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

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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.

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 of Adaptive Analyzer Technologies, Inc. (ATech) of New York, and Carl Zeiss, Germany for the loan of the Corona® NIR instrument for a two-month period and for technical support. We thank Brian Werner, Jon Gethner, and Dan Bruchez of ATech, and Jürgen Gobel and Michael Rode of Zeiss.

Tannys Moffatt and Sherri E. Woods assisted with data processing.

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 NH_4-N that binds to soil and is less prone to leaching to groundwater than NO_3-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 ~> 0.95, RPD ~> 4.0 (Table 1). Those developed for Ca, Cr, Ni, P, Sr, Zn, and Zr were successful (r^2 ~> 0.9, RPD ~> 3.0). Those for Li, Mn, Mo, Na, S and Si were moderately successful (with r^2 ~> 0.8, RPD ~> 2.25), and those for Be, B, and K may be useful (r^2 ~> 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**
r^2	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**
r^2	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**
r^2	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

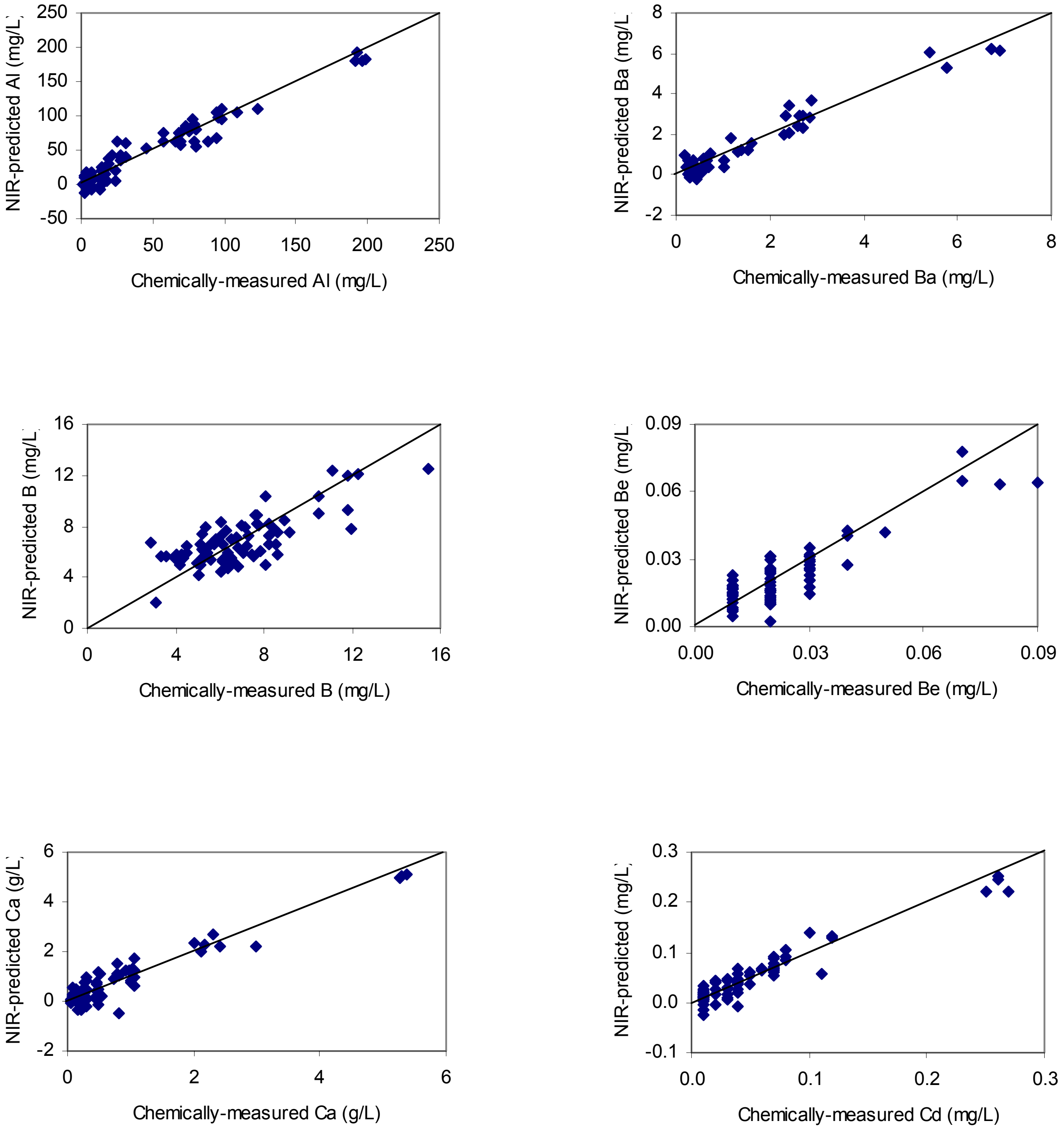


Figure 1. Linear regression relationships between the NIR-predicted and the chemically-determined values for each constituent in manure. The line is 1:1 and passes through the origin. R^2 and other statistics are given in Table 1.

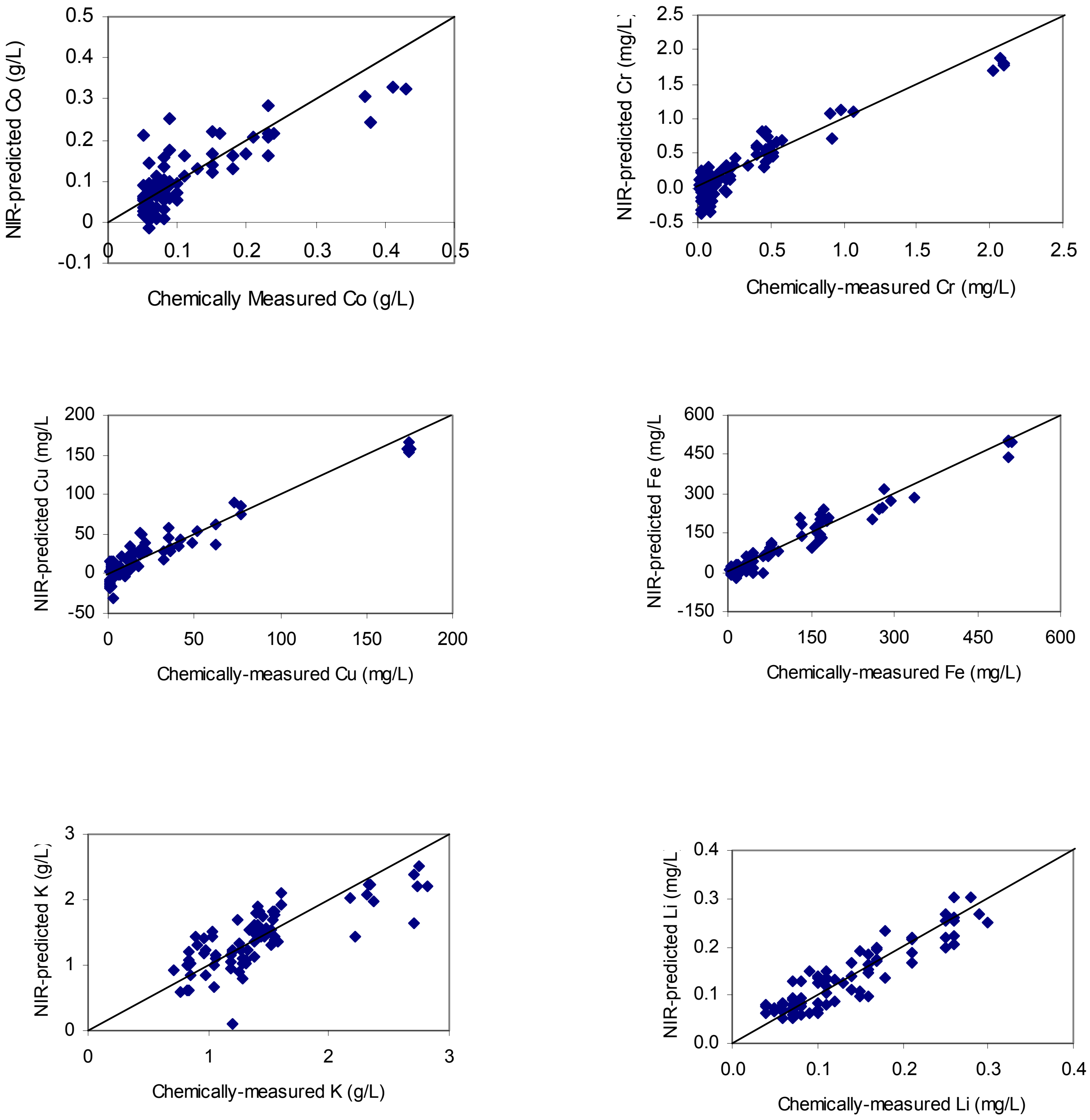
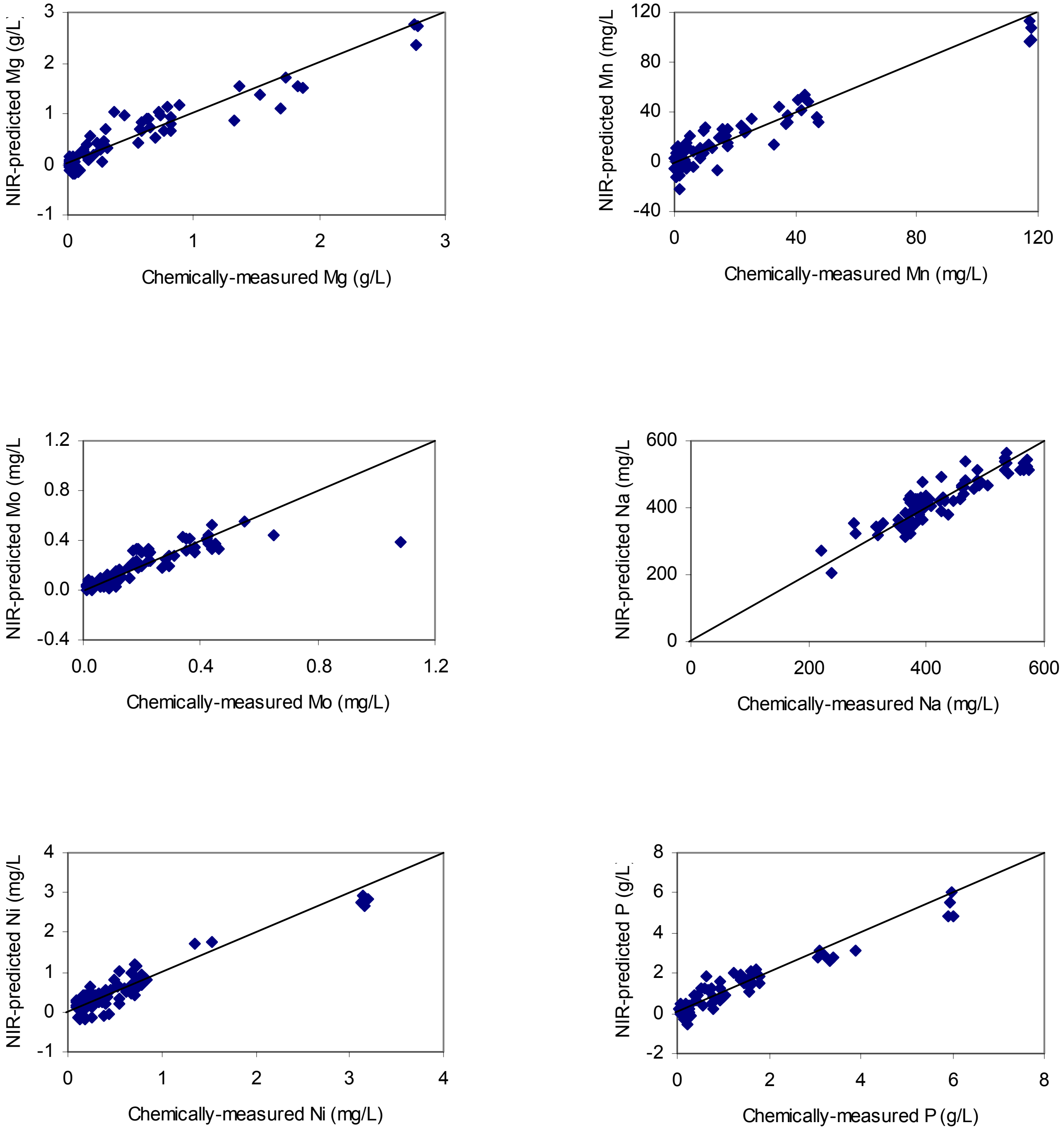


Figure 1. cont'd


NIR-predicted Mg (g/L
3
2
1
0
-1
0
1
2
3
Chemically-measured Mg (g/L)
NIR-predicted Mn (mg/L
120
80
40
0
-40
0
40
80
120
Chemically-measured Mn (mg/L)
NIR-predicted Mo (mg/L
1.2
0.8
0.4
0.0
-0.4
0.0
0.4
0.8
1.2
Chemically-measured Mo (mg/L)
NIR-predicted Na (mg/L
600
400
200
0
0
200
400
600
Chemically-measured Na (mg/L)
NIR-predicted Ni (mg/L
4
3
2
1
0
-1
0
1
2
3
4
Chemically-measured Ni (mg/L)
NIR-predicted P (g/L
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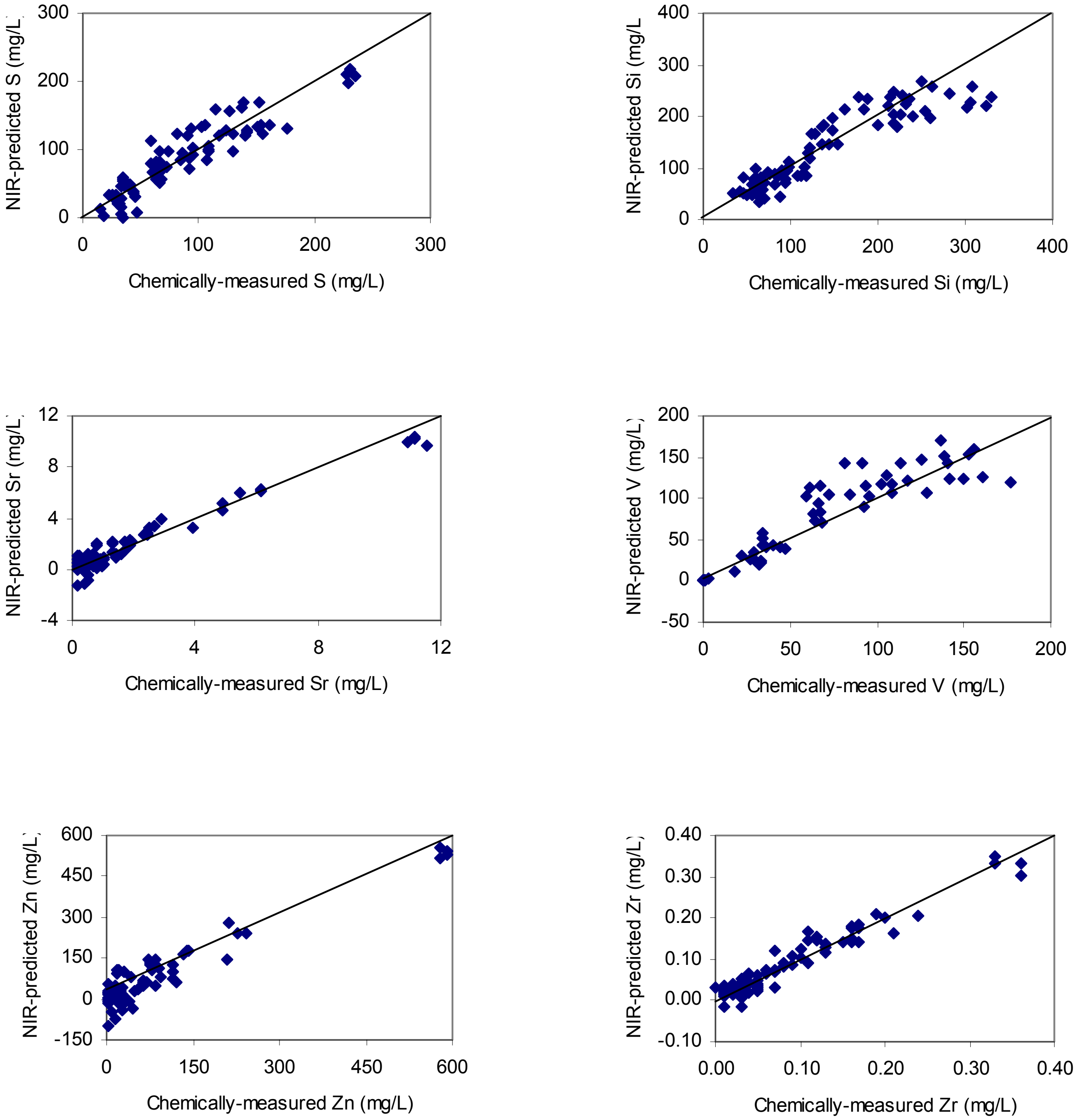
4
2
0
-2
0
2
4
6
8
Chemically-measured P (g/L)

Fig. 1. cont'd


NIR-predicted S (mg/L
300
200
100
0
0
100
200
300
Chemically-measured S (mg/L)
NIR-predicted Si (mg/L
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300
200
100
0
0
100
200
300
400
Chemically-measured Si (mg/L)
NIR-predicted Sr (mg/L
12
8
4
0
-4
0
4
8
12
Chemically-measured Sr (mg/L)
NIR-predicted V (mg/L)
200
150
100
50
0
-50
0
50
100
150
200
Chemically-measured V (mg/L)
NIR-predicted Zn (mg/L
600
450
300
150
0
-150
0
150
300
450
600
Chemically-measured Zn (mg/L)
NIR-predicted Zr (mg/L)
0.40
0.30
0.20
0.10
0.00
-0.10
0.00
0.10
0.20
0.30
0.40
Chemically-measured Zr (mg/L)

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, NH_4-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	**H_2O**	**Al**	**B**	**Ba**	**Be**	**Ca**	**Cd**	**Co**	**Cr**
r^2	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**
r^2	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**
r^2	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 NH_4-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.

References

Fitzgerald, M., and G.J. Racz. 2001. Long-term effects of hog manure on soil quality and productivity. Volume 1: Properties and composition of hog manure samples. Final Report Prepared for Agri-Food Research and Development Initiative, Project 98-124, April, 72 pp.

Malley, D.F. 1999. Rapid, accurate, on-site analysis of hog manure: A possibility with near-infrared spectroscopy. World Wise '99 Conference Proceedings, Winnipeg MB, 7-8 December 1999, Track 1C on CD ROM

Malley, D.F. and R.S. Currie. 1999. Feasibility study on the rapid analysis of available N and P in hog manure and manure-amended soils by near-infrared spectroscopy. Report to The Manitoba Livestock Manure Management Initiative Inc. and The Prairie Farm Rehabilitation Administration. March, 36 pp.

Malley, D.F., P.D. Martin, and L. Dettman. 2001. Analysis of nutrients in hog manure by field-portable near-infrared spectroscopy: Results for the Zeiss Corona® Spectrometer. Final Report to CETAC-West, July, 17 pp

Malley, D.F., R. G. Eilers, E. Rempel, M. Van Walleghem, and P.D. Martin. 1999. Rapid analysis of nutrient and salt concentrations in hog manure by near-infrared spectroscopy. Manure Management'99 Proceedings of a tri-provincial conference on manure management. Saskatoon, SK, 22-24 June 1999, p 633-641.

Malley, D.F., P.D. Martin, and T. Moffatt. 2001a. Analysis of nutrients in hog manure by field-portable near-infrared spectroscopy: Results for the Textron/Case NH ProSpectra™ Spectrometer Final Report to CETAC-West, July, 28 pp

Malley, D.F., P.D. Martin, and T. Moffatt. 2001b. 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 to Manitoba Livestock Manure Management Initiative Inc., July, 17 pp

Malley, D.F., P.D. Martin, and S.E. Woods. 2001. Analysis of nutrients in hog manure by field-portable near-infrared spectroscopy: Development of a mobile laboratory and results for Foss NIRSystems Inc. model 6500 spectrophotometer in the laboratory. Final Report to CETAC-West, July, 33 pp

Malley, D.F., P.D. Martin, S.E. Woods, and L. Dettman. 2001. 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 to Manitoba Livestock Manure Management Initiative Inc., July, 35 pp

Malley, D.F. and L. Vandenbyllaardt in collaboration with G. Racz, M. Fitzgerald, G. Plohman, and J. Hicks. 1999. Feasibility study on the rapid compositional analysis of hog manure by near-infrared spectroscopy. Report to The Manitoba Livestock Manure Management Initiative Inc. on Project 99-01-25. August. 31 pp.

Malley, D.F., L. Yesmin, and R.G. Eilers. Determination of N, P, and salts in hog manure and manure-amended soils using near-infrared spectroscopy. Soil Science Society of America Journal (submitted for publication).

Rode, M. 2001. NIR diode array spectrometers on agricultural harvest machines: overview and outlook. Abstract #O7-2 in Abstracts and Program of NIR-2001: Changing the World with NIR, 10th International Conference on Near-Infrared Spectroscopy, Kyongju, Korea, 10-15 June 2001.