POTENTIAL OF USING NIR TO PREDICT NITROGEN FERTILISER VALUE OF ORGANIC RESIDUES

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1 INTRODUCTION

Organic fertilisers based on waste products are frequently introduced in agriculture. Their nitrogen (N) fertilisation effect in relation to their total and mineral N content varies widely, and a demand has arisen for standardised laboratory methods to determine this. The fertilisation value of the nitrogen is likely to be affected by the C/N ratio and the forms of organic N and C present in the organic fertiliser. Measurement of total N and C content and their different forms involves expensive and time-consuming extractions. Near infrared reflectance (NIR) spectroscopy is a quick laboratory method without the need for extraction. It can be used in qualitative and quantitative characterisation of biological materials. The NIR spectrum is affected not only by the content of C and N but also by the forms. Near infrared spectroscopy is used for rapid analysis of forage, grains and soil, and has recently also been applied for determination of DM, NH_4-N and total N in manures (Kemsley et al., 2001; Sørensen et al., 2007). The objective of this study was to test whether the N fertilisation value of different organic residues could be predicted from NIR data and to compare the results with predictions based on C/N ratio and amino acid content.

2 MATERIALS AND METHODS

2.1 Fertiliser value of organic residues

The nitrogen fertiliser value of different organic residues was tested in pot experiments with ryegrass. Fifteen treatments received 70 kg total N ha^{-1} as organic residues and three additional treatments received 0, 35 or 70 kg N ha^{-1} as ammonium nitrate. The residues were blood meal, feather meal, bone meal, meat meal, cattle manure, pig slurry, mink manure, chicken manure, horse manure, sewage sludge, biogas residue, lucerne pellets, rapeseed cake, mussel compost and vinasse. The ryegrass was cut twice during a two-month period and the amount of harvested plant N measured. Plant N uptake in relation to added total N in organic fertiliser treatments was compared with the linear response of mineral N fertiliser. This allowed the mineral fertiliser equivalent (MFE), expressed as percentage of total N added, to be calculated. To separate the effect of ammonium N in organic fertilisers from that of mineralised organic N, the mineral fertiliser equivalent of the organic N (MFE_{org}) was calculated by subtracting the percentage of ammonium from the MFE.

2.2 Elemental analyses

The organic residues were analysed for total N, ammonium N, total C and amino acid N. Total N was analysed according to Kjeldahl and ammonium N by direct distillation on a Kjeltec analyser. Total C was analysed on dried and ground samples by elemental analysis using an Elementar VarioMax CHN. Amino acids were determined according to SS-EN ISO 13903:2005. From this, the C/N ratios and ammonium-N and amino acid N contents as a percentage of total N were calculated and related to MFE through linear regression.

2.3 NIR measurements

NIR measurements were made with the spectroradiometer *FieldSpec Pro FR* (Analytical Spectral Devices, Inc., Denver, Co) on all samples both before and after drying, except for vinasse, which would not dry. Liquid materials (pig slurry, cattle slurry and biogas residue) were shaken in closed bottles and then a 5 mm thick sample was poured into the black dish used for all samples during measuring. Just before measuring the sample was stirred to prevent sedimentation or floating particles. The instrument was equipped with a bare optic fibre connected to a probe with a 20 W tungsten light source positioned 7 cm over the rotating sample. The same spectroradiometer was used for the dried samples, but with the probe in direct contact with the sample and with a 50W halogen light source. Each spectrum consisted of 50 averaged sub-spectra. The range of measurement was 350-2,500 nm in 1.4-2.0 nm intervals, with a spectral resolution of 3-10 nm. A wavelength interval of 1 nm was interpolated to the instrument

output file. The potential of NIR to predict MFE was tested partial least square regression (PLS) performed on the first derivative of NIR absorbance data (900-2500 nm) with leave-one-out cross-validation. In addition to r^2 of calibration and r^2 of cross-validation, RMSE (root mean square error) and RPD (ratio between standard deviation and the RMSE) were calculated for both the calibration and the cross-validation. The larger the RPD value, the more successful the prediction achieved. A commonly used decision criterion is based on a ratio limit of 3 (Sørensen et al., 2007).

3 RESULTS AND DISCUSSION

3.1 Correlation between mineral fertiliser value and C/N ratio

The C/N ratio had a strong negative correlation (r^2=0.90) with MFE (Figure 1). Similar relations between MFE and C/N ratio were reported in Danish experiments with different pig slurries (Sørensen and Fernández, 2003) and cattle slurries (Sørensen et al., 2003), although the MFE values at different C/N ratios were about 20% higher in those experiments. This difference was probably due to the Danish studies measuring MFE in spring barley field experiments, as opposed to our measurements in ryegrass pot experiments. While the choice of crop and duration of the experiment can also influence the results, the relative differences between the organic fertilisers remain the same.

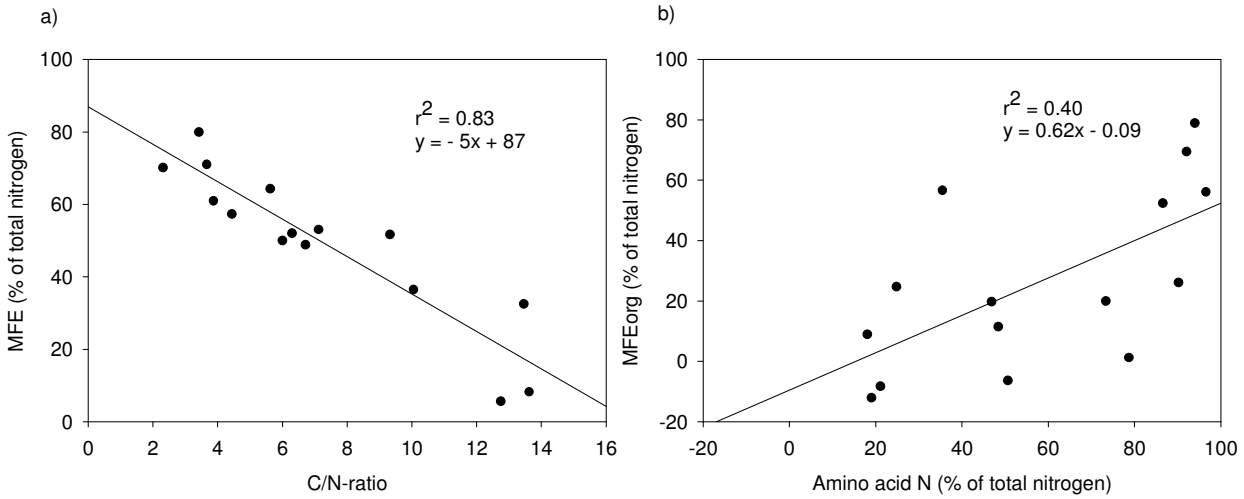

FIGURE 1 **Linear regression between a) C/N ratio and mineral fertiliser equivalent (MFE) and b) amino acid N and MFE of the organic N (MFE_{org}).**

3.2 Correlations between fertiliser value and amino acid nitrogen

The amino acid fraction of N did not correlate well to MFE_{org} (Figure 1b). In fact, the total organic nitrogen correlated better (r^2=0.46). Since the sum of ammonium N and amino acid N can be considered to be the potentially plant-available N, although influenced by the C content of the fertiliser. The correlation between MFE and the ratio between ammonium and amino acid N and total C was tested, but proved to have a weaker correlation (0.73) than the C/N ratio based on total N and C (Figure 1a).

3.3 Prediction with NIR

The prediction of C and N content per unit dry matter (DM) with NIR was not very successful from neither untreated samples (Table 1) nor from dried samples. This contradicts other investigations with manure (Kemsley et al., 2001), composts (Michel et al., 2006) and plant material (Bruun et al., 2005). The difference is probably due to the small amount of samples and the large variation in types of material. However, the predictive power of calibrations for both total N and C per unit wet weight of the untreated samples was high (Table 1). NIR is a good detector of water content, and the better prediction per unit wet weight is likely to be an effect of that, since The higher the water content, the more diluted N and other constituents will be per unit wet weight. However, the correlation between dry matter content and total N per wet weight (r^2=0.54) could not fully explain the high r^2 values obtained for both calibration and prediction of total N from NIR (Table 1).

TABLE 1 **PLS results for prediction from NIR on undried samples of different variables, expressed as percentage per unit wet weight (ww) and per unit dry matter (DM), where MFE is mineral fertiliser equivalent, MFE_{org} is MFE of the organic nitrogen, RPD is the ratio between the standard deviation and the root mean square error (RMSE) and cal and cval indicate whether r^2 and RPD refer to calibration or cross-validation respectively**

	r^2_{cal}	RPD_{cal}	r^2_{cval}	RPD_{cval}
MFE/DM	0.69	1.86	0.41	1.33
MFE_{org}/DM	0.90	3.29	0.66	1.77
Total C/DM	0.39	1.32	0.04	0.95
Total N/DM	0.67	1.81	0.37	1.27
Ammonium N/DM	0.31	1.24	0.07	1.02
MFE/ww	0.94	4.14	0.73	1.96
MFE_{org}/ww	0.95	4.87	0.77	2.13
Total C/ ww	0.87	2.85	0.72	1.96
Total N/ww	0.87	3.03	0.74	2.02
Ammonium N/ww	0.20	1.16	0.01	0.90
C/N ratio	0.51	1.48	0.16	1.07

The predictive power of the C/N ratio was not strong (Table 1). The possibilities for directly predicting MFE appeared better. NIR of dried samples showed potential for prediction of MFE_{org} per unit dry matter (Figure 2a), as did NIR of untreated samples (Figure 2b; Table 1), although not as accurately as the dried samples. NIR of untreated samples was not promising for prediction of MFE per unit dry matter (Figure 3a; Table 1), but better for MFE per unit wet weight (Figure 3b; Table 1). Even though the promising correlations are partly an effect of the covariation of nitrogen and dry matter content, the prediction of MFE_{org} from the dried samples proves that NIR detects properties of the organic N that relate to the mineralising capacity. Since other investigations show that N and C can be measured accurately with NIR, it should be possible to use different models on different materials to predict N and C and from these predictions calculate C/N ratio and thereby MFE.

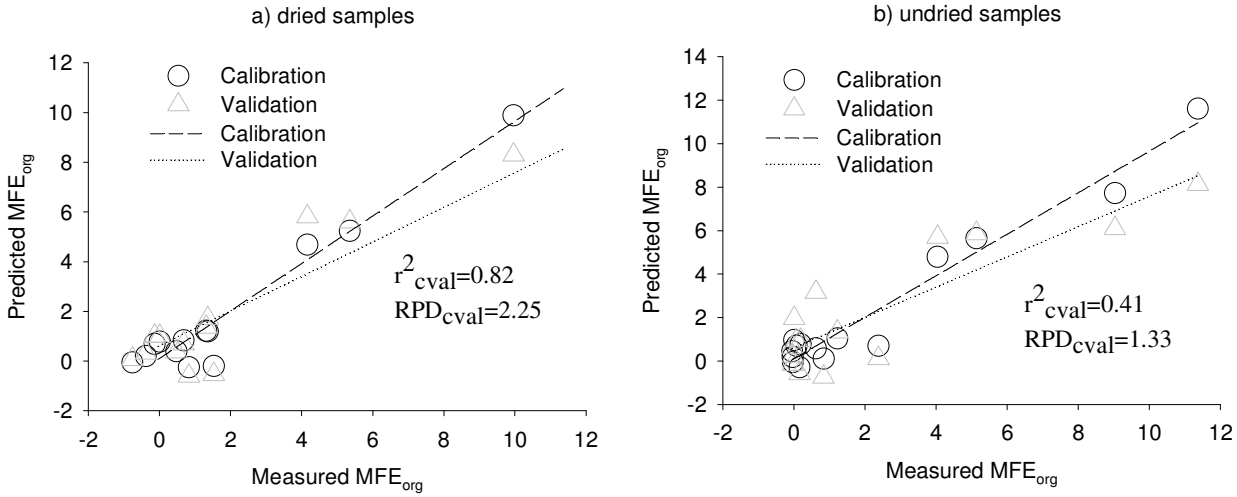

FIGURE 2 **PLS results for prediction of MFE_{org} per unit DM from NIR data from a) dried and b) undried samples**

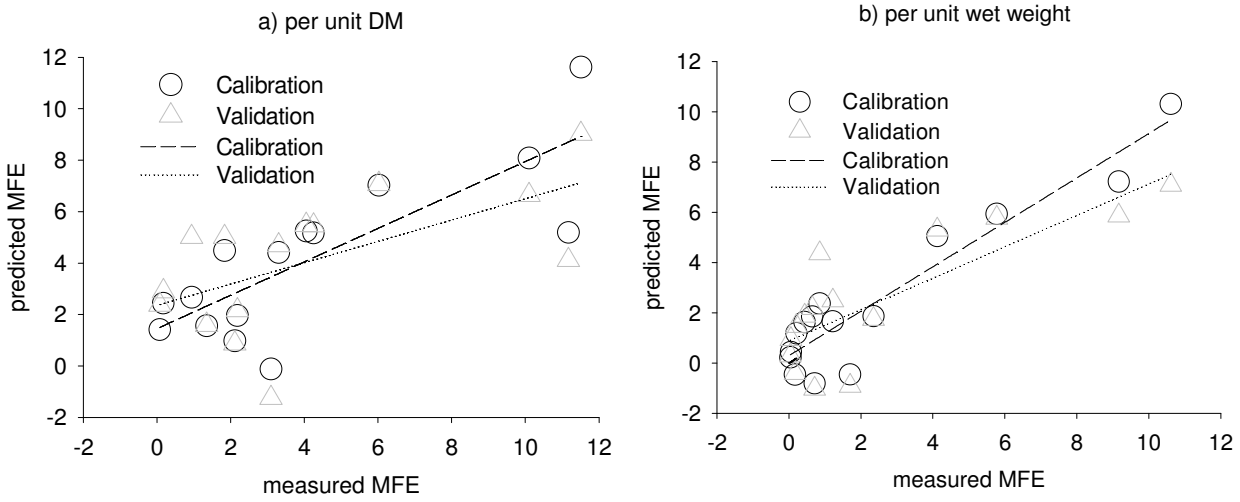

FIGURE 3 **PLS results for prediction of MFE a) per unit DM and b) per unit wet weight from NIR data taken on undried samples.**

4 CONCLUSIONS

The C/N ratio gave a good indication of the immediate plant availability of N in fertiliser, with a negative linear relationship where MFE ranged from 10% at C/N ratios around 14 to 75% at C/N ratios around 2. Amino acid content did not explain any further variation in MFE. The results indicate that nitrogen fertiliser values can be predicted from NIR data and that it may be worthwhile exploring this possibility within a larger distribution of data.

ACKNOWLEDGEMENTS

This project was funded by the Swedish Farmers' Foundation for Agricultural Research. The authors also want to thank all providers of fertilisers and Johanna Wetterlind for support concerning PLS calculations in Unscrambler.

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