

Visible near infrared diffuse reflectance spectroscopy (VisNIR DRS) for rapid measurement of organic matter in compost

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Amanda L McWhirt¹, David C Weindorf¹, Somsubhra Chakraborty² and Bin Li³

Abstract

Commercial compost is the inherently variable organic product of a controlled decomposition process. In the USA, assessment of compost's physicochemical parameters presently relies on standard laboratory analyses set forth in Test Methods for the Examination of Composting and Compost (TMECC). A rapid, field-portable means of assessing the organic matter (OM) content of compost products would be useful to help producers ensure optimal uniformity in their compost products. Visible near infrared diffuse reflectance spectroscopy (VisNIR DRS) is a rapid, proximal-sensing technology proven effective at quantifying organic matter levels in soils. As such, VisNIR DRS was evaluated to assess its applicability to compost. Thirty-six compost samples representing a wide variety of source materials and moisture content were collected and scanned with VisNIR DRS under moist and oven-dry conditions. Partial least squares (PLS) regression and principal component regression (PCR) were used to relate the VisNIR DRS spectra with laboratory-measured OM to build compost OM prediction models. Raw reflectance, and first- and second-derivatives of the reflectance spectra were considered. In general, PLS regression outperformed PCR and the oven-dried first-derivative PLS model produced an r^2 value of 0.82 along with a residual prediction deviation value of 1.72. As such, VisNIR DRS shows promise as a suitable technique for the analysis of compost OM content for dried samples.

Keywords

Visible near-infrared diffuse reflectance spectroscopy (VisNIR DRS), compost, organic matter, loss-on-ignition (LOI)

Introduction

Visible near-infrared (VisNIR) diffuse reflectance (DRS) spectroscopy is a rapid, proximal-sensing technology which has shown promise in a variety of agronomic and waste-management applications, including quantification of multiple soil properties, waste products, and environmental hazards (Weindorf et al., 2011). The interests of this study lie in the technology's ability to assess the organic matter (OM) content of finished composted materials for quality control purposes. Compost is an inherently variable product hewn from a wide variety of organic source materials known as feedstocks and, worldwide, serves as a means of recycling many types of organic wastes for use as soil-amendments and agricultural fertilizers. However, there are inherent risks in using certain types of waste products for feedstock material in compost production and the potential for contamination from commercial compost application is of concern (Plaha et al., 2002; Tomati et al., 2002). For this reason, in the USA and many countries across Europe, compost must be tested for basic parameters and possible contaminants before it can be sold (Brinton, 2000). Standards and protocols vary across national borders, though almost all have certifying agencies and requirements. The current USA standard is *Test Methods for the Examination of Composting and Compost* (TMECC), which provides the procedures and methods for compost analysis at certified laboratories as defined by the US Composting Council

(USDA-USCC, 2002). In the USA, compost quality is regulated as a biosolid or fertilizer, and regulations vary by state (Brinton, 2000). These established testing methods often require extensive laboratory preparation and analysis, which can interrupt or delay the abilities of compost producers to manage their product. As such, a means to quickly test a basic and important parameter of compost, such as OM, with little or no laboratory preparation, or ideally in situ could enable compost producers to more efficiently measure this aspect of their product in order to ready it for sale.

The majority of current knowledge concerning spectroscopy for compost analysis has utilized near-infrared spectroscopy (NIRS), which focuses on a narrower range of the electromagnetic spectrum (800–2500 nm) than VisNIR DRS (350–2500 nm). However, because the two technologies share a spectral range of interest, promising results involving NIRS are relevant

¹Louisiana State University Agricultural Center, Baton Rouge, LA, USA

²Ramakrishna Mission Vivekananda University, Narendrapur, Calcutta, India

³Louisiana State University, Baton Rouge, LA, USA

Corresponding author:

David C Weindorf, 307 Sturgis Hall – Louisiana State University, Baton Rouge, LA 70803, USA
Email: dweindorf@gagcenter.lsu.edu

to the use of VisNIR DRS for compost analysis. Near-infrared (NIR) spectroscopy has shown promising results in assessing organic matter, total organic carbon, nitrogen concentrations, physicochemical qualities (Vergnoux et al., 2009), nutrient metal content (Huang et al., 2008), and overall compost quality (Galvez-Sola et al., 2010). Sludges and compost–sludge mixtures have also been assessed with NIRS technology as to their carbon and nitrogen content (Albrecht et al., 2008), heavy metal content (Galvez-Sola et al., 2009; Moral et al., 2007), and humic acid contents (Polak et al. 2005).

Studies utilizing VisNIR DRS in the fields of agriculture or waste management have shown the technology's ability to identify organic and inorganic soil carbon for soil characterization (Brown et al., 2006; Morgan et al., 2009), clay mineralogic composition (Waiser et al., 2007), and in quantifying soil environmental contaminants, such as hydrocarbons (Chakraborty et al., 2010). The history of the technology with compost analysis, however, is more limited, though studies have proven its applicability in assessing microbial populations, nitrogen content, carbon content, pH, and compost salinity (Ben-Dor et al., 1997; Malley et al., 2005; Sharma et al., 2005). Sharma et al. (2005) obtained r^2 values of 0.852 for the correlation between predicted and measured values for quantification of the percentage of ash.

Whilst these studies indicate the potential of the technology, they have been limited by various factors. Ben-Dor et al. (1997) were focused on monitoring the material's composition and spectral changes throughout the composting process instead of analyzing the material once it had reached a finished state. Malley et al. (2005) obtained useful calibration data for total carbon, organic carbon, total nitrogen, carbon:nitrogen, sulfur, potassium, and pH, and Sharma et al. (2005) for pH, salinity, and percentage of ash. However, their studies were confined by studying only milled and dried samples from specific feedstocks and composting methods. Both groups noted the need for further study involving more varied sample sets and samples at variable moisture contents.

The moisture content of samples is of particular interest as moisture interference in spectral readings has been noted in many studies (Morgan et al., 2009; Stevens et al., 2006; Van der Meer and De Jong, 2000). However, it has also been shown that the influence of moisture on soil reflectance was stronger in the short-wave-infrared (SWIR) (1100–2500 nm) region than the VisNIR region (400–1100 nm) (Zhu et al., 2010). Other studies (Waiser et al., 2007) have indicated that air-drying of samples increases the accuracy of the prediction model because air drying reduces the intensity of bands that are related to water so signals associated with other physicochemical properties are not masked. The interaction between sample moisture and the assessment of sample parameters in compost warrants further study.

In order to build on previous results that indicate the potential use of VisNIR DRS as a viable tool in the rapid assessment of OM in finished composted materials, the objectives of this study were to: (i) determine the capacity of VisNIR DRS to quickly and accurately quantify OM in finished composted products; (ii) test un-ground samples at variable moisture contents to further assess

the applicability of the technology for in situ analysis; and (iii) to compare the accuracies of partial least squares (PLS) regression and principal component regression (PCR) in predicting OM in composts. If VisNIR DRS proves a reliable method for the quantification of OM in compost, it could replace more time consuming laboratory (loss on ignition) analysis and aid in compost product assessment.

Materials and methods

Samples

Thirty-six compost samples of diverse origin, feedstock, and composting method were collected from across the USA in the spring of 2011 (Table 1), including one sample from Canada. Compost samples were tested according to standard TMECC (USDA-USCC, 2002) laboratory procedures and later analyzed with VisNIR DRS. Diversity of sample type and composting method were ensured to test the applicability of the technology on a range of composted materials. Of the 36 samples, 3 were from a certified testing laboratory and were used to validate the accuracy of our laboratory results. Our results fell within the 95% confidence intervals set by the certified laboratory for most parameters. The 36 samples were divided into replicates and stored in plastic bags at 4°C upon receipt. Each replicate was tested independently and the resulting data were averaged to obtain a single data set for each parameter.

Standard laboratory testing

The TMECC standard method for loss-on-ignition (LOI) (Method 05.07-A) (USDA-USCC, 2002) was used to analyze the 36 samples for the percentage of OM in a muffle furnace using a 1-g sample (Fisher Scientific Isotemp Programmable Forced-Draft Muffle Furnace; Thermo Scientific Barnstead, Dubuque, IA, USA). An Orion 2-Star pH meter (Thermo Scientific, Waltham, MA, USA) was used to assess pH (Method 04.11-A 1:5 Slurry) (USDA-USCC, 2002). Electrical conductivity (EC) was tested via the same method on a model 4063CC digital salinity bridge (Traceable Calibration Control Company, Friendswood, TX, USA). The percentage of moisture was assessed via Method 03.09-A (USDA-USCC, 2002). Particle size divisions (Method 02.02-B; USDA-USCC, 2002) were determined using a sieve shaker with nested sieves (Model B Ro-Tap® Sieve Shaker; W.S. Tyler, Pleasant Prairie, WI, USA). Particle size, EC, pH, and moisture percentages were determined in order to evaluate the diversity of samples and thus to establish the applicability of the technology to all types of compost. Compost OM was calculated using equation (1):

$$OM = (1 - \text{AshW} \div dw) \times 100 \quad (1)$$

where OM is LOI organic matter in percent, AshW is sample net weight (g) after ignition at 550°C, and dw is sample net weight (g) after drying according to Method 03.09-A before ignition (USDA-USCC, 2002). The analysis was run twice to obtain an average for each sample.

Table 1. Composting method, feedstock, origin, pH, organic matter (OM), salinity, and moisture content data for 36 compost samples used in this study from various locations in the USA and Canada.

Sample	Compost method	Feedstock -% (If number given)-	Origin	pH	OM -%-	EC dS	Moisture -%-	Particle size ^a _-%-
1	Windrow	Grass, chicken litter, woodchip	Louisiana	7.1	64.1	0.7	45.8	49.3
2	Windrow	Paper manufacturing sludge, pine sludge	Louisiana	6.6	36.2	1.1	65.8	51.4
3	Windrow	40 paper sludge, bark woodchip	Louisiana	7.7	30.8	0.8	48.9	68.5
4	Pile	Poultry litter	Louisiana	8.6	71.2	21.9	29.1	65.6
5	Pile	Bagasse crop residue	Louisiana	6.4	86.0	0.1	61.5	90.4
6	Pile	Woodchip, bark mix	Louisiana	6.8	82.8	0.1	64.7	45.3
7	Windrow	Grass, chicken litter woodchip, cooking oil	Louisiana	7.3	51.1	2.1	44.4	67.2
8	Windrow	Bark, stall sludge	Louisiana	12.3	22.8	7.7	44.6	89.1
9	Windrow	Leaf, woodchip, chicken litter, glycerin	Louisiana	7.8	54.0	2.2	42.4	73.1
10	Unknown	Unknown	Pacific Northwest	6.7	81.7	1.9	75.7	51.8
11	Unknown	Unknown	Virginia	6.9	54.5	4.1	46.0	62.9
12	Unknown	95 Green waste, 4 biosolids, 1 wood	California	7.8	45.2	3.0	40.11	85.1
13	Unknown	Unknown	California	8.2	53.6	3.7	44.4	84.3
14	Unknown	Unknown	California	8.0	51.3	2.2	49.8	79.9
15	Unknown	Grape pumice	California	5.8	36.1	8.8	41.2	99.7
16	Unknown	Unknown	California	7.0	27.7	5.7	24.5	87.5
17	Unknown	Spent mushroom compost	California	8.1	55.1	8.9	59.0	57.8
18	Unknown	Unknown	California	7.6	61.3	1.9	31.8	85.6
19	Aerated static pile	40 biosolids, 60 hulls	Southern State	5.6	65.4	3.8	38.6	75.8
20	Windrow	Green wastes/food waste	California	7.8	55.8	3.6	47.9	88.8
21	Windrow	100 yard waste	Pacific Northwest	7.8	60.7	4.2	43.9	84.8
22	Unknown	Unknown	Pacific Northwest	7.4	58.6	2.2	55.0	59.5
23	Unknown	Unknown	Pacific Northwest	7.4	42.1	2.2	35.5	81.8
24	Unknown	Unknown	California	8.4	32.0	5.1	19.9	88.7
25	None	Sawdust	Louisiana	4.9	96.6	0.4	8.7	100.0
26	Unknown	Cow manure	Florida	7.8	24.8	0.5	38.7	89.6
27	Unknown	Spent mushroom	Florida	7.4	58.8	3.9	58.1	84.9
28	Unknown	Certified compost	Colorado	9.0	22.3	5.1	29.3	87.3
29	Unknown	Certified compost	Colorado	7.8	35.2	0.2	54.1	23.3
30	Unknown	Certified compost	Colorado	8.7	42.4	4.0	35.3	90.3
31	Pile	Dairy cow manure (grass fed)	Texas	9.2	37.2	5.8	17.9	91.4
32	Pile	Turkey manure and bedding	Texas	6.9	35.8	5.0	31.5	88.2
33	Pile	Mix:5 composts, granite, humate	Texas	8.4	42.8	2.6	32.2	86.9
34	Unknown	Cattle manure, cotton burr	Texas	8.4	57.6	6.4	59.5	63.8

^aPercent passing <5-mm sieve size.
EC, electrical conductivity.

VisNIR scanning

In the laboratory, the 36 compost samples were scanned using a field portable AgriSpec VisNIR spectroradiometer [Analytical Spectral Devices (ASD), CO, USA] with a spectral range of 350–2500 nm [ultraviolet/VisNIR (350–965 nm), short-wave infrared 1 (966–1755 nm), and short-wave infrared 2 (1756–2500 nm)] as given by ASD. The spectroradiometer had a 2-nm sampling interval and a spectral resolution of 3- and 10-nm wavelengths from 350 nm to 1000 nm and 1000 nm to 2500 nm respectively. Before

scanning, each sample was divided equally into two parts (weight basis). The first part was left intact to preserve the moist condition (as received), whilst the second part was oven dried at 70°C for 24 hours (Method 5.07-A; USDA-USCC, 2002). Both moist and oven-dried samples were allowed to assume room temperature and were then scanned with a contact probe that had a 2 cm diameter circular viewing area and built-in halogen light source (ASD). The contact probe was inserted into the plastic bag that held the sample and full contact with the sample was ensured to avoid outside interference. Each sample was scanned three times

with a 90° rotation between successive scans to obtain an average spectral curve. A spectralon panel with 99% reflectance served as the standard white reference material and was scanned every five samples to compensate for drift in spectrometer and source.

Pre-treatment of spectral data

For this study, derivative spectroscopy was used to pre-process compost spectra prior to analysis. Derivative spectra have the capability to improve the quantification accuracy by removing the baseline shift arising from detector inconsistencies, albedo, and sample handling (Demetriades-Shah et al., 1990). Raw reflectance spectra were processed via a statistical analysis software package, R version 2.11.0 (R Development Core Team, 2008) using custom 'R' routines (Brown et al., 2006). These routines involved: (i) a parabolic splice to correct for 'gaps' between detectors; (ii) averaging replicate spectra; (iii) fitting a weighted (inverse measurement variance) smoothing spline to each spectra with direct extraction of smoothed reflectance; (iv) first derivatives at 10-nm intervals; and, subsequently, (v) second derivatives at 10-nm intervals. The zero, first, and second order derivative spectra were calculated using spectra expressed as reflectance, R , as a function of wavelength, λ , using equations (2)–(4):

$$\text{Zero order, } R = f(\lambda) \quad (2)$$

$$\text{First order, } dR/d\lambda = f'(\lambda) \quad (3)$$

$$\text{Second order, } d^2R/d\lambda^2 = f''(\lambda) \quad (4)$$

The resulting 10-nm average reflectance, first-derivative, and second-derivative spectra were extracted and individually combined with the laboratory-measured OM. These processed data were used to build PLS regression and PCR prediction models. Reflectance data was chosen over absorbance spectra because of the advantages of the former for analyzing dark samples and avoiding the over-expression of weak features.

Multivariate modeling

Both PLS and PCR modes were employed to help in predicting OM using the 10-nm average reflectance, first-derivative, and second-derivative spectra of the 36 samples. Quantitative PLS modeling is a powerful multivariate statistical tool that has been successfully applied to VisNIR data (Chakraborty et al., 2010; Morgan et al., 2009; Vasques et al., 2009; Waiser et al., 2007). The full spectrum multivariate tool PLS combines the signal averaging advantages of principal component analysis and classic least squares (Haaland and Thomas, 1988). In the present study, to detect the effect of moisture on VisNIR DRS prediction of OM in compost, a total of 12 models (6 models each for PLS and PCR) were made using Unscrambler 9.0 (CAMO Software, Woodbridge, NJ, USA). The whole dataset (36 samples) was used for training with leave-one-out cross-validation and in selecting PLS latent factors. Models with as many as nine factors were considered, and the optimal model was determined by

selecting the number of latent factors with the first local minimum in root mean squared error of cross-validation (RMSEcv). The coefficient of determination (r^2), and ratio of standard deviation to root mean square error (RMSE) were used as measures in evaluating the quality of models in real-world situations. The significant wavelengths in the first-derivative PLS model for both moist and oven-dry pretreatments were plotted to identify what portions of the spectra were important for organic matter predictions. The significant wavelengths ($P < 0.05$) were selected by 'R' based on Tukey's jack-knife variance estimate.

Principal component regression provides a means of addressing ill-conditioned matrices. Instead of regressing with the reflectance, first-derivatives, and second-derivative on the response variable (OM) directly, the principal components (PCs) for each spectra of the whole dataset (36 samples) were used. Choosing the optimum number of PCs was based on leave-one-out cross-validation. As the principal scores for each spectra are orthogonal, the PCR is just a sum of univariate regressions and is used to address the problem of multicollinearity.

Results and discussion

Thirty-six compost samples were first analyzed, and PLS and PCR prediction models were subsequently created. The OM contents were widely and normally (Shapiro-Wilk test statistic: 0.93 at $P = 0.05$) distributed from 22.3% to 96.6%, which reflect different feedstocks, composting methods, and origins. Among other measured properties, soil pH varied from 4.8 to 12.3 (Table 1). The highest salinity (21.9 dS m⁻¹) (sample 4) was identified in a sample where poultry litter was the main feedstock. Considerable variability was also observed for moisture content (8.7–75.7 %). Particle sizes also demonstrated considerable variability with the percentage of a sample that passed a 5-mm sieve ranging from 45.3% to 100.0% (Table 1). While OM was better correlated to pH (correlation coefficient, $P = 0.48$) than moisture % ($P = 0.21$), no correlation was found between OM and EC ($P = 0.06$). No correlation between particle size and scanning results was investigated as the study was focused on general applicability of the technology to a wide range of samples and not on a comparison of milled versus un-milled samples.

An average of the reflectance spectra, first-derivative, and second-derivative with respect to the reflectance for all pretreatments is shown in Figure 1. Though fundamental vibration of organic molecules can be found in the mid-infrared region, their overtones and combination bands caused by the stretching and bending of N–H, C–H, and C–O groups occurred mostly in the VisNIR region. In the reflectance, first-derivative, and second derivative plots, the specific spectral signals for water (1400 nm and 1900 nm) were quite apparent. Any significant difference in overall reflectance (except 550–1050 nm and 1350–1550 nm) and first-derivative reflectance between moist and oven-dried compost could not be recognized. Perhaps the oven-drying of compost samples was responsible for increasing the average reflectance at ~1400 nm, which corresponds to water absorption.

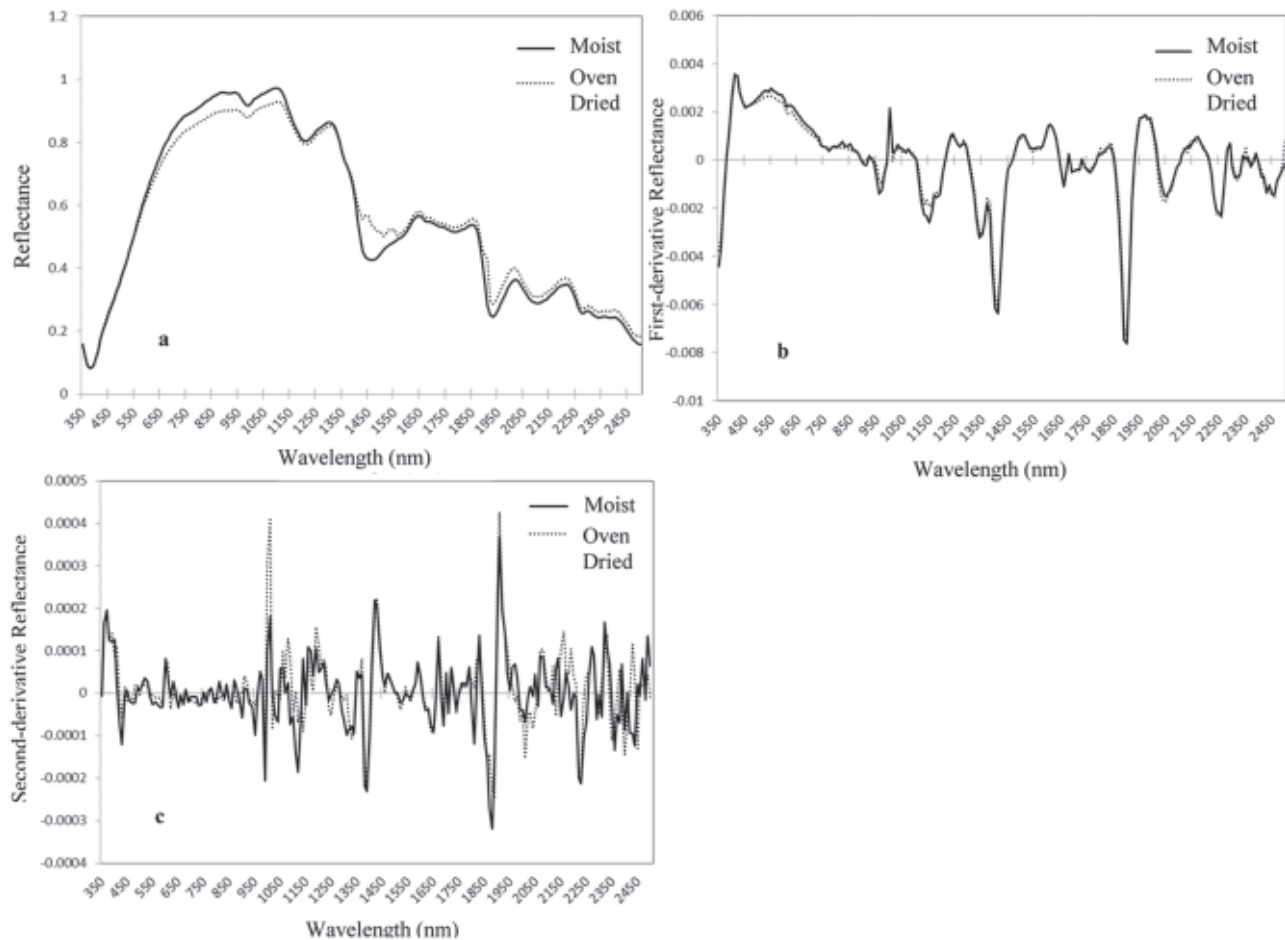


Figure 1. Averages of (a) reflectance, (b) first-derivative, and (c) second-derivative with respect to reflectance for moist and oven-dried compost samples analyzed by VisNIR spectroscopy.

Table 2. Partial least squares (PLS) and principal component regression (PCR) results of 36 compost samples from across the USA evaluated for organic matter using visible near-infrared diffuse reflectance spectroscopy.

	PLS Regression					PCR				
	Latent factors	r ²	RMSEcv [%]	RPD	Bias (10 ⁻¹⁵ %)	Principal components	r ²	RMSEcv [%]	RPD	Bias (10 ⁻¹⁶ %)
	<u>Moist</u>					<u>Moist</u>				
Reflectance	7	0.75	14.1	1.29	1.9	8	0.74	25.5	0.71	2.2
First-derivative	6	0.82	14.4	1.26	1.0	8	0.74	25.7	0.71	2.86
Second-derivative	4	0.77	13.7	1.33	1.7	6	0.58	18.7	0.98	2.93
	<u>Oven-dried</u>					<u>Oven-dried</u>				
Reflectance	5	0.71	12.3	1.48	8.0	7	0.66	14.3	1.27	3.4
First-derivative	4	0.82	10.1	1.72	-2.2	4	0.69	11.2	1.62	6.8
Second-derivative	2	0.74	12.0	1.49	3.7	1	0.42	22.5	0.81	4.5

RMSEcv, root mean square error of cross-validation; RPD, residual prediction deviation.

The accuracy and stability of both the PLS and PCR models were evaluated according to the residual prediction deviation (RPD) based guidelines by Chang et al. (2001). For spectroscopic modeling, a satisfactory prediction model is characterized by a RPD of >2.0 with r² of ~0.80–1.00, fair models with potential for prediction improvement consist of RPD values from 1.4–2.0, and erratic models have RPD values of <1.40. It must be noted that for the ideal application of these RPD values

an independent validation is recommended. However, with leave-one-out cross-validation these values are still suitable indicators for describing the potential of the technology, especially when considered with r² and additional error statistics, such as RMSEcv and bias (Table 2).

For moist sample scans, the first-derivative PLS model performed slightly better (r² = 0.82) than reflectance (r² = 0.75) and second-derivative (r² = 0.77) models (Figure 2; Table 2). Despite

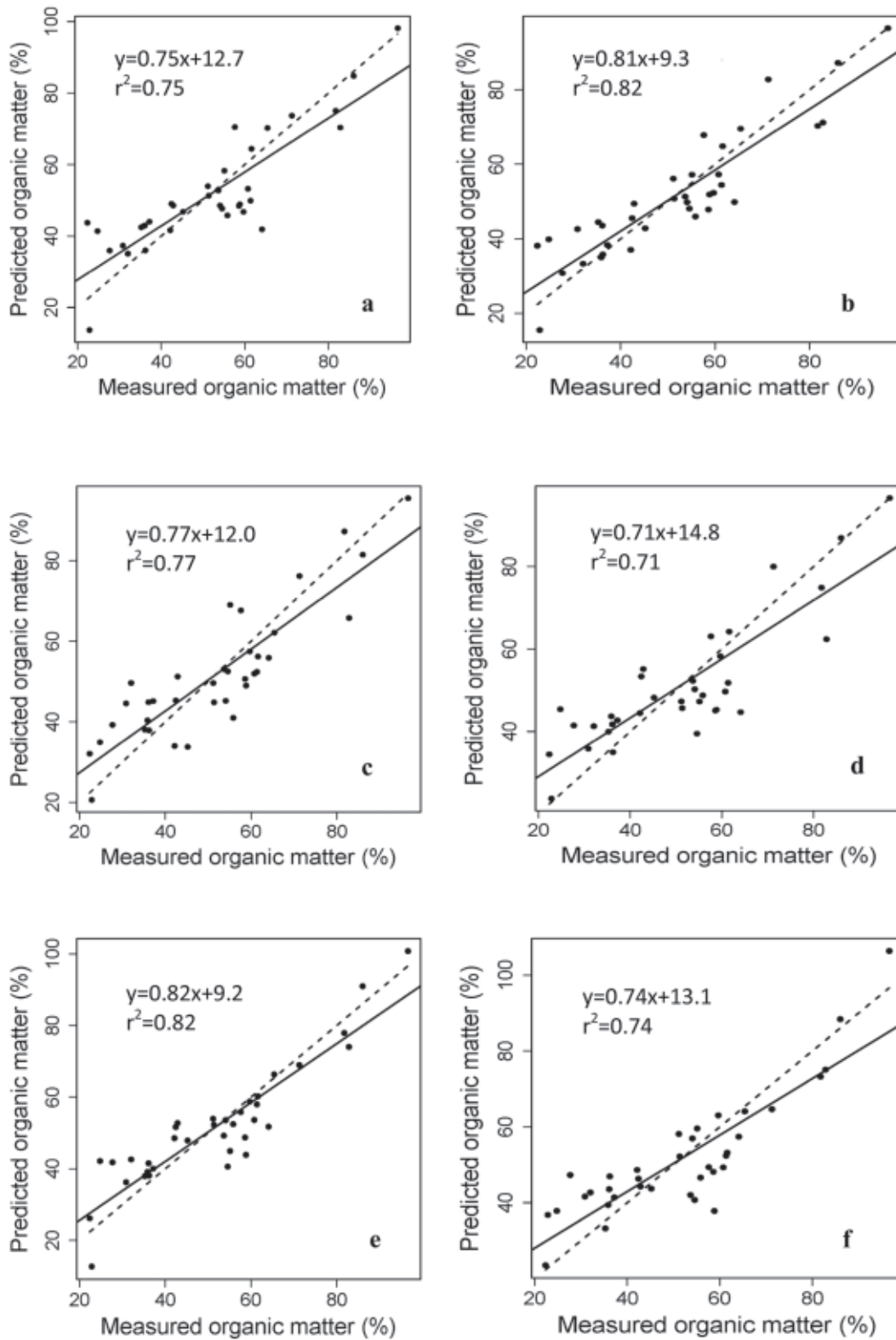


Figure 2. Predicted versus measured organic matter (%) for (a) moist reflectance, (b) moist first-derivative, (c) moist second-derivative, (d) oven-dried reflectance, (e) oven-dried first-derivative, and (f) oven-dried second-derivative partial least squares regression models for 36 compost samples. The solid line is the regression line and the dashed line is a 1:1 line.

the continuous reduction of PLS latent factors (rotation of principal components for a different optimization criterion) between the reflectance, first-derivative and second-derivative-based

models (Table 2), RPD values were less than 1.40 for all three cases. Oven-dried model results were promising as the use of first-derivative reflectance spectra outperformed reflectance and

the second-derivative-based model in terms of r^2 (0.82), RMSE (10.1%), and RPD (1.72). The trend of improvement of first-derivative models is consistent with other works using VisNIR, which also reported similar improvements (Brown et al., 2006; Chakraborty et al., 2010; Reeves and McCarty, 2001; Reeves et al., 1999). Notably, a reduction of PLS latent factors was observed in moist models with an increasing degree of higher derivative spectra, as was apparent in oven-dried models. It is possible that the use of a higher degree of spectrally-processed data helped to reduce the latent factors by removing viewing-geometry effects, as reported by Demetriades-Shah et al. (1990). According to the law of parsimony, in chemometric analysis, it is logical to choose a simpler model (smaller latent factors) assuming no substantial decrease in predictive performance. Plots of actual versus PLS predicted OM and fitted regression coefficient curves on the spectrum are presented in Figure 2. In the oven-dried first-derivative model, predictions of OM more closely approximated the 1:1 line and had negligible bias ($-2.2 \times 10^{-15}\%$) (Table 2). The fair RPD (1.72) indicated that there is sufficient possibility for model enhancement. We believe that although the RPD was not as high as obtained for other constituents of soils (Malley, 1998), the results are encouraging considering the complex and variable composition of compost.

For PCR, plots of actual versus predicted OM in compost samples and fitted regression coefficient curve on the spectrum are presented in Figure 3. Model statistics for the PCR models, summarized in Table 2, showed higher RMSE_{cv} compared with PLS models. Moreover, in most cases, PCR exhibited lower factors than PLS, which was also reported by Yeniay and Goktas (2002). Ignoring the variability of OM content whilst calculating the PCs may have some effects on the decreasing predictability of PCR compared with PLS (Martens and Naes, 1989). However, in terms of r^2 (0.69), RMSE_{cv} (11.2%), and RPD (1.62), the first-derivative of the oven-dried model somewhat confirmed the PLS trend. Hence, considering both PLS and PCR model statistics, the first-derivative oven-dried model seemed to perform most satisfactorily.

To investigate the rationale of the oven-dried first-derivative model's better performance over the moist first-derivative model, the significant regression coefficients (based on Tukey's jack-knife variance estimate, $P < 0.05$) of the first derivative PLS model from each pretreatment were plotted in Figure 4. Both the number and intensity of significant wavelengths changed markedly from moist to oven-dried models. We found more significant wavelengths for dried samples, which is the opposite of findings by Sakirkin et al. (2010, 2011) for manure. The change in numbers and intensities were apparent, specifically in the ~ 300 – 700 nm, 1700 nm, 1930 nm, 2000–2100 nm, 2200 nm, and 2400 nm regions, which could contain the spectral signatures of minerals (electronic transitions), alkyl asymmetric-symmetric doublets, carboxylic acids, amides, aliphatics, and carbohydrates, respectively, as defined previously by Viscarra Rossel and Behrens (2010).

This masking effect from water was somewhat expected, and, indeed, has been well documented in soils. Stevens et al. (2006) noted an increase of 0.93 g organic carbon kg^{-1} of soil in the

standard error of prediction between field-moist and dry sample states when analyzing organic soil carbon. Van der Meer and De Jong (2000) recognized the problem of quantifying organic soil carbon with VisNIR owing to the difficulty of isolating the reflectance of organic carbon from reflectance of water in a sample as they share some significant wavelengths and because of their effect on reflectance. Additionally, it has been observed that energy absorption by the water present in the sample can decrease the reflectance across the NIR range and that at high moisture levels the position of maximum reflectance may shift to shorter wavelengths (Bishop et al., 1994). Harris (1996) noted that the polarity of the water molecule can affect the re-distribution of electrons during excitations, owing to alterations in energy differences between the ground and excited states of the molecules, which affects the wavelength of the sample's absorbance or fluorescence.

Whilst a decrease in predictability in terms of RPD and RMSE_{cv} was noted for the moist-first-derivative PLS model compared with the oven-dried first-derivative PLS model, in terms of r^2 they did not perform significantly differently. Thus, whilst dry samples do permit a higher degree of accuracy, the convenience of using as received (moist) samples may, depending on the application, outweigh the slight loss in accuracy. Considering the heterogenous nature and volatility of OM in composts combined with the difficulty of replicating a given calculation, particularly for OM, our results show promise for the use of VisNIR DRS for the quantification of OM in composts. Whilst our results indicate drying of samples may still be required, the method of VisNIR DRS would still require less sample handling and, thus, there would be less chance of sample distortion than current standard methods, such as LOI. It has been noted that drying or other pretreatments to ready samples for carbon analyses can result in 'loss of volatile organic compounds or the decomposition and loss of other organic compounds present in the sample' (Schumacher, 2002). Indeed, LOI, whilst the least caustic method for organic carbon analysis, is also often considered the least accurate method of total organic carbon determination. In soils, studies done by the Environmental Protection Agency indicate that the percent coefficient of variation for LOI amongst replicate samples ranged from 2.7% to 5.6% (Schumacher, 2002). The borrowing of analytical methods from soils for analysis of compost and manures is common, and the same principles of the method apply to either material (Karam, 1993; Matthiessen, 2005; Schumacher, 2002). In our experiment, OM results from LOI fluctuated, on average, 8.1% among replicated samples. Thus, the advantages of VisNIR DRS for OM analysis are threefold: (i) speed of analysis and instantaneous obtainment of results; (ii) less sample handling required as samples need not be weighed or further subjected to heat after initial drying; and, most importantly, (iii) the ability to take replicate scans and obtain an average for the sample. Thus, VisNIR DRS shows promise as an addition to the TMECC-certified methods for compost analysis.

We acknowledge that the limited number of samples (36) somewhat constrains the global applicability of the dataset.

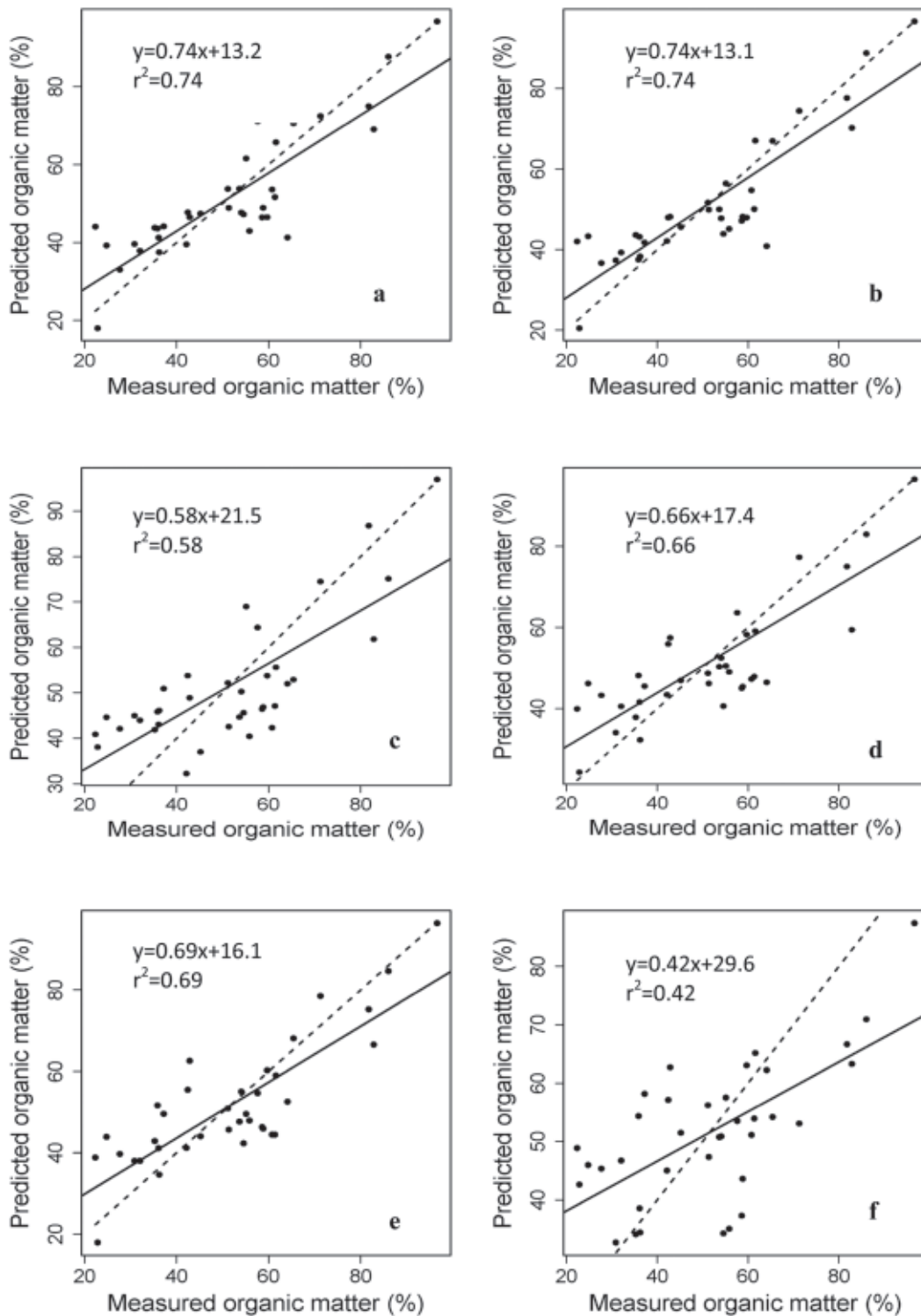


Figure 3. Predicted versus measured organic matter (%) for (a) moist reflectance, (b) moist first-derivative, (c) moist second-derivative, (d) oven-dried reflectance, (e) oven-dried first-derivative, and (f) oven-dried second-derivative principal component regression models for 36 compost samples. The solid line is the regression line and the dashed line is a 1:1 line.

However, this pilot research was intended to investigate the viability of VisNIR DRS spectroscopy to quantify compost OM content under varying sample moisture states and to further ascertain which spectral processing and moisture contents show the most promise for future investigation. Testing the chemical heterogeneity of the compost was beyond the scope of this project and

requires intensive studies before drawing stronger conclusions. More improvement could be achieved by increasing the sample number and building a spectral library targeting an even wider range of compost samples. That notwithstanding, these results are especially encouraging given the wide and dynamic range of OM levels and other variables in the samples tested.

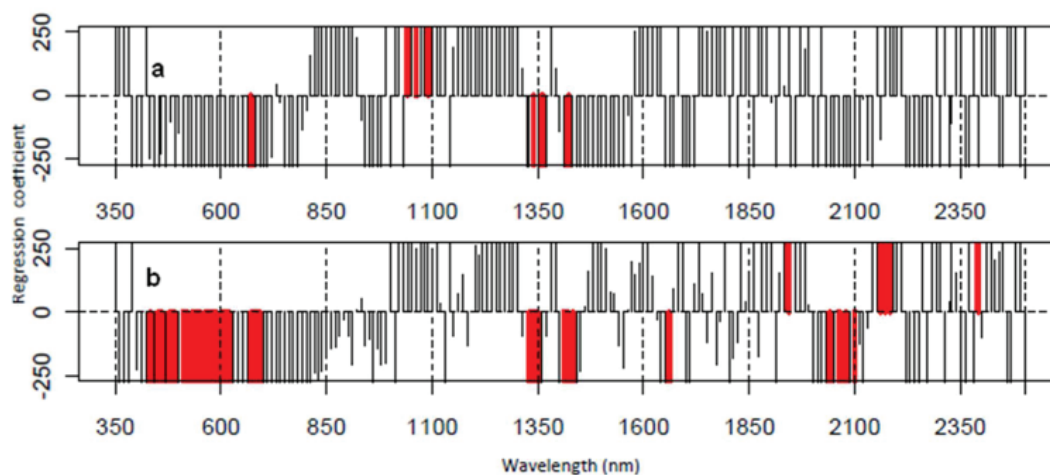


Figure 4. Regression coefficients (black) of the first-derivative partial least squares model of (a) moist first-derivative and (b) oven-dried first-derivative model of compost samples. The magnitude of the regression coefficient at each wavelength is proportional to the height of the bar. Significant wavebands ($P < 0.05$), as indicated by Tukey's jack-knife variance estimate procedure, are shown as thick, red bars. All plots are on the same x axis.

Conclusions

VisNIR DRS has shown the capacity to rapidly, reasonably, and non-destructively quantify the OM of composted materials. Given the field portability of the VisNIR spectroradiometer and our findings concerning the technology's accuracy with moist samples, further testing is warranted concerning the possibilities of its use in situ. When comparing PLS and PCR model statistics, first-derivative oven-dried models performed most satisfactorily for both model types, with PLS performing the best. Our results show promise for improving the speed of performing laboratory analysis and obtaining results almost instantly. Thus, we recommend the VisNIR DRS method, using dried samples, for further investigation concerning its possible inclusion among TMECC official testing methods and as a supplement to current, time-consuming laboratory methods. The goal for future research should be to develop a general model which can lead to reliable OM predictions under even more divergent compost matrix conditions.

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