavelength range.

As described for the results on nutrients (Malley, Martin and Dettman 2001), there are a number of steps to be taken in further evaluating the performance of the instrument. Further work with The Unscrambler by selecting wavelength regions rather than the entire 938 - 1700 nm region may improve the calibration success. To be applied in practice, however, calibrations to run the instrument must be developed in the operating software of the instrument or be importable into it. The calibrations based on the fall 2000 samples need to be validated using future samples scanned with this instrument.

Numerous ionic metals and non-metals in this study were found to be predictable by NIRS. Metals and ionic species do not absorb NIR light and are not directly measurable by NIRS. Nevertheless, these chemical species may be predictable 1.) if they are bound to organic components such as organic matter, NH₄-N, inorganic clays, or carbonates; 2.) if they are correlated with spectrally-active forms, or 3.) if they reproducibly change the spectrum of water.

It is expected that metals such as Ca, Zn, and Cu and the non-metal, P, are present in the manure because of the addition of mineral supplements to animal feed (Fitzgerald and Racz 2001). Cadmium, Pb, and Ni are probably in the manure because they are contaminants in the mineral supplements (Fitzgerald and Racz 2001). Some metals are present because of inclusion of minerals from clay-lined earthen manure stores, such as Al, Fe, and Si, perhaps as a result of agitation. Many of the constituents that were in the feed were highly correlated with one another. For example, Al, Fe, Zn, Ca, P (ICP), Cd, suspended P, suspended N, and suspended C and some others were highly inter-correlated (Malley, Martin, Woods, and Dettman 2001). It is not straightforward to determine which constituents are the spectrally-active substances responsible for the prediction of a group of inter-correlated constituents. Only spectrally-active substances, such as suspended C, N, and P in organic matter, will be measured dependably. The

Table 2. Accuracy of prediction for NIR calibrations for metals and minor elements in 80 samples of hog manure from fall 2000 developed from spectra obtained with the Foss NIRSystems model 6500 spectrophotometer.

Statistic	H₂O	Al	B	Ba	Be	Ca	Cd	Co	Cr
r²	0.97	0.92	0.62	0.94	0.88	0.97	0.99	0.76	0.97
SEP	0.49	14.6	1.56	0.44	0.006	0.208	0.007	0.043	0.084
RPD	5.60	3.57	0.92	4.21	2.89	5.96	8.29	2.04	5.75
RER	22.7	13.5	7.90	15.2	14.1	25.5	36.6	8.39	25.0

Statistic	Cu	Fe	K	Li	Mg	Mn	Mo	Na	Ni
r²	0.99	0.96	0.92	0.64	0.98	0.96	0.94	0.85	0.96
SEP	4.91	25.4	0.16	0.046	0.102	5.27	0.071	32.3	0.13
RPD	8.18	5.01	3.45	1.66	7.09	5.14	3.91	2.61	5.37
RER	35.6	20.0	13.1	6.35	27.2	22.3	17.3	10.3	24.5

Statistic	P	Pb	S	Si	Sn	Sr	V	Zn	Zr
r²	0.98	0.28	0.95	0.80	0.97	0.98	0.96	0.98	0.96
SEP	0.21	0.046	12.3	41.9	0.064	0.35	0.14	17.0	0.017
RPD	7.08	1.18	4.48	2.25	5.69	7.47	5.13	7.68	4.90
RER	28.3	3.89	17.6	9.53	15.7	32.9	19.6	34.6	20.4

From Malley, Martin, Woods and Dettman (2001)

predictability of non-spectrally-active constituents will depend upon the reliability of the chemical absorption or correlation relationships. Some constituents that were not predictable or not well predicted, such as B and Co, were poorly correlated with all other constituents. Considerable testing of the manure to be predicted by NIRS is required to determine the reliability with which non-spectrally-active constituents can be measured. Changes in the feed or method of handling and storing manure are more likely to impact the predictability of the non-spectrally-active constituents than those that are spectrally-active.

Potassium is often not predictable by NIRS. In this study, it was marginally predicted. The basis of this predictability may be the correlation with $\text{NH}_4\text{-N}$ or total dissolved N of 0.85-0.86 (Malley, Martin, Woods and Dettman, 2001). Sodium is also not usually predictable. Here it was not correlated appreciably with other constituents and may have been measurable because of its effect as a solute on the spectrum of water.

Ultimately, the decision to utilize NIRS for rapid, on-site analysis of hog manure, and the choice of instrument, will depend on the expectation of achieving economic, environmental, and/or regulatory benefits that exceed the cost of employing the technology. The choice among instruments and presentation methods will be guided in part by the accuracy that is required for various nutrients in various application situations.

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