Estimation of moisture, total nitrogen and total organic carbon in tropical livestock manures: Application of near Infrared Spectroscopy on wet and dry samples

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Abstract

Near infrared spectroscopy (NIRS) was used to analyse livestock manure. The purpose of this study was to evaluate the feasibility NIRS techniques for measuring moisture content (MC), total nitrogen (TN) and total organic carbon (TOC) in wet and dry manures. Forty four (44) samples of livestock manures from Reunion Island were analyzed by using NIRS : (i) on wet samples and (ii) on dry samples. Results showed that the NIRS method could provide accurate predictions of MC (R^2= 0.92, RPD = 3.5). The NIRS models on wet samples for TN and TOC allowed acceptable estimations with respectively R^2= 0.76, RPD= 2.1 and R^2= 0.81, RPD=2.3. The NIRS models built on dry manures were good for TN and TOC predictions, respectively R^2= 0.90, RPD=3.3 and R^2= 0.91, RPD= 3.5. For the future, the NIR technique can be recommended for estimation of MC, TN and TOC both on wet and on dry livestock manures because of its ability to provide rapid, and non-destructive measurements.

Keywords
Spectroscopy
Tropical environment
Wet manures
Dry manures
Predictive Models

1. INTRODUCTION

A variety of chemicals constituents contained in animal manures can be highly valuable to agriculture or energy production. In order to suggest the best way of re-using the animal manures, we considered three parameters which are crucial for decision-maker : moisture content (MC), total nitrogen (TN) and total organic carbon (TOC). MC is an important parameter because the handling and storage of manures depend on this value. In agricultural way, MC conditionned the techniques of spreading and for an energetic valorization, MC influenced the potential of manure to be burned or to be methanized (Chabalier, Van de Kerchove, and Saint-Macary 2006). TN played an important role in agriculture because the lack or the exces of this constituent may impact negatively the plants growths. Knowing TN is helpful to determine the capacity of microorganisms in methanation of manures. On one hand, TOC defined the way that manures will work as an amendment of soils and on the other hand, higher the TOC is, higher is the energetic potential of the manures (Ngnikam et al. 2002).

To reconcile precision and the potential negative environmental influences of animal manure, it is necessary to develop rapid and robust methods to evaluate the chemical composition of animal manure (Chen, Xing, and Han 2013; Reeves III 2007). The use of near infrared spectroscopy (NIRS) has many advantages for compositional analysis. NIRS technique is prompt for wide-spread usage. Numerous components concentration can be estimated once calibrations have been developed for the components of interest (Finzi et al. 2015). This technique has been used to determine the chemical composition of livestock manure (Reeves III and Van Kessel 2000; Malley et al. 2005; Reeves III 2007). The objective of this study was to investigate the feasibility of using NIRS to determine the nutrient composition of bovine manures both on wet samples and dried samples.

2. METHODOLOGY

2.1. Sample collection and preparation

Samples were collected from farms in Reunion Island (n=44). Samples were collected from manure storage facilities and ranged from slurries to solids. According to Van Kessel *et al.* (1999), samples were stored at 4°C at the laboratory. In this way, their storage can be lasted for several weeks with little or no change in the N composition.

2.2 Chemical analysis

Moisture (MC) or dry matter content was performed on wet samples by oven drying at 105°C to a constant wet. Total organic C (TOC) content and total organic N (TN) content were determined on samples dried at 40°C by using the Dumas method as described in NF ISO 13878 (ISO 1998) and NF ISO 10694 (ISO 1995) respectively. The measurement uncertainty for TOC and orgN was 7%.

2.3 NIRS measurements

NIR spectra were acquired using a laboratory spectrophotometer FOSS XDS (Foss NIRSystems, Silver Spring, MD, USA) working in a spectral range between with resolution of 2 nm and 32 scans per spectrum. All wet samples were scanned in triplicate as obtained, with no grinding or sample preparation other than mixing. Three different fillings were done and triplicate spectra of each sample were averaged. All dried samples (40°C) were ground through a 1mm screen, then packed into quartz ring cups and scanned in duplicate (two repacks, where the second scan was a completely different subsample from the first). Duplicate spectra of each sample were averaged.

2.4 Calibration development

The spectra were processed using Win ISI software (Infrasoft Int., Port Matilda, (PA), USA). The spectra were transformed: (1) using the standard normal variate and detrend transformation (SNVD) second derivative and smoothing calculated over five data points on both sides, which reduces baseline variation and enhances spectral features (J. Reeves, Mc Carty, and Mimmo 2002). Calibrations were performed by the stepwise multiple linear regression procedure in order to select the most informative wavelengths for building the model (Shenk and Westerhausv 1990).

In order to minimize the spectral errors, outliers were deleted during the calibration process. The statistical methods used to evaluate goodness of fit included the coefficient of determination and the root mean square error calculated for predicted values of the entire calibration set (R^2_C and SE_C, respectively) or during cross-validation (R^2_{CV} and SE_{CV}, respectively) after spectral and calibration outlier removal. In order to compare the quality of calibrations for variables with different units and ranges, the ratio of performance to deviation for cross-validation on the calibration set (RPD_{CV}) were calculated as the ratio between standard deviations (SD) of measured data and SE_{CV}.

The reliability and stability of calibrations for environmental or heterogenous samples (such as manure) were shown in **Table 1** according to the guidelines reported by Sakirkin *et al.* (2011).

Table 1: General guidelines for reporting the performance of calibration (Sakirkin et al. 2011)

RPD < 1.5	Model is not useful
1.5 ≤ RPD < 2.0	Model can possibly distinguish between high and low values
2.0 ≤ RPD < 2.5	Model can be applied to approximate or classify
2.5 ≤ RPD < 3	Model is good and can be used for quantitative prediction
3 ≤ RPD < 4	Model is excellent and can be used for reliable quantitative prediction
4.0 ≤ RPD	Model is reproductible and can be used reliably in commercial application

3. RESULTS AND DISCUSSIONS

3.1 Sample composition

The results in **Table 2** show the composition of the entire sample set. The compositions were different with MC, total C, and total N varying by approximately 2-, 50- and 30-fold respectively on wet basis. Based on dry samples, total C and total N ranged between 42 and 86% and between 21 and 45 ‰ respectively. In order to test the feasibility of developing NIR calibrations for manures, such wide range of samples were essential as reported in earlier findings (Reeves III and Van Kessel 2000; Finzi et al. 2015; Sakirkin et al. 2011)

Table 2 : Composition of studied manures

	Constituents	Units	Mean (SD)	Range (Min-Max)
Wet samples	Moisture	$g.100g^{-1}$ (wb)	76.64 (± 13.92)	41.91 - 98.57
	Total solids	$g.100g^{-1}$ (wb)	23.36 (±13.92)	1.43 – 58.09
	Total carbon	$g.100g^{-1}$ (wb)	7.61 (± 3.99)	0.44 - 20.77
	Total nitrogen	$g.kg^{-1}$ (wb)	5.34 (± 2.75)	0.43 - 13.63
Dry samples	Total carbon	$g.100g^{-1}$ (db)	67.06 (± 7.56)	41.77 - 85.70
	Total nitrogen	$g.kg^{-1}$ (db)	35.36 (± 5.62)	20.51 - 45.38

3.2 NIRS spectra

The difference between wet and dry samples can be seen in **Fig 1.** and **Fig 2.** when comparing the averaged spectra obtained by scanning each sample. Our results are consistent with those reported by Reeves (1995) who affirmed that the presence of water causes peak shifts in the spectra of liquid compounds.

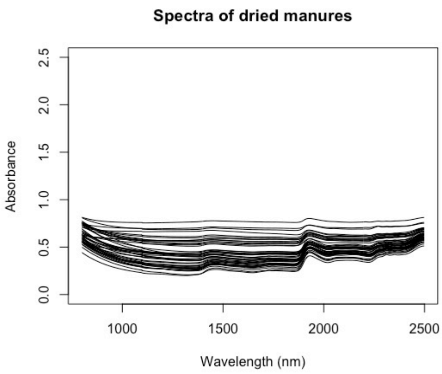

Fig. 1: Dried manures spectra

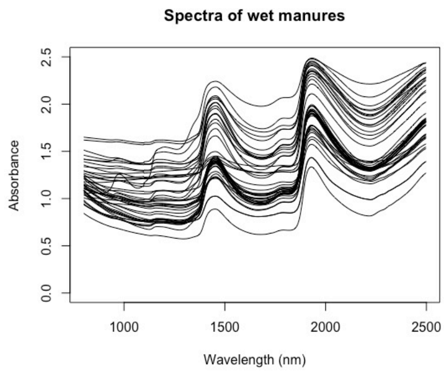

Fig.2 : Wet manures spectra

A principal component analysis (PCA) built with the sample absorbance (**Fig 3.**) confirmed also the characteristics of wet samples and dry samples. This analysis showed the feasibility of NIRS to distinguish wet and dry samples by only used the absorbance. As reported in other studies, NIRS can differentiate populations in a given data set (Jancewicz et al. 2017; Finzi et al. 2015; Tamburini et al. 2015).

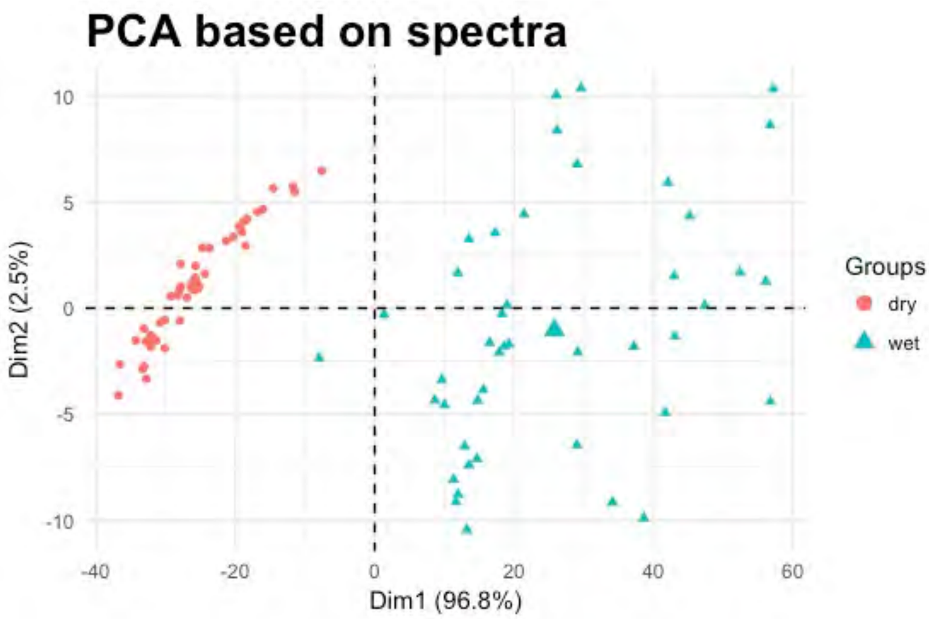

Fig 3. Score plot of the first two principal components of NIR spectra for the entire data set : wet samples and dry samples

3.3 NIRS calibration

The results of NIRS calibration were summarized in **Table 3** both for the dry samples and the wet samples.

3.3.1. Moisture content calibration

As shown in **Table 3** MC calibration gave good results with a SE_C of 3.47, a RPD_C of 3.5 and a R^2 of 0.93. According to the evaluation of the calibration, presented in Table 1, the model is excellent and can be used for reliable quantitative prediction. The R^2 found in our study is in accordance with the MC in dairy manures reported by Reeves (2007) when establishing the status of quick tests for on-farm analysis with emphasis on manures. Another study based on poultry manures showed that R^2 and SE_C were respectively 0.98 and 2.65 (Tamburini et al. 2015). However, these values were better than observed on bovine manures, such findings confirmed the helpfulness of NIRS to be used for predicting MC in manures.

3.3.2. Total nitrogen calibration

The calibration built with the wet samples gave the following results: RPD_C was 2.1 and a R^2 of 0.76 which can be considered as a model that can be applied to approximate or classify (Table 1). The performance of NIRS calibration to predict TN content of dried manures was $RPD_C = 3.3$ and a $R^2 = 0.90$. Such results meant that the model is excellent and reliable for quantitative prediction. Better performance was recorded for dried samples than for wet samples in our study.

For wet samples, our R^2_C was lower than those written by Reeves (2007) which was between 0.94 and 0.96. This can be justified by the fact of the very wide range values of our dataset when based on wet samples.

For dry samples, the results obtained were better than those reported (i) by Malley *et al.* (2005) who worked on diverse cattle manures (raw, stockpiled and composted) with $R^2 = 0.74$ and RPD = 2.14 and (ii) by Bastiannelli *et al.* (2010) who worked on poultry manures and recorded a R^2 of 0.8 and RPD of 2.8.

3.3.3. Total carbon calibration

TOC calibrations drove to these results: $RPD_C = 2.3$ and R^2 of 0.81; $RPD_C = 3.5$ and R^2 of 0.91 respectively for wet and dried samples. The model allowed a classification between high and low values for wet samples and is excellent and reliable for a quantitative prediction of TOC.

For wet manures, Reeves (2007) presented higher R^2 between 0.94 and 0.96. This author worked on more homogenous samples than ours.

For dry samples, our results were consistent than those reported in the literature: $R^2 = 0.91$ and RPD = 3.3 for Malley *et al.* (2005).

Table 3: Results obtained with NIRS calibration

	Parameters	Units	N	Outliers Spectral	Outliers Calibration	Mean	SD	SE_C	R^2_C	RPD_C	SE_{CV}	R^2_{CV}	RPD_{CV}	#
Wet samples	MC	$g.100g^{-1}$ (wb)	44	2	3	77.89	12.26	3.47	0.92	3.5	7.22	0.70	1.7	4
	Total N	$g.kg^{-1}$ (wb)	44	2	3	21.32	2.17	1.04	0.76	2.1	1.52	0.66	1.3	1
	Total C	$g.100g^{-1}$ (wb)	44	2	0	7.64	3.82	1.63	0.81	2.3	1.63	0.81	2.3	3
Dry samples	Total N	$g.kg^{-1}$ (db)	44	1	2	24.98	5.34	1.64	0.90	3.3	2.21	0.83	2.4	5
	Total C	$g.100g^{-1}$ (db)	44	3	3	36.76	6.86	1.98	0.91	3.5	3.41	0.75	2.0	3

N is the number of samples used in the dataset
SD is standard deviation
SE_C is the standard error of calibration
SE_{cv} is the standard error of cross-validation
R^2c and R^2cv are the coefficients of determination, respectively for calibration and cross-validation
RPD_C and RPD_{CV} are respectively the ratio between SD and SE_C and SD and SEcv indicating the model performance
is the number of wavelenghts taken into account in the model
wb : wet matter basis
db: dried matter basis

4. CONCLUSION

Our study aimed to investigate the feasibility of using NIRS to determine the nutrient composition of bovine manures. On the one hand and based on wet samples, which were only homogenized, excellent model was obtained for moisture prediction and allowed manures classification for TN and TOC. On the other hand and based on dried and ground samples, NIRS model for TN and TOC were both excellent and reliable for those constituents prediction. NIRS techniques were helpful for rapid determination of bovine manures characteristics in order to decide about the suitable re-use of them: agricultural or energetic way. Either on wet samples or dried samples, the feasibility of NIRS to predict crucial constituents in manures was confirmed.

5. References

Bastianelli, D., L. Bonnal, H. Juin, S. Mignon-Grasteau, F. Davrieux, and B. Carr, 2010. "Prediction of the Chemical Composition of Poultry Excreta by near Infrared Spectroscopy." Journal of Near Infrared Spectroscopy 18 (1): 69–77.

Chabalier, P. F., Van de Kerchove, V. and Saint-Macary H., 2006. Guide de La Fertilisation Organique à La Réunion. Edited by CIRAD Montpellier. La Réunion.

Chen, Longjian, Li Xing, and Lujia Han. 2013. "Review of the Application of Near-Infrared Spectroscopy Technology to Determine the Chemical Composition of Animal Manure." Journal of Environmental Quality , 42, 1015–28.

Finzi, A., R. Oberti, A.S. Negri, F. Perazzolo, G. Cocolo, F. Tambone, G. Cabassi, and G. Provolo, 2015. "Effects of Measurement Technique and Sample Preparation on NIR Spectroscopy Analysis of Livestock Slurry and Digestates." Biosystems Engineering 134 42–54.

Jancewicz, L.J., M.L. Swift, G.B. Penner, K. A. Beauchemin, K.M. Koenig, G.E. Chibisa, M. L. He, J.J. McKinnon, W. Z. Yang, and T A McAllister, 2017. "Development of Near-Infrared Spectroscopy Calibrations to Estimate Fecal Composition and Nutrient Digestability in Beef Cattle." Canadian Journal of Animal Science 97: 51–64.

Malley, D.F., C. McClure, P. D. Martin, K. Buckley, and W. P. McCaughey, 2005. "Compositional Analysis of Cattle Manure During Composting Using a Field-Portable Near-Infrared Spectrometer." Soil Science and Plant Analysis 36 (4): 455–75.

Ngnikam, E., P. Rousseaux, E. Tanawa, and R. Gourdon, 2002. "Multicriteria Analysis for Environmental Assessment of Solid Waste Management Systems in Tropical African Cities: Case Study of Yaoundé (Cameroon)." Journal of Decision Systems 11 (3–4): 479–98.

Reeves III, J. B. 2007. "The Present Status of 'Quick Tests' for on-Farm Analysis with Emphasis on Manures and Soil: What Is Available and What Is Lacking?" Livestock Science 112 (3): 224–31.

Reeves III, J B, and J S Van Kessel. 2000. "Near-Infrared Spectroscopic Determination of Carbon, Total Nitrogen, and Ammonium-N in Dairy Manures." Journal of Dairy Science 83 (8): 1829–36.

Reeves, J, G Mc Carty, and T Mimmo, 2002. "The Potential of Diffuse Reflectance Spectroscopy for the Determination of Carbon Inventories in Soils." Environmental Pollution 116 (1): S277–84.

Reeves, J. B, 1995. "Near- versus Mid-Infrared Spectroscopy: Relationships between Spectral Changes Induced by Water and Relative Information Content of the Two Spectral Regions in Regard to High-Moisture Samples." Applied Spectroscopy 49 (3). SAGE Publications Ltd STM: 295–303.

Sakirkin, S. L. P., C. L. S. Morgan, J. C. MacDonald, and B.W. Auvermann, 2011. "Effect of Diet Composition on the Determination of Ash and Moisture Content in Solid Cattle Manure Using Visible and Near-Infrared Spectroscopy." Applied Spectroscopy 65 (9). SAGE Publications Ltd STM: 1056–61.

Shenk, J. S., and M. O. Westerhausv, 1990. "Population Definition, Sample Selection, and Calibration Procedures for Near Infrared Reflectance Spectroscopy." Crop Science 31 (2): 469–74.

Tamburini, E., G. Castaldelli, G. Ferrari, M. Marchetti, P. Pedrina, and V. Aschonitis. 2015. "Onsite and Online FT-NIR Spectroscopy for the Estimation of Total Nitrogen and Moisture Content in Poultry Manure." Environmental Technology 36 (18): 2285–94.

Van Kessel, J. S., J. B. Reeves, and J. J. Meisinger, 1999. "Storage and Handling Can Alter the Mineralization Characteristics of Manure." Journal of Environmental Quality 28 (6): 1984–90.