



## Decomposition and mineralization of organic residues predicted using near infrared spectroscopy

K.D. Shepherd<sup>1,4</sup>, B. Vanlauwe<sup>2</sup>, C.N. Gachengo<sup>2</sup> & C.A. Palm<sup>3</sup>

<sup>1</sup>World Agroforestry Centre (ICRAF), P.O. Box 30677-00100, Nairobi, Kenya. <sup>2</sup>Tropical Soil Biology and Fertility Institute of CIAT (TSBF-CIAT), P.O. Box 30677-00100, Nairobi, Kenya. <sup>3</sup>The Earth Institute at Columbia University, P.O. Box 1000, Palisades, NY, 10964-8000, USA. <sup>4</sup>Corresponding author\*

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### Abstract

Characterization of decomposition characteristics is important for sound management of organic residues for both soils and livestock, but routine residue quality analysis is hindered by slow and costly laboratory methods. This study tested the accuracy and repeatability of near-infrared spectroscopy (NIR) for direct prediction of *in vitro* dry matter digestibility (IVDMD) and C and N mineralization for a diverse range of organic materials (mostly crop and tree residues) of varying quality ( $n = 32$ ). The residue samples were aerobically incubated in a sandy soil and amounts of C and N mineralized determined after 28 days. IVDMD and quality attributes were determined using wet chemistry methods. Repeatability was higher with NIR than the original wet chemistry methods: on average NIR halved the measurement standard deviation. NIR predicted IVDMD and C and N mineralization more accurately than models based on wet chemical analysis of residue quality attributes: reduction in root mean square error of prediction with NIR, compared with using quality attributes, was IVDMD, 6%; C mineralization after 28 days, 8%; and N mineralization after 28 days, 8%. Cross-validated  $r^2$  values for measured wet chemistry vs. NIR-predicted values were: IVDMD, 0.88; C mineralization, 0.82; and N mineralization, 0.87. Direct prediction of decomposition and mineralization from NIR is faster, more accurate and more repeatable than prediction from residue quality attributes determined using wet chemistry. Further research should be directed towards establishment of diverse NIR calibration libraries under controlled conditions and direct calibration of soil quality, crop and livestock responses in the field to NIR characteristics of residues.

### Introduction

Organic residues constitute a major source of nutrient inputs to both soils and livestock in small-holder tropical production systems. The quality of residues regulates the potential rate of decomposition and availability of those nutrients, both in the soil and in the rumen. Actual rate and degree of decomposition are moderated by the local activity

of the decomposer organisms and the environmental conditions, but residue quality is one of the factors most amenable to management in agricultural systems (Giller and Cadisch, 1997; Heal et al., 1997). From a synthesis of results from short-term incubation experiments with organic residues, Palm et al. (2001) developed a decision support model for predicting decomposition and net N mineralization/immobilization rates of organic residues from their concentrations of N, lignin and polyphenol. To provide a basis for more systematic development of predictive models, Palm et al.

\* FAX No: +254-20-524001.

E-mail: k.shepherd@cgiar.org

(2001) compiled the Organic Resource Database, which is a synthesis of data on quality characteristics of plant residues (including macronutrient, lignin, total soluble polyphenol concentrations) and decomposition behavior in soils. Short-term (28-day) incubation experiments using a diverse selection ( $n = 32$ ) of archived samples (mainly crop and tree residues) associated with the database (the same set of samples used for this study), confirmed the relation between C and N mineralization rates and N and polyphenol concentrations (Vanlauwe et al., 2005).

NIR has developed rapidly over the last several decades as a fast and robust analytical methodology and it is now used for the analysis of many agricultural and food products (Roberts et al., 2004). Although NIR has been used extensively for the analysis of forages, including determination of crude protein, lignin and digestibility (Roberts et al., 2004), there has been little work on NIR prediction of plant residue quality for soil improvement. Because the basic quality attributes determining decomposition and N release are the same in the soil as in the rumen, we expect NIR to predict decomposition well in soils. NIR analysis of manure quality, including N and lignin concentrations, has been demonstrated (e.g. Malley et al., 2002; Reeves et al., 2002). For a wide range of organic residues from a temperate region ( $n = 249$ ), Stenberg et al. (2004) showed stable NIR calibrations for C and N fractions obtained by stepwise chemical digestion. In tropical regions, using a large collection (319 samples) of organic residues from the Organic Resource Database, Shepherd et al. (2003) demonstrated NIR analysis of N, total soluble polyphenol and lignin concentration across a wide range of residue types (including crop residues, leafy and woody tree residues, and animal manures) and residue attribute values. However, there have been few studies on NIR prediction of decomposition and N mineralization of residues in soils (Bruun et al., 2005; Gillon et al., 1999).

The utility of NIR as a rapid analytical tool depends on errors in relation to the intended application. Error in NIR analysis is associated with accuracy, repeatability, and reproducibility (Workman and Shenk, 2004). Accuracy is the agreement between the NIR predicted value and the reference (wet chemistry) method. Repeatability is the agreement between NIR results for the

same sample analyzed repeatedly by the same method, instrument and team of operators. Reproducibility is the agreement between NIR results for the same sample analyzed on different instruments or in different laboratories. The repeatability of NIR analysis is usually excellent (coefficients of variability  $<1.5\%$ ) and often superior to that of wet chemistry methods (Williams and Norris, 2001). For this reason it is theoretically possible for NIR calibration equations to produce predictions that are more accurate than the laboratory reference values used in the calibration set (Naes et al., 2002). Accuracy of NIR to determine a reference value is limited by the noise in the reference and the adequacy of the mathematical model. If the reference method is unbiased, and a good linear calibration model is achieved, increasing the number of calibration samples averages out errors in the reference. Therefore, the lack of repeatability in the reference method can be compensated for by using many calibration samples, with the result that the accuracy of the calibration method is better than that of the reference (Naes et al., 2002). Although very few studies have tested this possibility, Aastveit and Marum (1991) found that NIR predicted digestibility of fodder grasses more accurately than the *in vitro* reference method. Furthermore, we can expect that functional attributes, such as decomposition, may be predicted more accurately by NIR than from predictive models based on wet chemistry measurements of residue quality attributes (e.g. lignin and polyphenol concentration). This is not only because NIR is highly repeatable but also because it integrates broad information on biochemical composition and thus may include additional information on decomposition than that provided by a limited number of quality attributes determined by wet chemistry.

The broad objectives of this study were to (1) predict organic residue quality attributes using NIR, and (2) compare NIR with wet chemistry reference methods for estimating residue decomposition and mineralization. The specific objectives were to (1) test the accuracy and repeatability of NIR for direct prediction of *in vitro* dry matter digestibility and C and N mineralization of organic residues, (2) evaluate the accuracy and repeatability of NIR for estimating residue quality attributes, and (3) evaluate whether NIR can predict decomposition and

mineralization of organic residues more accurately than predictive models that are based on residue quality attributes determined using wet chemistry methods.

## Materials and methods

### *Wet chemistry methods for residue quality*

Thirty-two samples were selected from the residue database, described by Palm et al. (2001), to

represent combinations of high and low N, soluble polyphenol and lignin concentrations (Table 1). The 32 residue samples were analyzed for quality attributes using wet chemistry methods (Figure 1). The samples consisted of crop residues and tree prunings, one farmyard manure sample and one sawdust sample. The materials represent potentially available sources of organic inputs for soil improvement in tropical farming systems, sampled from different parts of Kenya, and are fully described by Vanlauwe et al. (2005).

Table 1. Selected characteristics of organic residues used in the decomposition study

No.	Species	Plant part	C g kg <sup>-1</sup>	N	Sol C <sup>a</sup>	PP <sup>b</sup>	PBC <sup>c</sup>	Lignin
1	<i>Zea mays</i>	Stover	413	6	48	11	15	46
2	<i>Croton megalorapus</i>	Leaves	416	34	75	31	36	87
3	<i>Senna spectabilis</i>	Leaflets	443	42	119	27	19	82
4	<i>Lantana camara</i>	Leaves	410	34	84	62	48	116
5	<i>Calliandra calothyrsus</i>	Leaflets	445	41	76	95	164	88
6	<i>Senna siamea</i>	Leaflets	449	29	98	72	24	113
7	<i>Crotalaria ochroleuca</i>	Leaflets	455	53	104	31	22	36
8	<i>Crotalaria grahamiana</i>	Leaflets	378	34	101	28	21	48
9	<i>Tithonia diversifolia</i>	Leaves	398	33	92	60	29	82
10	<i>Gliricidia sepium</i>	Leaflets	437	38	138	29	29	108
11	<i>Gliricidia sepium</i>	Leaflets	405	36	119	26	21	157
12	<i>Senna siamea</i>	Leaflets	436	20	119	81	22	104
13	<i>Flemingia macrophylla</i>	Leaflets	404	29	114	86	171	16
14	<i>Senna spectabilis</i>	Leaflets	465	34	129	37	12	96
15	<i>Calliandra calothyrsus</i>	Leaves	438	30	114	140	295	98
16	<i>Calliandra calothyrsus</i>	Leaflets	419	35	92	100	118	145
17	<i>Calliandra calothyrsus</i>	Leaves	464	30	128	145	288	62
18	<i>Calliandra calothyrsus</i>	Leaflets	463	31	120	148	322	121
19	<i>Calliandra calothyrsus</i>	Leaves	451	26	104	123	280	129
20	<i>Calliandra calothyrsus</i>	Leaflets	445	32	95	95	198	158
21	<i>Saccharum officinarum</i>	Stover	402	12	49	15	19	47
22	<i>Lantana camara</i>	Leaves	437	45	85	52	13	62
23	<i>Lantana camara</i>	Stems	426	10	31	15	21	164
24	<i>Cattle manure</i>	–	370	25	37	10	48	173
25	<i>Tithonia diversifolia</i>	Leaves	377	42	95	48	24	46
26	<i>Gliricidia sepium</i>	Stems	421	16	50	13	26	204
27	<i>Senna spectabilis</i>	Leaves	455	46	99	19	26	113
28	<i>Sesbania sesban</i>	Leaves	370	45	151	23	30	25
29	<i>Gliricidia sepium</i>	Leaflets	407	38	116	35	34	167
30	<i>Sesbania sesban</i>	Stems	444	8	32	8	25	151
31	<i>Eucalyptus saligna</i>	Leaf litter	461	10	89	108	183	237
32	<i>Eucalyptus saligna</i>	Sawdust	486	1	14	17	20	295

<sup>a</sup>Soluble C.

<sup>b</sup>Soluble polyphenol.

<sup>c</sup>Protein binding capacity measured as bovin serum albumin.

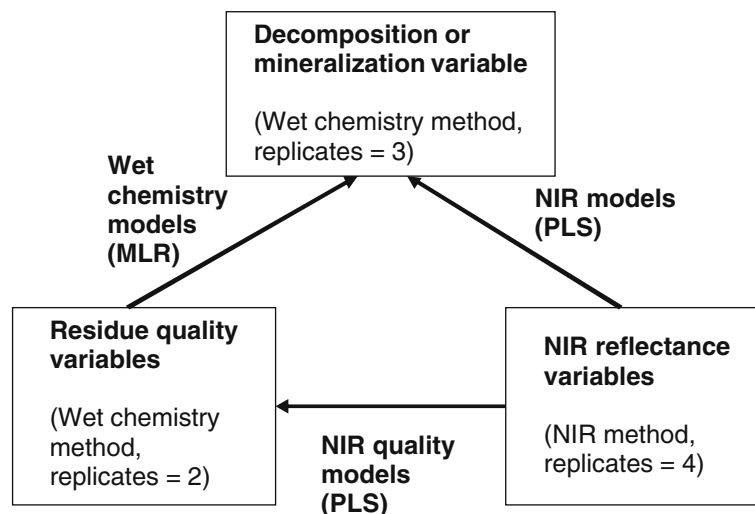


Figure 1. Analytical scheme for comparing models to predict residue decomposition and mineralization variables using models based on either residue quality using wet chemistry methods or the NIR method. Arrows denote direction from independent to dependent variables. MLR, Multiple linear regression; PLS, partial least squares regression.

Wet chemistry analysis of residue quality attributes was done on oven dried materials (35 °C) ground to pass through a 1 mm sieve. Samples were stored in sealed polythene bags at 20 °C. N was analyzed after complete oxidation of the plant materials by Kjeldahl digestion using an auto analyzer; total carbon using potassium dichromate; water-soluble carbon by wet oxidation using potassium dichromate; total soluble polyphenol content by the Folin–Ciocalteu reagent against a tannic acid standard after extraction with a methanol–water mixture, reported in tannic acid equivalents; lignin content by the acid detergent fibre route; and protein binding capacity (PBC) of soluble polyphenols using reaction with bovine serum albumin (BSA). With the exception of protein binding capacity all analyses were run on duplicate samples so as to assess error in the wet chemistry methods. The methods are fully described by Vanlauwe et al. (2005).

#### *Methods for decomposition and mineralization*

Residue decomposition and mineralization were measured by aerobic incubation. A rate of residue equivalent to 5 t ha<sup>-1</sup> dry weight was incubated for 28 days at 25 °C in 50 g of sandy soil in 60 ml bottles. The soil was pre-incubated at 40% water-holding capacity for 2 weeks prior to incubation. Control soils did not receive any residues.

The bottles were placed in incubation jars (250 ml glass bottles) containing NaOH traps, which were used to measure CO<sub>2</sub> released during decomposition. Sufficient jars were set up to allow for four destructive sampling times, replicated three times (12 jars per treatment). The jars were arranged in a completely randomized design. Jars without soil added were used as blanks. After 3, 7, 14, and 28 days, CO<sub>2</sub> trapped in the sodium hydroxide solution was determined by titrating the excess base with HCl, and all NaOH traps were replaced (except at day 28). On the same dates, three jars per treatment were destructively sampled for mineral N determination. Mineral N was also determined at the beginning of the experiment. Ammonium-N and nitrate-N in the soil was determined after extracting fresh soil with KCl. Nitrate N was determined through cadmium reduction of nitrate to nitrite, and the nitrite and ammonium N concentrations determined colorimetrically.

To smooth noise in the decomposition data, a standard exponential curve was fitted to the accumulated C (log<sub>e</sub> transformed) and soil N concentrations over time for each replicate. The fitted curves closely estimated the time trends for all samples with no consistent bias: comparison of predicted versus actual values gave coefficient of determination ( $r^2$ ) = 0.98 and root mean square error (RMSE) = 30 mg C kg<sup>-1</sup> for CO<sub>2</sub> evolution,

and  $r^2 = 0.97$  and  $RMSE = 3.1 \text{ mg N kg}^{-1}$  for mineral N concentration. The fitted values were used to calculate the total amounts of C and net N mineralized after 3 and 28 days, expressed as a percentage of the respective initial amounts added in the organic residues, after subtracting the amounts mineralized in the soil controls. To characterize the early decomposition dynamics, the amounts of C mineralized at day 3 (by which on average 46% of the total C released had occurred; range 13–65%) were expressed as a percentage of the amounts mineralized at day 28 as described by Vanlauwe et al. (2005).

*In vitro* dry matter digestibility (IVDMD), a laboratory assay commonly used as a quality index for animal feed by animal nutritionists, was determined using standard methods as described by Vanlauwe et al. (2005). During the first digestion phase, organic residues were incubated for a 48-h period at 39 °C, under anaerobic conditions, with rumen liquor and microorganisms. This was followed by a 24-h acid/pepsin digestion phase that maintained the same temperature and anaerobic conditions. Oven-dry weight of plant material remaining and their ash contents were then determined. Control bottles followed exactly the same procedure but were incubated without plant material. IVDMD was calculated as dry matter as a percentage of the original dry matter on an ash-free basis. The procedure was done on two replicate samples to assess error in the wet chemistry method.

#### *Near infrared reflectance measurements and preprocessing*

Diffuse reflectance spectra were recorded for four replicate sub-samples of each residue sample using a FieldSpec™ FR spectroradiometer (Analytical Spectral Devices Inc, Boulder, CO) at wavelengths from 1.0 to 2.5  $\mu\text{m}$  at interpolated 1 nm intervals as described by Shepherd et al. (2003). Enough plant-sample was placed into 7.4 cm diameter Duran glass Petri dishes to give a sample thickness of about 1 cm. The samples were scanned through the bottom of the Petri dishes using a high intensity source probe (Analytical Spectral Devices Inc, Boulder, CO). The probe illuminates the sample (4.5 W halogen lamp giving a correlated color temperature of 3000 K; WelchAllyn, Skaneateles Falls, NY) and

collects the reflected light from a 3.5 cm diameter sapphire window through a fiber-optic cable from a sample area of 1.2 cm diameter.

To sample within dish variation, reflectance spectra were recorded at two positions, successively rotating the sample dish through 90° between readings. The average of 25 spectra (the manufacturers default value) was recorded at each position to minimize instrument noise. Before reading each sample, 10 white reference spectra were recorded using calibrated spectralon (Labsphere®, Sutton, NH) placed in a glass Petri dish. Reflectance readings for each wavelength band were expressed relative to the average of the white reference readings. With this method, a single operator can comfortably scan several hundred samples a day.

The raw spectral reflectance data was pre-processed prior to statistical analysis as follows. The density of data was reduced by selecting every 10th-nanometer value from 1.0 to 2.5  $\mu\text{m}$  to ease data handling and match the data more closely to the spectral resolution of the instrument (3–10 nm). Tests showed that there was no loss in prediction performance compared with using the 1-nm values. The reflectance values were then transformed with first derivative processing (differentiation with 2nd order polynomial smoothing with a window width of 20 nm) using a Savitzky-Golay filter, as described by Fearn (2000). Derivative transformation is known to minimize variation between samples caused by variation in grinding and optical set-up (Marten and Naes, 1989). Multiplicative scatter correction (used to compensate for additive and/or multiplicative effects in spectral data) and normalization (sample-wise scaling) of the reflectance data (both described in Vandeginste et al., 1998) did not improve calibrations and so were not used. Three noisy bands were omitted: 1.00–1.01  $\mu\text{m}$  due to splicing between the individual spectrometers, and 2.50  $\mu\text{m}$  due to low signal to noise ratio (Analytical Spectral Devices Inc., 1997) leaving 148 wavebands for analysis.

#### *Near infrared calibration*

The data from the wet chemistry methods were calibrated against the 148 NIR reflectance wavebands (Figure 1) using partial least squares regression (PLS), implemented in The Unscrambler

(Camo ASA, Oslo) software. PLS is an extension of multiple linear regression in the form:

$$Y = XB + E, \quad (1)$$

where  $Y$  is an  $n$  cases by  $m$  variables response matrix,  $X$  is an  $n$  cases by  $p$  variables predictor matrix, and  $B$  is a  $p$  by  $m$  regression coefficient ( $b$ ) matrix, and  $E$  is an error term for the model that has the same dimensions as  $Y$ . The algorithm used is fully described in Martens and Martens (2000).

Hold-out-one full cross-validation with jack-knifing (Martens and Martens, 2000) was used to evaluate the stability of the calibrations and to eliminate unreliable (non-significant) wavebands in the calibrations. In this procedure the data set is repeatedly re-calibrated by successively deleting one sample at a time and using the resulting model to predict the value for the held-out sample. The RMSE is based on the differences between the predicted and actual values, after all the samples have been held out once. Jack-knifing makes use of the hold-out-one method to estimate the uncertainty variances for the regression coefficients (Martens and Martens, 2000). A  $t$ -test is used to test the significance of the regression coefficient for each waveband. A variable was deleted if the uncertainty variance was two standard deviations larger than the regression coefficient.

Prediction success was evaluated on wet chemistry and actual observations using  $r^2$ , RMSE and bias for the cross-validation data. Box-Cox transformation (Box and Cox, 1964) of the wet chemistry variables was used to obtain a multivariate normal distribution of the data. Predicted values were first back-transformed prior to calculating these prediction statistics.

RMSE was calculated as

$$\text{RMSE} = \sqrt{\sum_{i=1}^n (\hat{y}_i - y_i)^2 / n}, \quad (2)$$

where  $\hat{y}_i$  and  $y_i$  are predicted and measured wet chemistry values and  $n$  is the number of samples. To compare RMSE between dependent variables the ratio error range (RER) was used, which was defined as the ratio of the range of the sample set to RMSE.

For the tests of NIR repeatability, the cross-validation and jack-knifing were done on sepa-

rate PLS models built for each individual residue sub-sample, but using the wet chemistry data averaged over replicate determinations. The predicted values from each of the four separate models were then used to assess repeatability. However, in all the other tests the replicated spectral measurements were averaged before fitting the models.

For the tests to assess the accuracy of the NIR method, both the spectral data from the four replicate sub-samples and the wet chemistry data from replicate determinations were averaged before fitting the PLS models. Thus the term 'NIR method' used in this paper includes error due to sub-sampling of residues for spectral measurement.

#### Repeatability calculation

Repeatability in the wet chemistry method for the residue quality and decomposition variables was estimated using a mixed effects model with estimation of variance components using residual maximum likelihood, implemented in Genstat version 6.1 (Lawes Agricultural Trust), as follows:

$$y_{ij} = s_i + \varepsilon_{ij}, \quad (3)$$

where  $y$  is the wet chemistry variable observation with  $i$  samples (number of organic resource samples used) and  $j$  replicates,  $s$  is the random term for the effect of sample, and  $\varepsilon$  is the residual error. Total variance (Var) in the data is expressed as:

$$\text{Var}(y_{ij}) = \sigma_s^2 + \sigma_{\text{error}}^2 \quad (4)$$

where  $\sigma_s^2$  is the variance component for sample and  $\sigma_{\text{error}}^2$  is the residual variance. Repeatability was then expressed as the residual standard deviation (SD), and its standard error (SE) calculated as:

$$\text{SD} = \sqrt{\sigma_{\text{error}}^2} \quad (5)$$

$$\text{SE} = \frac{\text{SE}_{\text{var}}}{2^* \sqrt{\sigma_{\text{error}}^2}}, \quad (6)$$

where  $\text{SE}_{\text{var}}$  is the standard error of  $\sigma_{\text{error}}^2$ .  $\text{SE}_{\text{var}}$  quantifies the uncertainty in the estimate of the residual variance and is output by the Genstat REML procedure.

Repeatability of the NIR method was calculated in the same way as for the wet chemistry methods but using the predicted values from NIR calibrations for replicated residue sub-samples. Using these estimates, the repeatability of NIR was then compared with the repeatability of the wet chemistry method for the different residue quality and mineralization properties. Repeatability for PBC was not calculated as the wet chemistry method was not replicated.

#### *Calculations for comparing NIR and wet chemistry accuracy*

NIR could be used to increase the accuracy of wet chemistry methods in at least two ways. In the first scenario, a NIR calibration is performed for an individual batch of wet chemistry samples. The calibration line (fitted using cross-validation to avoid over-fitting) is used to produce an 'improved' estimate of the wet chemistry reference values. The hypothesis is that wet chemistry data is more likely to have outliers and has lower repeatability than the NIR data, so errors in the wet chemistry data can be averaged out by using the corresponding estimates from the NIR calibration line (Naes et al., 2002).

In the second scenario, a previous calibration is used to predict the wet chemistry values. The hypothesis in this case is that use of a previous calibration based on many wet chemistry analyses can compensate for the lack of repeatability in the reference method. This assumes that the samples being predicted belong to the same population of samples used for establishing the calibration.

Because samples with high  $y$ -residuals in the NIR calibration are likely to have high error in the wet chemistry data, for both scenarios, the NIR calibration can be additionally used as a tool to screen samples that have seemingly high error. These samples can then be re-analyzed by the wet chemistry method and accuracy thereby further improved.

Assessing the accuracy of NIR involves comparison of NIR results with reference results, which themselves contain noise. Therefore when evaluating the accuracy of NIR against the accuracy of the reference method, it is preferable to subtract out the reference error from the NIR error term. This will give an NIR error result

similar to the case where the reference value is close to its true value. Thus to assess the NIR accuracy for the two scenarios, assuming no bias in the wet chemistry method, RMSE was corrected for error in the wet chemistry method as

$$\text{RMSE}_{\text{corr}} = \sqrt{\text{RMSE}^2 - \sigma_{\text{error}}^2/r}, \quad (7)$$

where  $\sigma_{\text{error}}^2$  is the residual variance in the wet chemistry method and  $r$  is the number of wet chemistry method replicates. To evaluate whether NIR improved accuracy, the  $\text{RMSE}_{\text{corr}}$  (or residual standard deviation) for NIR was compared with the SD of the wet chemistry measurements for the different residue quality and mineralization properties.

To test the first scenario above, the corrected RMSE for the calibration data was compared with the SD of the wet chemistry data, because the calibration line for the same batch of samples is simply being used to average out errors in the wet chemistry data. For the second scenario, the corrected RMSE for the validation data was compared with the SD of the wet chemistry data, assuming that the cross-validated RMSE provides a reasonable estimate of prediction error outside the batch. Ideally this would be done using an independent calibration data set, but this was not available in this study. However, cross-validation prediction errors have often been found to give reasonable estimates of prediction error on new samples from the same population as the calibration samples.

#### *Multiple linear regression*

Graphical modeling, implemented using MIM 3.1 (Edwards, 2000), was used to explore conditional associations between mineralization and residue quality variables and select explanatory variables for inclusion in multiple linear regression (MLR) models. Graphical modeling is a form of multivariate analysis that uses graphs to represent models. Graphical models allow depiction of factor associations using graphs of arcs connecting nodes (factors) that are significantly conditionally associated. Hence they provide a compact representation of joint probability distributions. This method offers important insight into variable associations that cannot be provided by standard correlations. For

example, pairwise correlation is frequently a spurious indicator of influence within multivariate data because of mutual dependence on a third variable. The partial correlations which are provided by this graphical modeling method provide better insight into pairwise influence after controlling for other factors.

Box–Cox transformation (Box and Cox, 1964) of variables was used to obtain a multivariate normal distribution of the data. Replicate laboratory measurements were averaged before analysis. Starting with saturated models, in which arcs connect all variables with each other, stepwise deletion was used to iteratively remove those arcs for which conditional associations were non-significant. Standard F-tests were used as the deletion criterion. This is an empirical procedure for variable selection and there is no objective way of setting the F-test criteria. However the procedure enables weak associations and conditional independence between variables to be identified to produce a parsimonious model.

Significant ( $P = 0.05$ ) associations between decomposition and mineralization and residue quality variables were used as a basis to select quality variables for inclusion in MLR models, which were implemented in The Unscrambler software using full hold-out-one cross-validation. Independent variables with non-significant ( $P = 0.05$ ) regression coefficients were omitted. Performance of models predicting decomposition and mineralization from either residue quality variables ('wet chemistry models') or NIR spectra ('NIR models') were compared (Figure 1) in terms of cross-validation  $r^2$  and RMSE values.

## Results and discussion

### *Residue quality and decomposition prediction using NIR*

NIR gave high accuracy in prediction of N concentration despite the wide range of materials used (Table 2 and Figure 2), and reasonable accuracy for polyphenol and soluble C. Predictions for lignin, carbon and PBC would be adequate for separating samples into broad classes. The high  $r^2$  values for PBC (Table 2) are a result of clustering of the data into two groups (Figure 2), and the scatter in actual vs. predicted values was high in the high range. These results for N, polyphenol and lignin are consistent with those obtained for a larger set of samples ( $n = 319$ ) from the same library (Shepherd et al., 2003). For a wide range of temperate organic residues, Stenberg et al. (2004) also obtained comparably robust NIR calibrations for N (cross-validated RMSE = 2.9, RER = 20). Few attempts have been made to calibrate plant N concentration across a wide range of organic residues, and although RMSE values in our studies are typically two to three times larger than for more narrow-based forage calibrations, the RER values are similar (Stenberg et al., 2004). Stenberg et al. (2004) considered their soluble C calibrations to be unstable (cross-validated RMSE = 28, RER = 8) and their RMSE was more than double that of our calibration, although their range was also larger so that RER values in the two studies were also similar. Stenberg et al. (2004) obtained better

Table 2. Statistics for full cross-validation models for predicting residue wet chemistry values from near infrared reflectance

Wet chemistry method <sup>a</sup>	Mean	No. PLS factors <sup>b</sup>	$r^2$	RMSE <sup>c</sup>	RER <sup>d</sup>
C, g kg <sup>-1</sup>	428	4	0.76	14.4	6.6
N, g kg <sup>-1</sup>	29.6	4	0.97	2.06	23.0
Polyphenol, g kg <sup>-1</sup>	55.9	5	0.93	11.1	12.6
Lignin, g kg <sup>-1</sup>	116	8	0.70	32.6	6.5
Soluble C, g kg <sup>-1</sup>	91.2	3	0.84	13.4	8.9
PBC, g BSA kg <sup>-1</sup>	81.3	3	0.91	29.5	10.5

Both replicate spectral sub-samples and replicate wet chemistry measurements were averaged before fitting the models.

<sup>a</sup>BSA, bovin serum albumin; IVDMD, *in vitro* dry matter digestibility; PBC, protein binding capacity.

<sup>b</sup>PLS, partial least squares regression.

<sup>c</sup>RMSE, root mean square error.

<sup>d</sup>RER, range in wet chemistry method per unit RMSE.



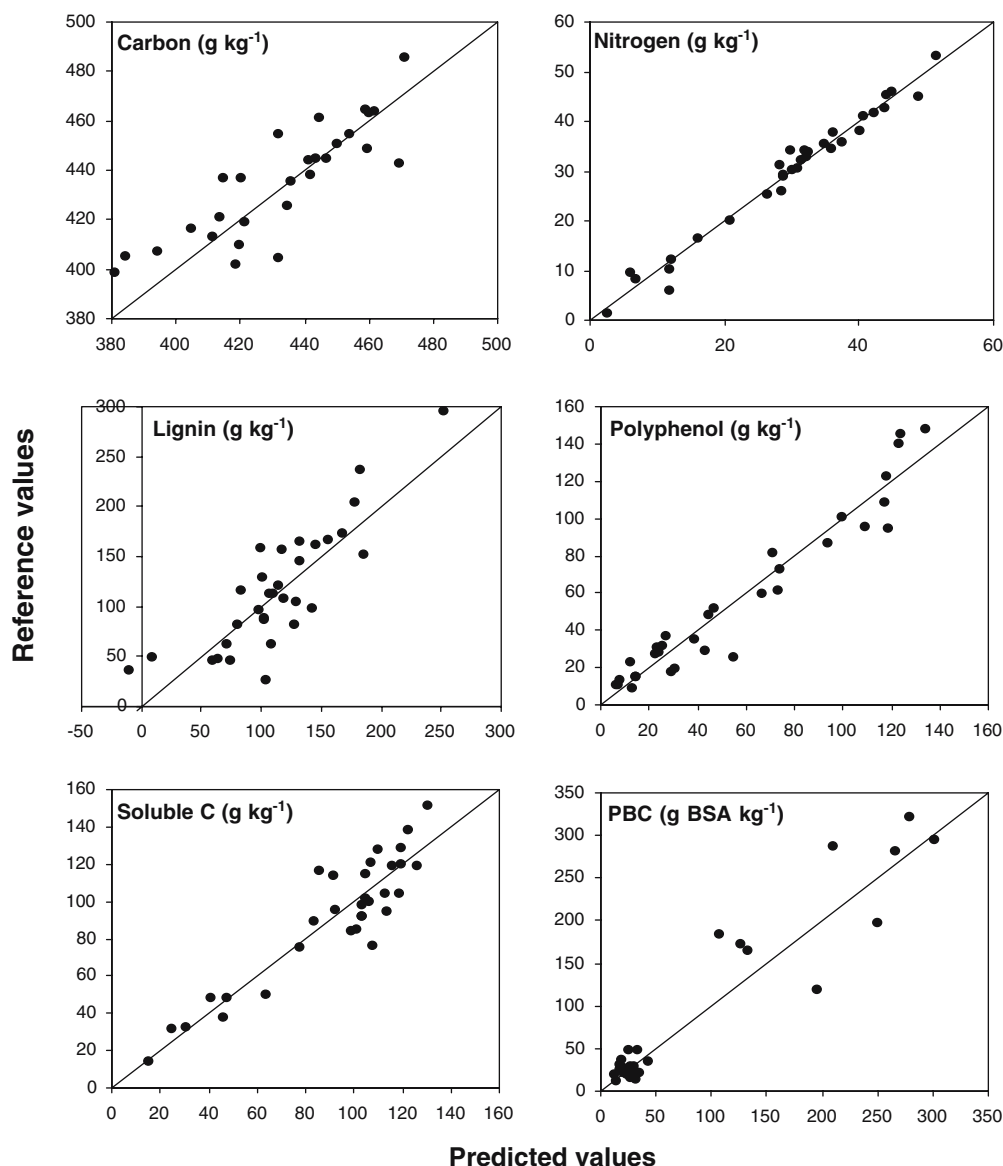


Figure 2. Scatterplots of wet chemistry values against NIR predicted values for residue quality variables. The NIR predicted values were obtained using hold-out-one, full cross-validation. The 1:1 line is also shown. Both replicate spectral sub-samples and replicate wet chemistry methods were averaged before fitting the models. PBC is protein binding capacity in units of bovin serum albumin (BSA).

prediction performance for lignin C (cross-validated RMSE = 10, RER = 10) than we did for total lignin (RMSE = 33, RER = 6). Joffre et al. (1992) also demonstrated good NIR calibrations for C and N for the litter of eight species of evergreen and deciduous trees, conifers and shrubs.

The PLS models relating the decomposition and mineralization variables to NIR also

produced robust predictive models (Table 3 – NIR columns, and Figure 3). The robust NIR calibrations for IVDMD are in agreement with a number of previous studies, which have demonstrated NIR prediction of IVDMD with high  $r^2$  and low error (Roberts et al., 2004).

Large and significant absolute regression coefficients occurred at wavelengths 1.43, 1.65, 1.68, 1.94, and 2.12  $\mu\text{m}$  for C mineralization and 1.48,

1.70, 1.72, 1.93, 2.06, 2.15, and 2.29  $\mu\text{m}$  for N mineralization (Figure 4). The diagnostic bands for C mineralization corresponded with those associated with the dependent residue quality variables: the bands at 1.43 and 1.94  $\mu\text{m}$  corresponded with dominant bands in the PLS model for soluble C (not shown), and the 1.65  $\mu\text{m}$  band is closely associated with total soluble polyphenols (Shepherd et al., 2003). Although the 1.68  $\mu\text{m}$  band has been reported to be associated with lignin (Shenk et al., 2001), it was not a significant band in the lignin PLS model in this study. The diagnostic bands for N mineralization were closely associated with those for residue N, in agreement with the MLR model, as previously reported (Shepherd et al., 2003).

By demonstrating good calibration of C and N mineralization across a wide range of residue qualities our results generally support the findings of the few previous studies conducted on calibration of mineralization of organic residues to NIR (Bruun et al., 2005; Gillon et al., 1993, 1999; Joffre et al. 2001). Gillon et al. (1999) incubated 34 litter samples of diverse biochemical composition in microcosms for 8 weeks. They found that the amount of litter weight loss at different sampling times and the decomposition exponential decay constant were strongly related to the NIR reflectance of the initial residues.

Using a set of 1235 samples of litter, Joffre et al. (2001) showed how NIR analysis of initial

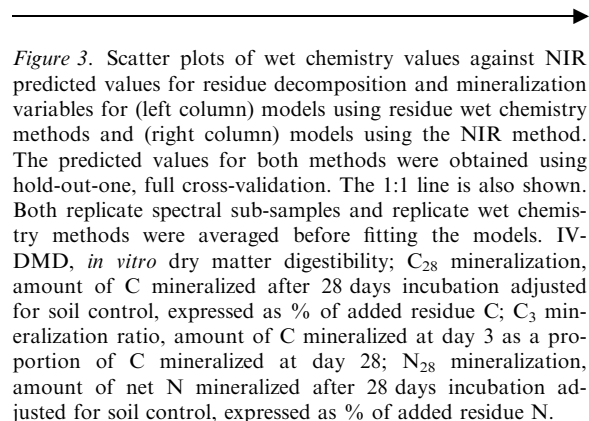


Figure 3. Scatter plots of wet chemistry values against NIR predicted values for residue decomposition and mineralization variables for (left column) models using residue wet chemistry methods and (right column) models using the NIR method. The predicted values for both methods were obtained using hold-out-one, full cross-validation. The 1:1 line is also shown. Both replicate spectral sub-samples and replicate wet chemistry methods were averaged before fitting the models. IVDMD, *in vitro* dry matter digestibility; C<sub>28</sub> mineralization, amount of C mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue C; C<sub>3</sub> mineralization ratio, amount of C mineralized at day 3 as a proportion of C mineralized at day 28; N<sub>28</sub> mineralization, amount of net N mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue N.

litter quality can be related to a theoretical litter organic matter quality. The theoretical framework considers decomposition as a continuous change in litter quality and a loss of total carbon. Organic matter quality is defined as a measure of substrate availability to the decomposer community, and can be related to the number of enzymatic steps required to release a carbon atom from an organic compound (Ågren and Bosatta, 1996). Experimentally, the initial quality of litter was calculated from mass loss data during decomposition, whereby the percent remaining carbon in a litter at a given time is a function of the ratio of the quality of litter at that time to the initial litter quality. Joffre et al. (2001) demonstrated that the amount of ash-free litter remaining at any time, adjusted for species

Table 3. Prediction of decomposition and mineralization of organic residues using either residue quality variables based on wet chemistry methods or NIR models

Decomposition variable <sup>a</sup>	Mean	$r^2$		RMSE <sup>b</sup>		RER <sup>c</sup>	
		Wet chemistry	NIR	Wet chemistry	NIR	Wet chemistry	NIR
IVDMD, %	48.3	0.87	0.88	6.40	6.03	9.6	10.2
C <sub>28</sub> mineralization, %	31.8	0.78	0.82	5.30	4.87	7.5	8.2
C <sub>3</sub> mineralization ratio, %	46.4	0.78	0.88	6.40	4.66	5.5	7.6
N <sub>28</sub> mineralization, %	-6.51 <sup>d</sup>	0.86	0.87	15.4	14.2	9.4	10.2

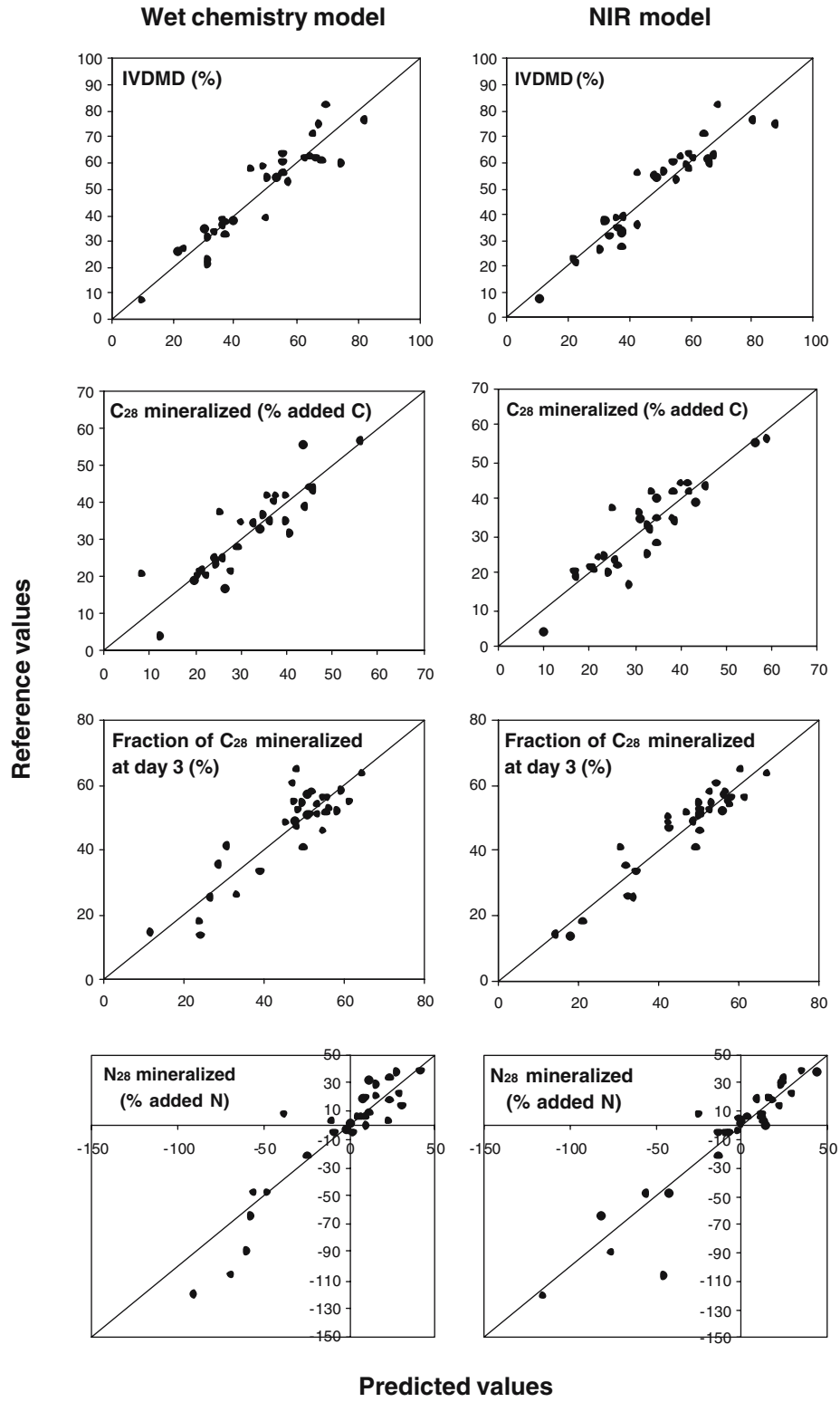
Cross-validated multiple linear regression models were used for the wet chemistry method models and cross-validated partial least squares regression models for the NIR models. Validation statistics are shown. Replicate spectral measurements and replicate decomposition/mineralization measurements were averaged before fitting the models.

<sup>a</sup>IVDMD, *in vitro* dry matter digestibility; C<sub>28</sub> mineralization, amount of C mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue C; C<sub>3</sub> mineralization ratio, amount of C mineralized at day 3 as a proportion of C mineralized at day 28; N<sub>28</sub> mineralization, amount of net N mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue N.

<sup>b</sup>RMSE, root mean square error.

<sup>c</sup>RER, range in wet chemistry method per unit RMSE.

<sup>d</sup>Range -120.5 to 38.4.



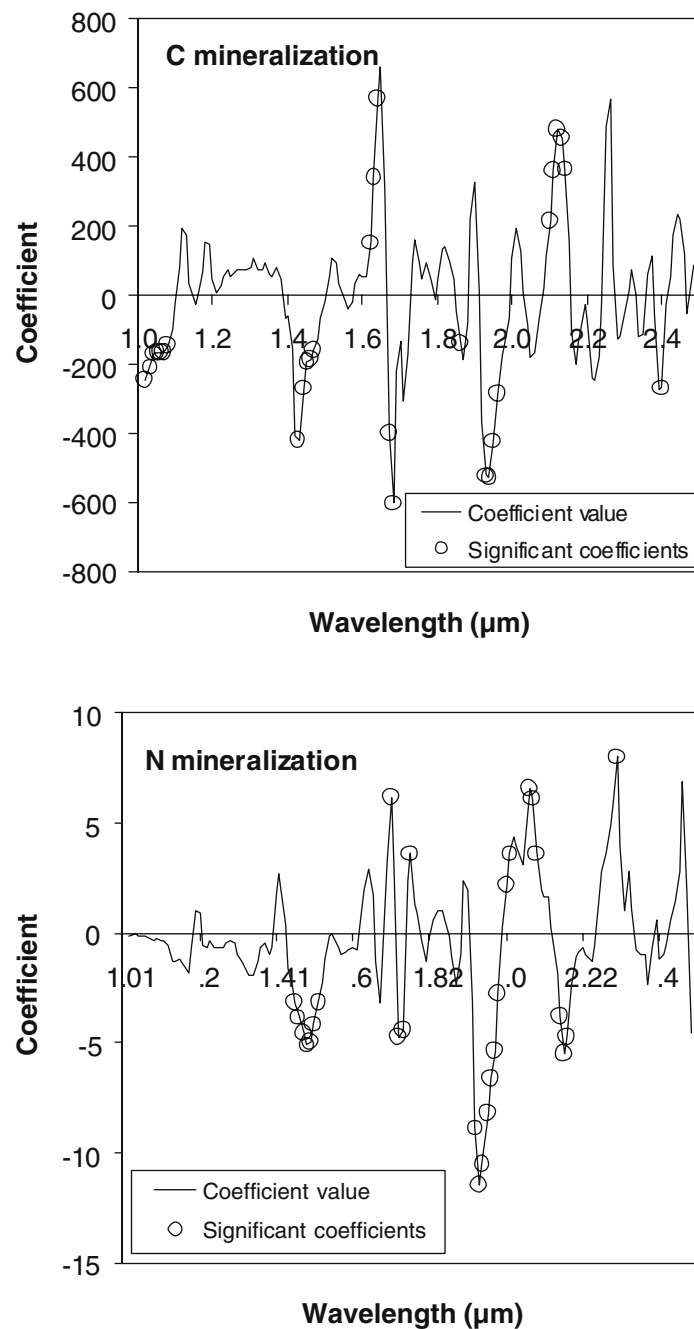


Figure 4. Partial least squares regression (b) coefficients against wavelength for prediction of C and N mineralization from NIR spectra. Significant ( $P = 0.05$ ) coefficients were identified by jack-knifing using full hold-out-one cross-validation.

using a single parameter, could be calibrated well (validation  $r^2 = 0.94$ ) to NIR. NIR was found to provide much better prediction of decomposition than using three chemical fractions. This was attributed to the rich information on bio-

chemical composition than can be obtained from NIR spectra compared with elemental analysis.

Bruun et al. (2005) in an incubation experiment using materials from a wide range of agricultural plants and plant parts from Europe,

found as in our study that NIR was able to predict C mineralization patterns well (validation  $r^2 = 0.92$ ), but results were poorer for N mineralization ( $r^2 = 0.45$ ) compared with our results. As noted by Bruun et al. (2005), net N mineralization, being the result of mineralization and immobilization processes, is a more complex process than C mineralization and therefore more easily influenced by external factors and experimental conditions. For example in their study nitrogen was added to avoid nitrogen limitation of micro-organisms, which was not done in our study.

#### NIR repeatability

NIR repeatability always exceeded the repeatability of the wet chemistry method (Table 4) despite the possibility of variation in sample packing density in the sample holders with the NIR method used (samples scanned in open Petri dishes). A similar conclusion was reached for studies on IVDMD of forage samples by Aastveit and Marum (1991), who obtained a SD of 1.24 for the wet chemistry method and 0.35 for NIR, although over a narrow range of IVDMD (67–82%) compared with this study (7–82%). Sørensen (2002), using silage samples, reported a SD of 1.7 for three replicate analyses of IVDMD determined on different days (although NIR analysis was performed on the same sub-sample as the wet chemistry method)

which is comparable with our wet chemistry SD value of 2.0. The improvements in repeatability with NIR were greatest (> 50% reduction in SD) for C, N, lignin, and C mineralization. The replicate wet chemistry methods were conducted within the same batch in this study, but measurement error would be expected to be higher if different batches analyzed over longer time periods were considered. Batch-to-batch variation within the same laboratory is typically much higher for wet chemistry methods than for NIR (e.g. Aastveit and Marum, 1991).

#### NIR accuracy relative to wet chemistry methods

Using the NIR calibration values to smooth the wet chemistry data improved accuracy of the wet chemistry method for C, N, and lignin concentrations, and C mineralization (Table 4). For C and N concentration, the improvement was large in absolute terms (> 60% reduction in SD). Thus using NIR in combination with these methods could lead to higher accuracy than using the wet chemistry method alone.

Using the NIR validation values to simulate use of a previous calibration to estimate the wet chemistry values (Table 4), NIR significantly improved the accuracy of the original wet chemistry method for C (by 33%) and N concentration (by 5%) but not for the other variables. Across all variables, SD values for NIR were 0.67 to 3.3

Table 4. Repeatability and accuracy of wet chemistry and NIR methods for determination of residue quality and mineralization properties

Wet chemistry method <sup>a</sup>	Min	Max	NIR SD	Wet chemistry SD	NIR RMSE <sub>corr</sub> calibration	NIR RMSE <sub>corr</sub> validation
C, g kg <sup>-1</sup>	370	486	3.8 (0.33)	14.8 (1.85)	2.67	9.89
N, g kg <sup>-1</sup>	1.4	53.2	0.70 (0.062)	1.74 (0.217)	0.69	1.65
Polyphenols, g kg <sup>-1</sup>	8.4	148	3.56 (0.316)	5.33 (0.667)	6.13	10.4
Lignin, g kg <sup>-1</sup>	25.4	295	5.7 (0.51)	16.9 (2.11)	9.71	30.3
Soluble C, g kg <sup>-1</sup>	14.0	151	2.40 (0.212)	4.02 (0.503)	11.0	13.1
IVDMD, %	7.0	82.4	1.85 (0.164)	1.99 (0.249)	3.74	5.86
C <sub>28</sub> mineralization, %	3.7	56.5	1.08 (0.095)	3.41 (0.305)	2.43	4.45
N <sub>28</sub> mineralization, %	-120.5	38.4	4.40 (0.388)	6.17 (0.545)	11.9	13.7

To evaluate repeatability for the two methods, compare NIR standard deviation (SD) with wet chemistry SD. To evaluate accuracy for the two methods, compare wet chemistry SD with NIR error corrected root mean square error (RMSE<sub>corr</sub>) using either calibration results (Scenario 1: within batch calibration) or validation results (Scenario 2: previous calibration). Standard errors are given in parentheses.

<sup>a</sup>IVDMD, *in vitro* dry matter digestibility; C<sub>28</sub> mineralization, amount of C mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue C; N<sub>28</sub> mineralization, amount of net N mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue N.

times higher than the wet chemistry method. Sørensen (2002) reported for IVDMD in silage samples that NIR prediction error estimated by cross-validation for samples from the same population gave a relatively precise estimate of the prediction error on completely independent test samples collected after the calibration period. However, further studies using independent sample sets are needed to objectively assess potential improvements in accuracy of NIR compared with wet chemistry methods when previous calibrations outside the batch are used.

The results suggest that using NIR in conjunction with the wet chemistry method within the same batch of samples could be useful for detection of outliers due to measurement error in the wet chemistry data. However, this strategy would not work if the whole batch was in error, caused for example by variation due to different operators or over time within the same laboratory.

The prospects for improving accuracy of the wet chemistry reference method using previous NIR calibrations showed less promise, although this strategy may be useful as a screening tool to detect drift in wet chemistry analyses over time or between different operators or laboratories. Environmental factors (e.g. temperature, humidity) will affect NIR repeatability over time and transfer of calibrations across NIR instruments between laboratories is also a source of error in the NIR method. Although variation over time and between laboratories is expected to be greater for wet chemistry methods than for the NIR method, NIR also requires calibration data sets that adequately sample the full variation in conditions to be expected, and this may be challenging for decomposition and mineralization incubations, which are easily influenced by environmental and experimental factors. However, where good calibrations can be obtained for standardized wet chemistry methods, for example as in this case for residue total N, large centralized calibration libraries would be feasible and could be used for continuous quality control in wet chemistry laboratories.

#### *Residue decomposition prediction using wet chemistry methods*

The graphical model used to select residue quality variables for prediction of mineralization and

decomposition variables is shown in Figure 5. Although C and N mineralization and IVDMD were highly inter-correlated, the three variables were statistically independent when residue quality variables were included in the model. IVDMD was shown to be dependent on C, N, polyphenol, lignin, soluble C, and PBC concentrations. C mineralization was dependent on soluble C, lignin, and polyphenol; and N mineralization was associated with polyphenol and N. Although the conditional relationships in the graphical models may also be dependent to some extent on the errors in the individual measurements, the relationships agree well with previous work on the effect of residue quality on decomposition. For instance, C mineralization has been found to be positively related to soluble C concentration and negatively to the lignin and polyphenol concentration of the residue (Giller and Cadisch, 1997). The fact that C mineralization was not related to residue N concentration suggested that N was not limiting C release during the incubation. Our results generally support the recent findings of Jensen et al. (2005), who found for a broad range of plant materials and plant parts that neutral detergent soluble C and N were among the best predictors of decomposition and N mineralization, respectively, and that these were in turn related to residue total N concentration. Contrary to previous work, they found that C/N and lignin/N ratios had little ability to predict decomposition and N mineralization. Soluble C and total N were important predictors of decomposition and N mineralization, respectively, in our study, although modified by lignin and polyphenol concentrations. The dependence of IVDMD on PBC may reflect the influence of tannin-like polyphenols that can provide protection against decomposition (Vanlauwe et al., 2005).

The MLR models relating the decomposition and mineralization variables to the residue quality variables, measured using wet chemistry methods, gave robust models with cross-validated  $r^2$  values for wet chemistry vs. predicted values of between 0.78 and 0.86 ('wet chemistry' columns in Table 3 and Figure 3). Using the same sample set, Vanlauwe et al. (2005) observed that polyphenol concentration also had an influence on N mineralization for samples with positive values, but the data was not partitioned in this study due to the small number of samples for NIR calibration.

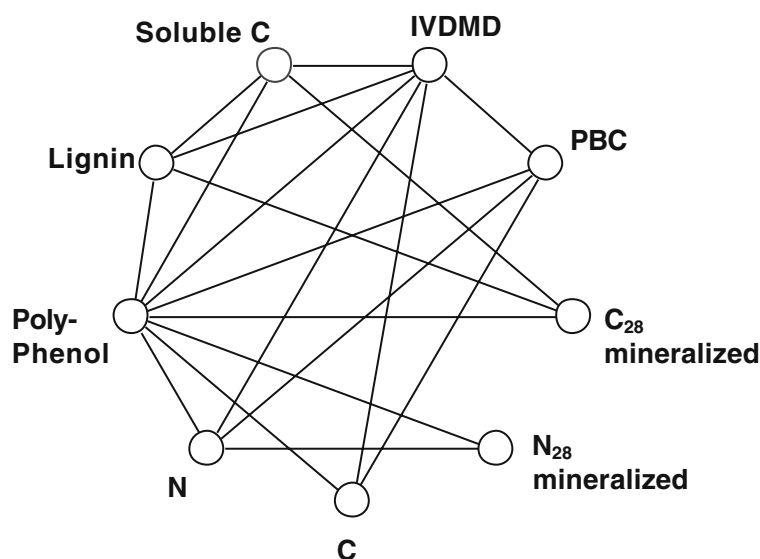


Figure 5. Graphical model showing conditional associations between C and N mineralization and residue quality variables. Arcs represent conditional node association at  $P = 0.05$  significance level.  $C_{28}$  mineralized, amount of C mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue C;  $N_{28}$  mineralized, amount of net N mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue N; IVDM, *in vitro* dry matter digestibility; PBC, protein binding capacity.

#### Comparison of wet chemistry and NIR models for predicting decomposition

For prediction of decomposition and N mineralization, the NIR models had consistently higher  $r^2$ , and lower RMSE values than the wet chemistry models, which were based on the residue quality variables measured using wet chemistry methods (Table 3). On average, NIR reduced cross-validation RMSE by 12% compared with the wet chemistry models. Note that the RMSE term already includes error due to bias (Naes et al., 2002). These findings generally concur with the results of Gillon et al. (1999) and Joffre et al., (2001) who also suggested that NIR may predict litter decomposition more accurately than the chemical composition of the initial litters by standard chemical methods. This is because NIR may capture broader information on biochemical composition than the conventional laboratory methods, provided by overtones and combination bands of stretching and bending vibrations from major OH, CH and NH groups (Shenk et al., 2001).

The reduction in error with the NIR models was relatively even across the full range of wet chemistry values, in terms of reduced scatter of

points about the 1:1 line in Figure 3, as opposed to being confined to either high or low ranges. For net N mineralization, there was more scatter in the NIR calibration in the negative than positive range of wet chemistry values, most likely reflecting lack of repeatability in the laboratory measurements at very low plant nitrogen concentrations, but the wet chemistry method model showed some systematic bias in the residuals in the negative range (Figure 3).

Graphical models were further used to test the hypothesis that given the NIR prediction of decomposition and mineralization, the wet chemistry methods added no further predictive information. Thus the NIR predicted values of decomposition were added to the graphical models of the decomposition and the dependent quality variables (Figure 6). The initial saturated models have arcs connecting all the nodes, but after stepwise deletion of non-significant arcs, only conditional relationships remain. Absence of an arc between two variables in the model implies that the two variables are independent (i.e. independent in the conditional probability distribution) given the other associations in the model (i.e. conditional independence, Edwards, 2000). For example, absence of an arc between the

mineralization variable and the residue quality variables would indicate their independence given the inclusion of the NIR method in the model. Therefore, if we know the NIR prediction, information about the wet chemistry variables is irrelevant for knowledge of mineralization. It also follows that given the information on the wet chemistry variables, NIR did provide additional information on mineralization, otherwise arcs connecting mineralization and the wet chemistry variables would have remained after backward deletion. In all cases (Figure 6) the graphical models showed that the strongest association was between mineralization or decomposition and the NIR method, and that inclusion of wet chemistry variables provided no additional information on decomposition or mineralization.

These results confer with the lower RMSE values for the NIR models than for the wet chemistry models for prediction of decomposition and mineralization. Therefore the results of this study provide strong evidence that residue decomposition and mineralization can be determined more accurately by NIR than through predictions based on determination of residue quality variables by wet chemistry methods. This may be a combined result of the fact that NIR integrates information on a larger number of biochemical attributes of residues than those included in the wet chemistry models and the greater repeatability of NIR compared with the wet chemistry methods themselves. However, another recent study did not support our finding. In the study of Bruun et al. (2005), NIR was able to predict C mineralization patterns marginally better than stepwise chemical digestion or C/N

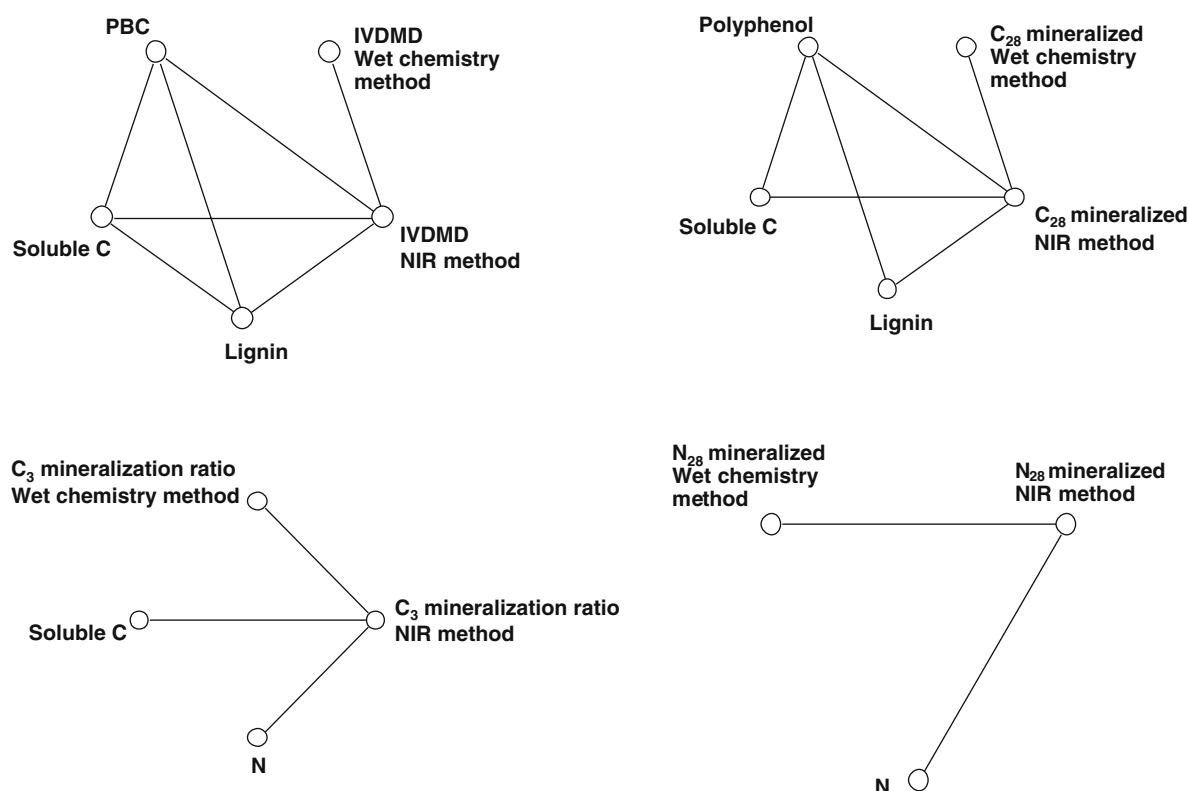


Figure 6. Graphical models showing conditional associations between residue quality variables, and residue decomposition or mineralization variables determined by the wet chemistry method and predicted by the NIR method. Arcs represent conditional node association at  $P = 0.05$  significance level. IVDM, *in vitro* dry matter digestibility;  $C_{28}$  mineralized, amount of C mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue C;  $C_3$  mineralization ratio, amount of C mineralized at day 3 as a proportion of C mineralized at day 28;  $N_{28}$  mineralized, amount of net N mineralized after 28 days incubation adjusted for soil control, expressed as % of added residue N.



ratios, but the reverse was true for prediction of N mineralization. However, they did not test conditional dependence assumptions. They concluded that the speed and cheapness advantages of NIR outweighed any loss in prediction accuracy.

An implication of these results is that NIR calibration libraries could be used to increase sampling efficiency and reduce analytical costs in time consuming decomposition studies using stratified and two-phase or double sampling schemes (Cochran, 1977). With this approach, NIR is used to thoroughly sample the variability of the target material in a given area or application. From the resulting spectral library (e.g. Shepherd and Walsh, 2002) a subset of samples is selected for the decomposition study, chosen to sample the spectral diversity (e.g. based on predicted decomposition values). NIR calibrations based on this subset of samples are then used to predict decomposition values for the entire spectral library. From this data, mixed effects variance-component models (e.g. Pinheiro and Bates, 2000) can be used to analyze the numbers of NIR and decomposition samples required to achieve a given level of accuracy in future studies. Trade-offs between cost and accuracy can then also be calculated. Used in this framework, NIR can enable risk-based approaches to soil and plant quality assessment that allow prediction uncertainty to be incorporated in decision-making. This double sampling approach can increase the efficiency of virtually any study where good NIR calibrations are obtained and precludes the need for establishment of large reference data sets, as used for example in the food and forage industry.

However, there is need to establish standardized assays for organic residue decomposition and nutrient release characteristics to help make results generalizable to the broadest possible range of conditions. To achieve this there is need to take account of not only the chemical composition of the substrate, which is what is predicted by NIR, but also effects of temperature, humidity and soil conditions on the rate of decomposition. To control for such external factors the results of NIR should be expressed in some values that are independent of these factors, for example using the framework suggested by Joffre et al. (2001).

NIR-predicted residue N concentration appears to be a useful indicator of N mineralization potential. In our study, N mineralization was predicted well by residue total N concentration alone. Jensen et al. (2005) found that neutral detergent water soluble N was the best predictor of N mineralization, and this was also closely related to plant total N. Shepherd et al. (2003) also demonstrated robust NIR prediction of residue N, over a more diverse range of residue composition and origin than used in this study. The results reported here further suggest that NIR may predict residue N to as good or better accuracy as the wet chemistry method. Therefore diverse centralized NIR calibration libraries for residue N prediction would appear to be a good investment.

## Conclusions

For determining residue quality attributes (as opposed to decomposition and mineralization variables), NIR was more precise, but generally not more accurate than the wet chemistry reference methods. Where high accuracy or standardization across laboratories is required, NIR could be usefully applied in conjunction with wet chemistry methods to improve quality control. Where high accuracy is not required, NIR alone provides a rapid and cheap method for determination of residue quality.

For determination of decomposition and mineralization, using NIR is both more accurate and more precise than using predictive models that are based on litter quality attributes determined using conventional wet chemistry methods. NIR proved to be rapid and robust, over a wide range of organic residue types and quality, involving only a single measurement, whereas several wet chemistry measurements were required to estimate IVDMD and C mineralization to a similar level of accuracy.

Potential applications of NIR include rapid characterization of diverse organic residues for livestock feed and as inputs for soil fertility improvement, including animal manures, composts, green manures, crop residues, and urban organic wastes. In particular, residue N provided a good indicator of N mineralization potential, and therefore NIR could be readily used to

directly characterize organic residues into the management categories proposed by Palm et al. (2001) in terms of fast or slow N mobilization or immobilization.

The potential for widespread use of NIR for measuring residue quality and decomposition characteristics is expected to increase over the next several years with developments towards cheaper and more portable spectrometers, coupled with more flexible software and easier calibration methods. Future efforts should be directed towards the establishment of centralized spectral calibration libraries using standardized methods designed to sample the widest possible range of materials. NIR should also be used in double sampling schemes to increase efficiency of residue decomposition studies. Further research should be directed towards direct calibration of soil quality, crop and livestock responses in the field to NIR characteristics of residues.

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