

ANALYSIS OF MANURES AND BIOSOLIDS VIA NEAR INFRARED REFLECTANCE SPECTROSCOPY (NIRS)

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1 INTRODUCTION

Current methods of laboratory analysis for organic materials are slow, relatively expensive and can give inconsistent results for solid and semi-solid materials. Consequently, they are rarely analysed. The resulting uncertainty means that farmers and growers are unaware of the nutrient content of organic materials and, therefore, generally fail to adequately allow for the nutrients supplied following the application of manures to land. Growers therefore tend to apply unnecessarily high rates of inorganic fertilisers (Anon, 2008), as “insurance” for optimal yields, in addition to the often substantial nutrient supply from the organic materials. However, interest in manures as nutrient sources reached unprecedented levels in 2008-09, as a result of substantially increased fertiliser prices. Whilst prices peaked in late 2008 and have fallen progressively since that time, interest appears to have remained high and farmers are more receptive to the use of practical aids for improved recycling of manures.

Near infrared reflectance spectroscopy (NIRS) has greatly improved precision and reliability in the analysis of forages and is now used routinely for the analysis of grain. More recently, NIRS has shown considerable potential for estimating the nutrient content of manures and slurries from multiple, rapid, scanning of fresh samples (Reeves and Van Kessel, 2000; Smith *et al.*, 2005). The main aim of the project is to extend substantially the sustainable recycling of organic manures and residues through the development of NIRS as a robust and reliable technology for multi-nutrient analysis. The initial focus of the research was on the development of robust calibration models for estimation of manure content of dry matter (DM), total N, NH₄-N, SO₃, P₂O₅, K₂O, MgO and pH; covering a range of manure types, including cattle and pig slurries and farmyard manures, and a range of treated biosolids. In addition to the conventional analysis capability, the research aims to develop a calibration model for the estimation of N release from the organic component of manure N, using data from small scale studies on N recovery by ryegrass following mineralisation of the organic N content of selected manures and biosolids.

2 MATERIALS AND METHODS

2.1 Development of NIRS calibration model for manure nutrient analysis

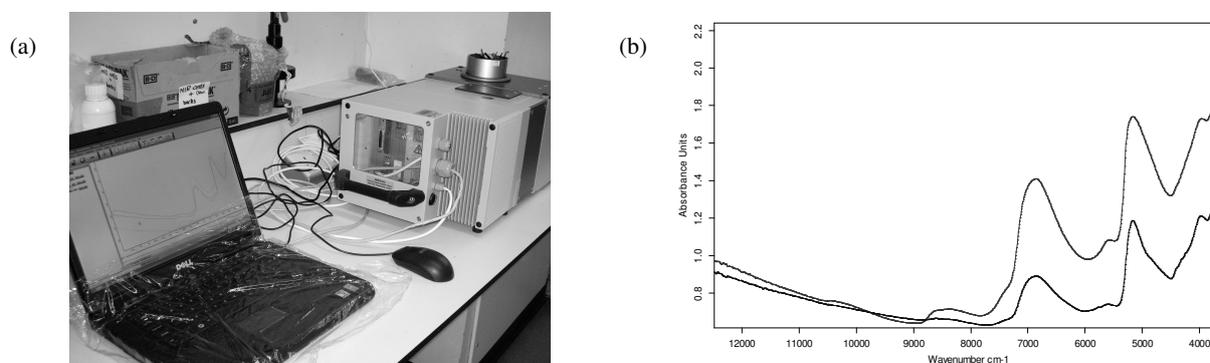


FIGURE 1 Scanning of manure samples for nutrient content (a) using the Bruker Optics Matrix-I NIRS; (b) NIR spectra of two cattle manure samples.

Within this research, the NIRS analyses were performed using a FT-NIR instrument, the Matrix-I (Bruker Optics UK, Ltd) (Figure 1). The samples are placed in a sample cup, with clear quartz base which allows the sample to be irradiated from below and the reflected IR spectra recorded, with the results of multiple scans integrated using the Opus software (version 6 © Bruker Optics). The Matrix-I, which has been used previously for analysis of immature grain samples, was chosen due to its robustness, sensitivity and its potential for on-farm measurement. Samples are routinely scanned three times, though in the case of potentially heterogeneous manure samples, a 6x scanning procedure has been used.

In each of the first two years of the research, a target total of 1050 samples of manures and biosolids were to be collected from across the UK, with the aim of covering the anticipated range in variability in the manures, both in terms of chemical and physical characteristics, and NIRS spectral variability. The projected sample totals for individual manure types were 250 of both pig and cattle FYM, 150 of both pig and cattle slurries and 250 biosolids samples, reflecting the anticipated variability of these different materials. A detailed sampling protocol was drafted to ensure a consistent approach for the collection, labelling, storage and submission of samples. Screw-top polythene bottles (*ca.* 1 litre) and strong plastic bags for collection of samples, together with card labels and information collection forms (separate forms for slurry, FYM and biosolids samples) were distributed. The methodology included guidance on sample size (*ca.* 1 kg for solids; 0.8 l for slurries), labelling, and despatch via courier services to the laboratory. All samples were logged on receipt and scanned as soon as possible thereafter. After initial scanning, the samples were frozen and stored until selection of a subset for full chemical analysis by conventional laboratory methods. A combination of Principal Component Analysis (PCA) and outlier analysis based on preliminary models was used to select the sample subsets for calibration (*ca.* 120 samples, *i.e.* 24 of each manure type in each of the two years). This approach facilitated a wide range of spectral variability and analyses and, hence, the development of robust nutrient calibration models. After thawing, the selected samples were multi-scanned (6x) and analysed by wet chemistry, the solids after rapid freezing in liquid nitrogen and homogenisation using a technique developed in previous research (Smith *et al.*, 2005).

2.2 Development of NIRS calibration model for manure organic nitrogen

Ryegrass grown in large pots (10 litre) has been used to track the release of N from manures with 30 selected manures applied to 3 different soil types (clay loam, sandy loam, loamy sand) at each of two sites: ADAS Boxworth, Cambs and North Wyke, Devon, for 3 years (180 manures in total). As far as possible, manures for this phase of the research were selected by discriminatory analysis of the spectral database for samples collected for the conventional analysis calibration models. The aim was to include three groups of manure types, *i.e.* those likely to be fast, moderate or slow releasers of N from the organic component of manure N. There were three replicates of each of the 30 manure treatments on each soil type and including controls, giving a total of 297 pots at each site in each year. The experiments were based in plastic tunnels, with overhead, sprinkler irrigation, to ensure that moisture was not limiting to grass growth.

Dry matter yield and N offtake were recorded for each cut of grass at the two sites. Based on the N recovery data, a total of six of the more recalcitrant N-source manures from the first- and second-year experiments were also kept on, at both sites, in order to assess the residual N release from the manure applications made in the previous year. The experiments will thus provide N release data for one season after application, across a total of 180 manures (on three soil types over three years) and second season N release data from a further 24 manures. The experiment will provide a basis for developing an NIRS model for the prediction of the longer term N release characteristics of manures. Air temperature within the tunnels has been recorded throughout the growing period, so that the influence of thermal time can be considered in relation to the results on N mineralization from the manures.

3 RESULTS AND DISCUSSION

3.1 Manure nutrient analysis by NIRS

A total of 1019 samples were collected and scanned between January and June 2008, with the active support of the project partners. The total comprised 190 pig FYM, 134 pig slurry, 338 cattle FYM, 176 cattle slurry and 181 biosolids samples. Principal Component Analysis (PCA) was used to select a total of 118 samples to represent the spectral variability and range of manure analysis, in order to assemble preliminary nutrient calibration models. These samples, comprising 14 pig FYM, 41 pig slurry, 20 cattle FYM, 22 cattle slurry and 21 biosolids, were multi-

scanned (6x) and analysed by wet chemistry, the solids following homogenisation. The multiple scans were spectrally averaged before performing model regression. In 2009, a total of 1154 samples were collected and scanned between January and July 2009; the total comprising 254 pig FYM, 135 pig slurry, 373 cattle FYM, 145 cattle slurry and 247 biosolids samples. Principal Component Analysis was again used in combination with outlier analysis to select a further subset of 120 samples (24 of each manure type) for chemical analysis, to expand the range of spectral variability and analyses and continue the development of robust nutrient calibration models.

Following this second year calibration analyses, refinement of the calibration models was undertaken with expert chemometrics input from Bruker Optics. Calibration optimization was performed with 50% of the data used as a test set. Model regressions were run with this test set selected by both analyte value and by PCA. Those models optimized by the test set selected by analyte value gave the most stable results. The removal of some samples from the calibration set was necessary and included slurry samples of very low solids content, in fact “dirty water” samples and also samples with very low nutrient content (at ppm level). Some of these samples were almost translucent and, hence, unsuitable for reflectance-based analysis. The resulting calibration graphs for sample DM and total N content are shown in Figures 2a and 2b.

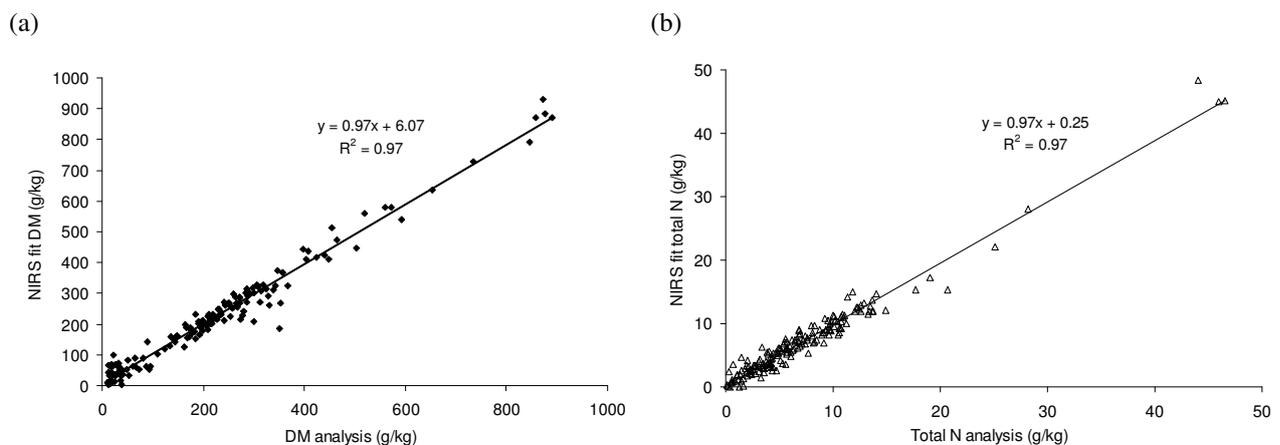


FIGURE 2 Second year calibration models for manure analyses: (a) DM content and (b) total N content.

From the statistics associated with the validation procedure, Malley *et al.* (2005) proposed the following guideline for describing the performance of calibration models for environmental samples, based on the r^2 (correlation coefficient) and RPD statistic (standard deviation of the analyte set divided by standard error of prediction): $r^2 > 0.95$, RPD > 4 - *excellent*; $r^2 = 0.9-0.95$, RPD 3-4 - *successful*; $r^2 = 0.8-0.9$, RPD 2.25-3 - *moderately successful*; $r^2 = 0.7-0.8$, RPD 1.75-2.25 - *moderately useful*. It was considered that some calibrations with $r^2 < 0.7$ may be useful for screening purposes. On this basis, performance of the calibrations for conventional analysis of manure and biosolids samples, at the current stage, was as follows: *excellent* - DM, total N; *successful* - $\text{NH}_4\text{-N}$, P_2O_5 ; *moderately successful* - SO_3 ; *moderately useful* - K_2O , MgO .

Near infrared radiation ($9000\text{cm}^{-1} - 4000\text{cm}^{-1}$) is absorbed by various chemical bonds, mainly C-H, N-H, O-H, all of which are characteristic of organic matter. It is therefore no surprise that the calibrations have been particularly successful for dry matter (moisture), nitrogen, ammonium-N and phosphate content, but rather less so for minerals, potassium and magnesium. However, the success of the models for DM, N, $\text{NH}_4\text{-N}$ and P content is perhaps remarkable, bearing in mind the range of materials represented by these calibrations, from dirty water with $< 0.5\%$ solids content at one extreme and extending to dried biosolids products with up to 80-90% DM. Performance for pH was unsatisfactory ($r^2 < 0.3$, RPD 1.2), which was not a surprise given the limited range in pH (almost all between pH 6.5 and 9.0) even within the very large range of samples scanned and analysed.

3.2 NIRS calibration model for manure organic nitrogen

Observations on N release from the manures have been similar across the first two years of results, with greatest recovery in the first grass cut from slurries, elevated N offtake from FYM samples extended to second and third cuts and a more even N release observed across all cuts from conditioned biosolids. An example of the N recovery from pig FYM is shown in Figure 3, with N uptake in the harvested grass expressed as % of manure N applied, across the three soil types used in the experiments. It is hoped that similar N release data for the 180 manure/biosolids samples

will provide a good basis for developing an NIRS calibration and, hence, a method for predicting the mineralization of organic N from these materials. A similar approach has been shown to have great potential for prediction of the performance of horticultural, organic potting mixes (Smith *et al*, 2001).

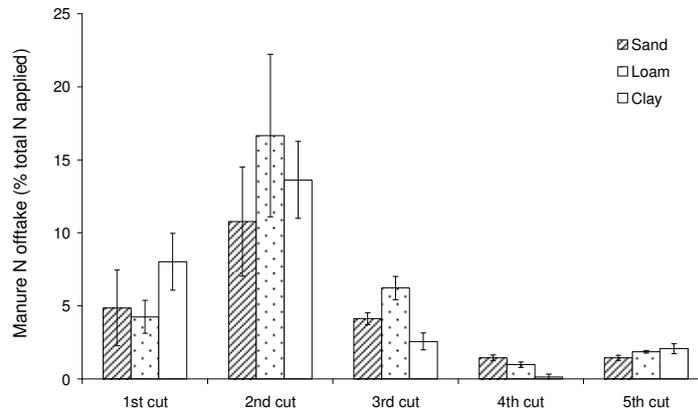


FIGURE 3 Nitrogen recovery from pig FYM across five cuts of ryegrass (year one 2008)

4 CONCLUSIONS

The research has confirmed the potential of NIRS to provide a rapid, reliable and reduced cost analysis capability for farm manures, slurries and biosolids. The calibration models for conventional analysis parameters were improved by the exclusion of very dilute effluents, where the low solids content and very low nutrient content appears to reduce the reliability of the reflectance assessment. It is therefore suggested that a threshold limit of ca. 0.5% solids be set, below which NIRS should not be used for sample analysis. It is envisaged that the development of a predictive capability for mineralization of manure organic N will enhance interest in NIRS as an analytical tool.

The high level of interest in the research at local and national farming events, confirms the potential of the technique to encourage manure analysis as a strategic tool to improve manure and nutrient management, resulting in economic benefits at the farm level and a significant contribution to reducing environmental emissions.

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