



## The potential of NIR spectroscopy to predict nitrogen mineralization in rice soils

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### Abstract

Prediction of nitrogen (N) mineralization is important for specifying the optimum rate of N fertilizer for flooded rice at the time of sowing. To develop a predictive test, soils (0–0.1 m) were sampled from 22 farms throughout the rice-growing region of southern Australia over a 4-year period. Near infrared reflectance (NIR) spectra of the soils were compared with sixteen biological and chemical soil tests for the prediction of N-uptake by rice plants from these soils in the field and glasshouse. The aim of the study was to develop a soil-NIR calibration as an accurate, rapid and economical mineralization test. Nitrogen uptake by field-grown and glasshouse-grown plants was poorly correlated ( $r = 0.30$ ), even though significant NIR calibrations were developed with both. Since N uptake by rice in the field was affected by varying weather and management, the field calibration is probably spurious. The calibration of soil NIR spectra with N uptake by glasshouse plants was satisfactory, with a standard error (SE) of 13 kg ha<sup>-1</sup> over a range of 11 – 95 kg ha<sup>-1</sup>, and a correlation between calculated and measured N uptake ( $r = 0.87$ ,  $P < 0.001$ ). An even better soil-NIR calibration was found with N-mineralization after 21 days of anaerobic incubation (SE 16 mg kg<sup>-1</sup>, range 52–175 mg kg<sup>-1</sup>). Analysis of the soil spectra showed that similar wavelengths were correlated with both plant-N uptake and mineralization. NIR spectroscopy shows considerable potential to predict soil N mineralization, and may assist future fertiliser decision support.

### Introduction

Prediction of the supply of nitrogen (N) by the soil is needed to specify the optimum amount of fertilizer N, and to minimise environmental degradation from excess N. There are many tests of plant-available N from the soil, as well as direct and indirect measures of plant N uptake (Bundy and Meiseinger, 1994; Drinkwater et al., 1996). Most N tests apply to upland crops and aerobic soils, which differ in critical respects from flooded soils used for growing lowland rice. For upland crops, mineral N accumulated before sowing is mostly available for plant uptake, either directly from the topsoil or from the subsoil after leaching. In con-

trast, for lowland rice, any nitrate accumulated before sowing is lost by denitrification at the time of flooding. Furthermore, mineral N in the subsoil is mostly unavailable because of the shallow roots of lowland rice (Heenan and Thompson, 1984).

The most appropriate soil N tests for lowland rice are therefore those that predict the supply of mineral N during crop growth. These include measures of potentially mineralizable N, as defined by Stanford and Smith (1972), and by aerobic or anaerobic incubations (Campbell et al., 1997; Curtin and Wen, 1999; Jalil et al., 1996; Narteh and Sahrawat, 1997; Sahrawat, 1983). The limitations of soil mineralization for a commercial test are the time and cost of measurement, even for short-duration incubations such as the 2-day test proposed by Sahrawat (1998). Alternatively,

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promising results have been obtained with chemical extractants (Gianello and Bremner, 1986; Hong et al., 1990; Smith and Shengxiu Li, 1993) and the use of hot 2M KCl for releasing ammonium has been promoted by Jalil et al. (1996) and Campbell et al. (1997).

There has been less attention to the use of near infrared reflectance (NIR) techniques as tests of soil-N supply. NIR spectroscopy offers the advantages of rapid and low-cost analysis, and is currently used for the routine analysis of grain, stockfeed, food and pharmaceutical products (Batten, 1998). NIR spectroscopy has been evaluated for soil testing by Meyer (1989) who found a high correlation with mineralizable N, defined as the ammonium-N liberated upon Walkely-Black digestion. NIR spectra have also been correlated with N uptake by wheat (Börjesson et al., 1999) and rice (Dunn et al., 2001), in both cases for soils collected from a small area.

The objective of this study was to evaluate NIR spectroscopy as a commercial pre-sowing test for soil-N supply to irrigated rice in south-eastern Australia. Rice is produced on about 8000 fields each year and on a wide range of soil types in a region that extends over 40 000 km<sup>2</sup>. The average annual application of fertilizer N is about 110 kg ha<sup>-1</sup> and the range is from zero to 200 kg ha<sup>-1</sup>. Much of the N fertilizer is top-dressed at the panicle initiation stage, with the optimum application rate specified by a plant test and decision support system (Angus et al., 1996; Batten et al., 1991). However, N fertilizer incorporated in the soil before sowing is used more efficiently by rice crops than N top-dressed at the panicle initiation stage, provided that the application rate is not excessive (Angus et al., 1990). The reason that top-dressing has persisted is that there is less risk of over-fertilizing, which leads to yield loss from lodging and increased cold damage (Heenan and Lewin, 1982; Williams and Angus, 1994). A test to predict soil-N supply is needed to specify the optimum rate of N fertilizer applied at the time of sowing.

## Materials and methods

### *Soil and plant data*

Soil samples were collected from 22 field experiments conducted on commercial farms throughout the Riverina region of southern New South Wales between 1995 and 1998. The fields were selected to represent the wide geographical distribution of rice-growing and

the diverse crop sequences in the industry, from continuous rice-growing to rice grown after a long period of pasture. The control plots in each experiment were about 70 m<sup>2</sup> in area (10 m × 7 m) and the soil sample from each plot consisted of a composite of 10 cores, 0.1 m deep, collected with a 50 mm diameter sampling tube. Soil samples were air dried in a glasshouse for 3–4 weeks, then crushed, sieved (<2 mm) and milled in a centrifugal grinder with a 2 mm mesh. The prepared samples were stored air-dry in re-sealable plastic bags. Sub-samples of these soils were analysed for the following general soil properties: available phosphorus (modified bicarbonate or Colwell method), cation exchange capacity (cec), and pH (CaCl<sub>2</sub>, 0.01 M) by standard methods (Rayment and Higginson, 1992) in a commercial laboratory.

Within a week of soil sampling, the experimental areas were flooded and broadcast with pre-germinated rice (*Oryza sativa* cv. Amaroo) seed by aircraft at a rate of 120 kg ha<sup>-1</sup>. At each experimental site the above-ground N uptake in the crop was measured at panicle initiation, a developmental stage about 10–11 weeks after sowing. Panicle initiation N (PIN) uptake was calculated as the product of plant tissue N concentration, derived by NIR spectroscopy (Batten et al., 1991), and above-ground dry weight. This measure was obtained from duplicate 1 m<sup>2</sup> quadrat cuts within each control plot in each of three replicates of the experiment.

### *Glasshouse study*

In a glasshouse controlled to keep the temperature between 20 and 30 °C, triplicate samples (300 g) of the soils from each experimental site were mixed with fine sand (1:1) inside plastic bags and placed into small pots within a 1 m<sup>2</sup> basin. The base of each soil bag was pierced in three places and the basin filled with water to the height of the pots (95 mm). Five pre-germinated seeds were placed on the surface of each pot, the water level maintained just above the soil surface for the first week and then raised to at least 0.05 m above the soil surface for the duration of the study. Ten weeks after commencement, at about the panicle initiation stage, the rice shoots were harvested at the soil surface, dried (70 °C for 48 h), weighed, replicates bulked, finely ground and analysed for total N by combustion (Europa Scientific ANCA-NT preparation module, Crewe, UK).

### Soil tests

Soil tests were made on the 22 soils and the data related to N uptake by plants in the field and glasshouse experiments. The soil tests consisted of biological methods based on aerobic and anaerobic incubation, soil chemical analyses, and calibrations of soil NIR spectra against plant N uptake measures.

### Biological tests

Ten soil biological tests were evaluated for their relationship with rice N uptake (Table 1). Soils were incubated both aerobically and anaerobically simultaneously in a constant-temperature cabinet. Aerobic incubations were conducted on 5 g of soil mixed with 10 g fine quartz sand and 2 mL of deionized water in a 70 mL vial. The vials were then enclosed inside 500 mL sealed glass jars to which 5 mL of water had been added to reduce evaporative loss from the soil. The jars were opened and aired every 4 days to prevent development of anaerobic conditions. Anaerobic incubations were conducted in 70 mL vials to which 5 g of soil and 30 mL of deionised water were added, the vials sealed and incubated (Waring and Bremner, 1964). All soils were incubated in duplicate at 40 °C and the inorganic N content was measured after 10 and 21 days. Un-incubated and incubated samples were extracted with 2 M KCl solution, the solutions filtered and analysed for ammonium-N and nitrate-N by a segmented flow auto-analyser (Alpkem, Wilsonville, OR, USA).

The biological tests determined in this study were based on the aerobic (O=Oxic) or anaerobic (A=Anaerobic) incubations after 10 and 21 days, for both the gross (G) and net (N) accumulation of inorganic N after incubation (Table 1).

### Chemical tests

Six soil chemical tests were evaluated for their relationship with rice N uptake. These included: initial ammonium-N ( $\text{NH}_4^+$ -N) content, total soil carbon (TSC), total soil nitrogen (TSN), the soil carbon to nitrogen ratio (C:N), and two measures derived from a hot KCl ammonium-N extraction method (Gianello and Bremner, 1986). Ammonium-N was measured as described above and TSC, TSN and C:N were measured by Dumas combustion analysis. For the tests involving hot KCl, 5 g of soil and 30 mL of 2 M KCl were placed in 100 mL acid digestion tubes, the tubes were mixed individually by vortex, fitted with

glass funnels, placed in a block digester and boiled ( $\sim 120^\circ\text{C}$ ) for 4 h. The samples were then cooled to room temperature, made up to 100 mL with 2 M KCl, mixed, allowed to settle, filtered, refrigerated and analysed for  $\text{NH}_4^+$ -N. Two estimates of hot-KCl extraction are presented from these data: gross (HKG) and net (HKN), where net extraction was calculated as  $\text{HKN} = \text{HKG} - \text{NH}_4^+\text{-N}$ .

### Soil NIR calibration

Soil NIR spectra were evaluated for their relationship with rice N uptake. A near infrared scanning spectrometer (model 6500, NIRSystems Inc., Silver Spring, MD, USA) was used to obtain soil absorption spectra at 2 nm wavelength intervals from 400 to 2500 nm. Each spectrum was the average of 30 scans of a standard sample cell with a quartz front containing  $\sim 10$  g of soil. Each sample was scanned in duplicate and the spectra averaged. NIR calibrations were performed by partial least squares (PLS) regression using 'The Unscrambler' Version 7.01 (Camo A/S, Trondheim, Norway). According to Börjesson et al. (1999)

'PLS is a multivariate linear calibration technique that produces projections in a few dimensions of a data matrix with many variables. Thus, a large number of variables are reduced to a few latent variables (components). These orthogonal components are used in the regression and problems with the otherwise strong dependence between wavelengths are avoided'.

The PLS models were validated using full cross validation, explained as follows by Börjesson et al. (1999):

'With this technique, models were constructed leaving one sample out each time and then the models were tested on the omitted sample. This was repeated until all the samples had been tested once. The number of components to be used in the PLS-models was selected according to maximum explained variance in the cross-validated samples'.

The calibrations were evaluated from their standard errors of cross-validation (SECV) and correlation coefficients ( $r$ ) between measured and calculated values. The  $r$  values provide a comparison of the NIR calibrations with the biological and chemical soil tests.

The best calibration was judged to be the one with the lowest SECV, and in this study 8 calibrations were evaluated. These calibrations tested four mathematical treatments of two spectral bands (400–2500 nm and 1100–2500 nm), all with full cross validation.

Table 1. Summary statistics for the general soil properties, rice nitrogen uptake measures, and the biological and chemical soil tests ( $n = 22$ )

Name	Property	Units	Mean	CV (%)	Min.	Max.
<b>General soil properties</b>						
P	Available phosphate (Colwell)	mg kg <sup>-1</sup>	31	n.a.	8	91
cec	Cation Exchange Capacity	cmol kg <sup>-1</sup>	20	n.a.	7	30
pH	Soil pH		6.2	n.a.	5.0	8.6
<b>Nitrogen uptake by rice plants at panicle initiation</b>						
PIN-Field	Panicle Initiation Nitrogen in Field Plots	kg ha <sup>-1</sup>	45	14	13	76
PIN-GH	Panicle Initiation Nitrogen in Glasshouse	kg ha <sup>-1</sup>	56	15	11	95
<b>Biological soil tests</b>						
O10G	Gross after 10 days aerobic incubation <sup>a</sup>	mg kg <sup>-1</sup>	62	10	33	110
O21G	Gross after 21 days aerobic incubation	mg kg <sup>-1</sup>	85	20	40	144
A10G	Gross after 10 days anaerobic incubation	mg kg <sup>-1</sup>	93	9	53	142
A21G	Gross after 21 days anaerobic incubation	mg kg <sup>-1</sup>	112	12	52	175
O10N	Net after 10 days aerobic incubation <sup>b</sup>	mg kg <sup>-1</sup>	44	14	16	90
O21N	Net after 21 days aerobic incubation	mg kg <sup>-1</sup>	66	25	22	123
A10N	Net after 10 days anaerobic incubation	mg kg <sup>-1</sup>	84	9	49	130
A21N	Net after 21 days anaerobic incubation	mg kg <sup>-1</sup>	103	13	52	157
OD	Difference between 10 and 21 days-aerobic	mg kg <sup>-1</sup>	23	73	0	50
AD	Difference between 10 and 21 days-anaerobic	mg kg <sup>-1</sup>	19	69	-1	45
<b>Chemical soil tests</b>						
NH <sub>4</sub> -N	Ammonium nitrogen	mg kg <sup>-1</sup>	9	9	3	22
TSC	Total soil carbon	g kg <sup>-1</sup>	16	n.a.	9	22
TSN	Total soil nitrogen	g kg <sup>-1</sup>	1.5	n.a.	0.9	2.6
C:N	Soil carbon to nitrogen ratio		10.2	n.a.	8.6	11.7
HKG	Hot KCl - NH <sub>4</sub> <sup>+</sup> -N, gross	mg kg <sup>-1</sup>	84	4	37	127
HKN	Hot KCl - NH <sub>4</sub> <sup>+</sup> -N, net	mg kg <sup>-1</sup>	70	5	37	98

n.a.: not available.

<sup>a</sup> Gross = total concentration of inorganic-N.

<sup>b</sup> Net = total concentration of inorganic-N minus the original concentration.

The mathematical treatments were; nil, multiplicative scatter correction, standard normal variate, and first derivative. The predictive ability of NIR calibrations for different constituents (ie properties) were compared by the range error ratio (RER), defined as the range of data divided by SECV (Starr et al., 1981).

#### Data analysis

Inorganic-N liberated by the biological and chemical methods was expressed as mg kg<sup>-1</sup>. Plant N uptake in the field and glasshouse was expressed as kg ha<sup>-1</sup>. In the case of glasshouse plants, these values were calculated from the plant uptake per pot, assuming that the N was extracted from a land area containing the

weight of soil in the pot, that the bulk density was 1.3 g cm<sup>-3</sup>, and the effective rooting zone was 0.1 m. This bulk density and a high concentration of roots in the top 0.1 m have been observed in this region by Angus et al. (1994) and Heenan and Thompson (1984).

The precision of the soil and plant tests is presented as coefficients of variation, calculated from analysis of variance of all data sets from the 22 experimental sites and the replicate measurements.

#### Results

The soils varied widely in all properties measured, as did plant N uptake (Table 1). None of the gen-

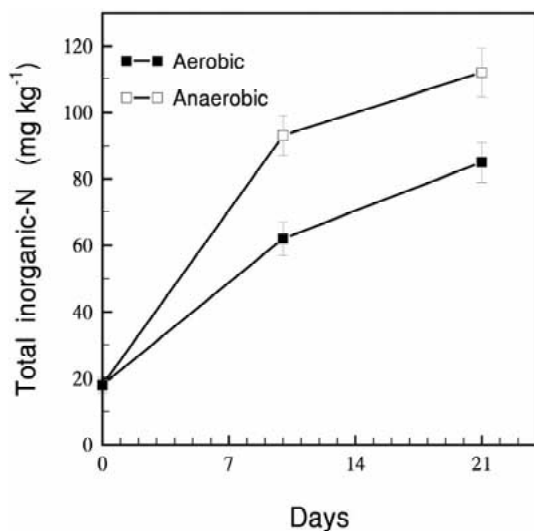


Figure 1. Mean accumulation of inorganic-N during incubation under aerobic and anaerobic conditions for the 22 soils. Bars indicate standard errors of the mean.

eral soil properties (ie available phosphorus, cation exchange capacity or pH) were correlated with plant N uptake or the soil N tests ( $P < 0.05$ ). Plant N uptake in both the field and glasshouse exhibited a similar precision of measurement, with coefficients of variation around 15% (Table 1). For gross mineralization measures, the coefficients of variation ranged from 9 to 20%, but estimates of net mineralization were less precise. Mineralization measures determined over 10 days incubation were generally more precise than those derived from 21 days incubation. The most precise measurements were the chemical extractions,  $\text{NH}_4^+$ -N, HKG and HKN.

#### Incubation dynamics

Inorganic-N accumulation was measured after 10 and 21 days of incubation under aerobic and anaerobic conditions. After 21 days, the amounts accumulated ranged from 40 to 144  $\text{mg kg}^{-1}$  under aerobic conditions and from 52 to 175  $\text{mg kg}^{-1}$  under anaerobic conditions. These amounts represented less than 10% of the organic N in the soils. Averaged over the 22 soils, accumulation under anaerobic conditions was about 30  $\text{mg kg}^{-1}$  greater than under aerobic conditions at both sampling times (Figure 1). Mineralization was about four times more rapid during the first 10 days of incubation than the following 11 days, and about 80% of the inorganic N accumulated during the first 10 days (Figure 1). The amounts of inorganic

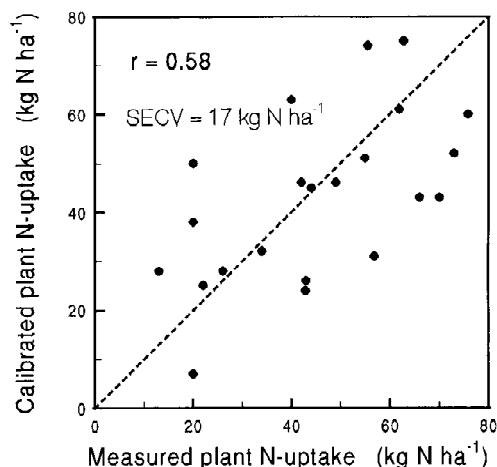


Figure 2. Calibration of soil NIR spectra with N-uptake by rice plants in the field at the panicle initiation stage (PIN-Field), using a one-out cross-validation routine. The broken line shows the 1:1 relationship, SECV = standard error of cross validation.

N liberated under aerobic and anaerobic conditions were correlated after incubation for 10 days ( $r = 0.81$ ,  $P < 0.001$ ) and 21 days ( $r = 0.77$ ,  $P < 0.001$ ). Nitrate-N comprised about one half of the inorganic-N prior to incubation, one third after aerobic incubation, and was undetectable after 10 and 21 days of anaerobic incubation (data not shown).

#### Plant N uptake and soil tests

Although the N uptake by field-grown and glasshouse-grown plants were of similar magnitude and range, they were poorly correlated ( $r = 0.30$ ). Nitrogen uptake by plants in the field was not correlated with any biological or chemical soil test ( $P < 0.05$ ). Conversely, correlations occurred between all soil tests and plant N-uptake in the glasshouse ( $P < 0.05$ ). A correlation matrix of soil tests that were correlated ( $P < 0.001$ ) with PIN-GH, along with their correlations with PIN-Field, is outlined in Table 2. In general, the biological tests were more highly correlated with PIN-GH than the chemical tests, and the anaerobic tests had higher correlations than the aerobic tests.

For both PIN-Field and PIN-GH, the best calibrations with soil NIR spectra resulted from a first derivative transformation of the 1100–2500 nm spectra. The calibration for PIN-Field had a SECV of 17  $\text{kg N ha}^{-1}$  over a data range of 13 – 76  $\text{kg N ha}^{-1}$ , giving a RER of 3.7 which is an unpromising basis for a calibration (Figure 2). The soil NIR calibration of PIN-GH was better than PIN-Field, with a RER of

Table 2. Correlation matrix for nitrogen uptake by plants grown in the glasshouse (PIN-GH), field (PIN-Field) and soil tests for which the correlation with PIN-GH was  $P < 0.001$  ( $r > 0.63$ ). The last row shows the correlations between the NIR calibration for N uptake by glasshouse grown plants (PIN-GH) and the other tests. The abbreviations are as for Table 1

	PIN-GH	PIN	O10G	O21G	A10G	A21G	A21N	TSC	TSN	HKG	NIR-GH*
PIN-GH	1.00										
PIN-Field	0.30	1.00									
O10G	0.82	0.01	1.00								
O21G	0.80	-0.10	0.91	1.00							
A10G	0.81	0.04	0.81	0.73	1.00						
A21G	0.92	0.16	0.83	0.77	0.93	1.00					
A21N	0.89	0.20	0.80	0.74	0.94	0.99	1.00				
TSC	0.77	0.07	0.71	0.63	0.73	0.79	0.76	1.00			
TSN	0.76	0.14	0.75	0.65	0.77	0.82	0.79	0.96	1.00		
HKG	0.74	0.08	0.68	0.59	0.73	0.79	0.74	0.89	0.85	1.00	
NIR-GH <sup>a</sup>	0.87	0.58	0.74	0.72	0.77	0.85	0.82	0.75	0.71	0.69	1.00

<sup>a</sup>NIR-GH = Predictions from the calibration of soil NIR spectra against PIN-GH.

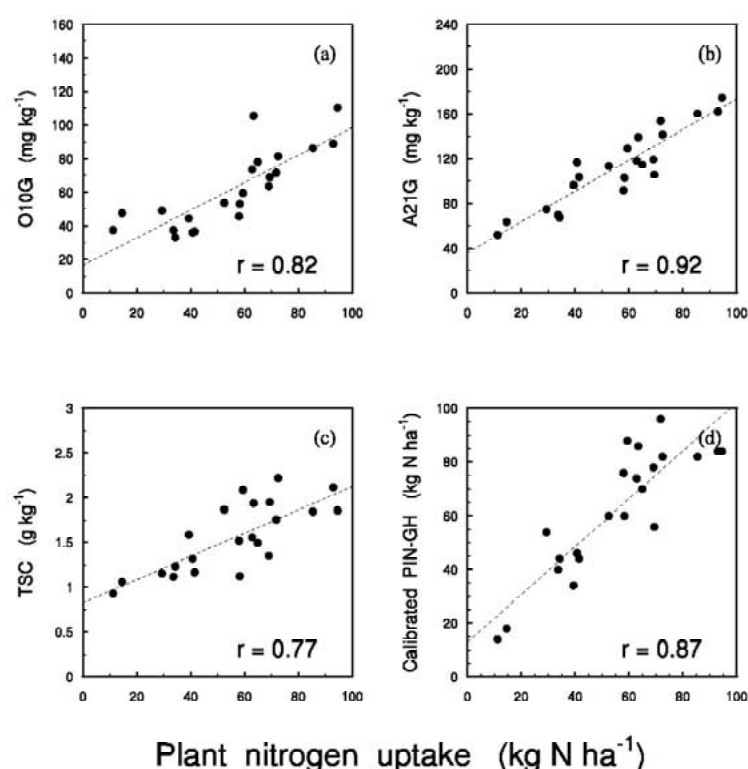


Figure 3. Relationships between the plant N-uptake of rice grown in the glasshouse (PIN-GH) and (a) aerobic incubation (O10G), (b) anaerobic incubation (A21G), (c) total soil carbon (TSC), and (d) NIR calibration. Variables allocated to Y axes are defined in Table 1. Broken lines are the lines of best fit.

6.5, based on a SECV of  $13 \text{ kg ha}^{-1}$  over a range of  $11 - 95 \text{ kg N ha}^{-1}$ .

The best tests from the four categories of aerobic incubations, anaerobic incubation, chemical and NIR, were selected for closer examination on the basis of their correlations with PIN-GH. The relationships

between PIN-GH and these tests are shown in Figure 3. Scrutiny of the data showed that there were no consistent outliers.

Due to the strong association between PIN-GH and A21G (Table 2 and Figure 3), soil NIR spectra were calibrated against A21G. This calibration gave a

SECV of  $16 \text{ mg N kg}^{-1}$ , over a data range from 52 to  $175 \text{ mg N kg}^{-1}$ , which yielded an RER of 7.7 and a high correlation ( $r = 0.89$ ) between measured and calculated A21G (Figure 4). This was the strongest NIR calibration identified in the study.

A correlation analysis of PIN-GH and A21G, with the absorption at individual wavelengths across the soil spectra (first derivative, 1100–2500 nm), showed remarkably similar patterns (Figure 5). The  $r$ -values from the two parameters were themselves correlated ( $r = 0.90$ ,  $P < 0.001$ ). The wavelengths that correlated most strongly with both properties formed a broad range from 1950 to 2100 nm and a sharp peak around 2250 nm. These areas contrast markedly with the active wavelengths for nitrogen mineralisation of upland soils reported by Börjesson et al. (1999).

## Discussion

NIR spectra can be calibrated against the supply of mineral nitrogen to flooded rice, as measured by soil tests and plant-N uptake. NIR spectroscopy therefore cannot directly provide a nitrogen availability index as defined by Bundy and Meisinger (1994), but may provide data correlated with such an index. The important question for this study is whether NIR is likely to lead to a reliable soil test for N supply to rice. The number of data points needed for a commercial NIR-based test is usually in the hundreds or thousands, rather than the 22 available here, so this study is intended to assess the feasibility of a test rather than develop a commercial test.

The ideal NIR-based test would be one that predicted N uptake by rice plants in the field. At first glance, the correlation ( $r = 0.58$ ) in Table 2 suggests that the NIR calibration with N-uptake in the field is promising. However, there was low correlation ( $r = 0.30$ ) between N uptake by plants growing in the field and in the same soils in the glasshouse. It is unlikely that the association was low because of imprecise data, since the coefficients of variation for the field and glasshouse data were similar and less than 15%. The probable reasons for the poor association is that field-grown plants experienced varying environmental conditions and their roots were in contact with subsoils, while glasshouse-grown plants experienced the same environment and their roots made no contact with the subsoil. The environmental factors were presumably the effects of temperature on N mineralization, and the effects of temperature and solar

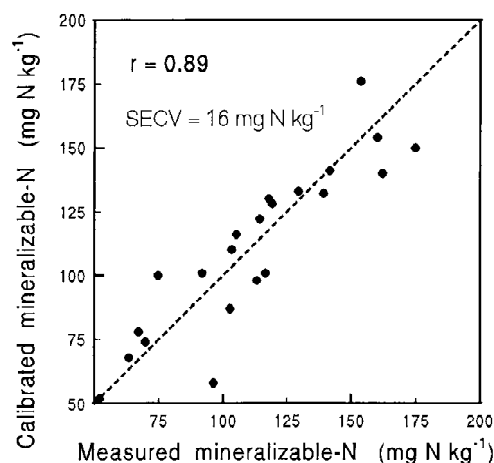


Figure 4. Calibration of soil NIR spectra with mineralizable-N (A21G) using a one-out cross-validation routine. The broken line shows the 1:1 relationship, SECV = standard error of cross validation.

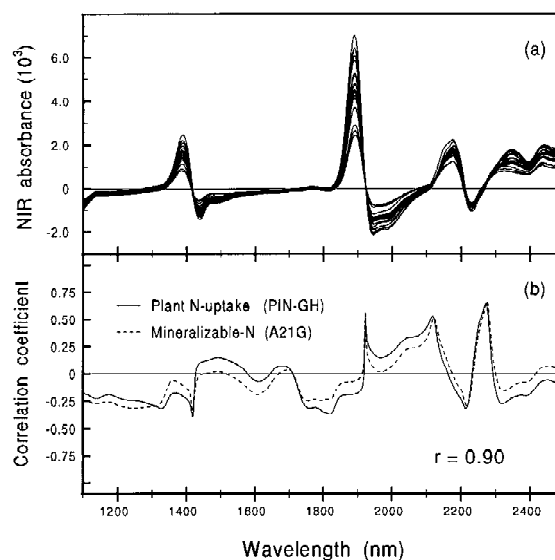


Figure 5. Soil NIR absorbance spectra, (a) first derivative of the spectrum for each soil, and (b) their correlation with measures of plant N-uptake (PIN-GH) and mineralizable-N (A21G) across the spectrum (i.e. 1100–2500 nm).

radiation on plant growth and N demand. The soil factors were probably related to topsoil depth, which is affected by whether the sampling point was exposed subsoil (scrape) or additional topsoil (fill) during the process of levelling. The puzzling aspect is how there could be satisfactory NIR calibrations for N uptake of plants in the field and glasshouse, when the correlation between these two sets of data was so low. The correlation between NIR spectra and N-uptake in the field

(Figure 1), although significant, is probably spurious because of over-fitting NIR with a small number of samples. A NIR-based soil test calibrated on plant-N uptake is therefore unlikely to be suitable for commercial use. The low initial levels of ammonium-N in the soils suggest they had dried out sufficiently quickly to prevent appreciable mineralization. The initial amount of ammonium-N in the soil was 8% of that available after 21 days of anaerobic incubation, equivalent to 24% of N uptake by rice plants in the glasshouse. N-uptake in the glasshouse was effectively unrelated to initial ammonium-N content ( $r = 0.25$ ) while the process of mineralization during 21 days of anaerobic incubation was closely related to N uptake ( $r = 0.89$ ).

The strong association between N uptake in the glasshouse and all the biological indices suggests that incubating soils at temperatures as high as 40 °C does not select microbial communities too divergent from those in the soils sown to rice in the glasshouse. Sahrawat (1998) and Angus et al. (1994) have previously investigated incubation temperatures as high as this for rice soils.

The high correlation and close approximation of inorganic-N accumulation between the anaerobic and aerobic incubations suggests that the two systems mineralised the same N substrates. The rate of anaerobic mineralization was greater than the aerobic mineralization for the first 10 days, but after that the rates were similar. The reasons for the difference are not clear. However, the higher correlations between anaerobic incubation and N uptake, suggests that anaerobic rather than aerobic incubation should be the preferred basis for a soil test.

The association between N uptake and the 21-day incubations were generally greater than for the 10-day incubation, suggesting that a soil test should be based on long-duration incubations, even though the precision of these tests was inferior. Other research suggests that short-duration incubations do not necessarily reflect the long-term N-supplying capacity and that the true rate of mineralization is revealed only after transient effects of crop residue, sample preparation and moisture content at sampling have passed (Hasegawa and Horie, 1994; Stanford and Smith, 1972). However, the later stages of incubation alone are not reliable indicators of mineralization, as shown by the lack of correlation of OD and AD with plant N uptake and their low precision.

The chemical extraction methods were much poorer than the incubation methods, supporting the results of Gianello and Bremner (1986) and Douglas

and Magdoff (1991). Presumably the advantage of incubation tests is that they simulate the action of soil microbes on N release. Even TSC was more highly correlated with crop N uptake than the chemical extraction methods. TSC has the additional advantage that it can be measured rapidly and cheaply by combustion.

The best soil NIR calibrations were derived from first derivative transformations of the 1100–2500 nm spectra. This mathematical treatment of soil spectra has previously been observed to give the best relationships with other soil properties (Reeves et al., 1999). Since there were high correlations between anaerobic incubation, plant N uptake in the glasshouse and the values for both, calculated from NIR calibrations, it is likely that these NIR calibrations detected the same fraction of soil N that is available for plant uptake and mineralization. The remarkable similarity in the correlations of soil spectra with plant-N uptake and anaerobic incubation supports this conclusion. Anaerobic incubation is quicker and cheaper to measure than plant-N uptake, and so is a preferred basis for developing an NIR calibration. Soil NIR calibrations have previously been performed only over the limited variation of soil type found in a single field (Dunn et al., 1999), adjacent fields (Börjesson et al., 1999), a single location (Malley et al., 1999) or two research sites (Reeves et al., 1999).

Whether an NIR-based prediction of mineralization is satisfactory depends on the accuracy of the test compared with the accuracy required for a recommendation. The use of RER as an estimate of accuracy is inadequate in this respect since the SECV refers to only one side of the error. The range of error is therefore twice the SECV. In this case the RER value of 7.5 shows that mineralization of soils in the region can be divided into about 4 classes. A classification into seven classes would be optimal for fertiliser recommendations, given that rice-growers typically specify N applications in increments of 30 kg ha<sup>-1</sup> and the range of applications is between 0 and 200 kg ha<sup>-1</sup>. However, a classification of even four categories would be an improvement on the present system in which rice-growers typically under-fertilize at the time of sowing and top-dress at the panicle initiation stage when nitrogen use efficiency is low. Continued development of an NIR-based calibration with a greater number of samples could lead to improved accuracy in predicting mineralization. Further development is also needed to extend the prediction of mineralization to a fertilizer recommendation. The method proposed is to extend



the simulation of crop-N in a decision support system (Angus et al., 1996).

## Conclusions

NIR spectroscopy has become a preferred method for plant chemical analyses in many laboratories. Batten (1998) listed the advantages as '(a) minimal sample preparation, (b) a short turn around time at the laboratory, (c) the need for only basic buildings, (d) minimal training of staff and (e) simultaneous determination of several constituents in every sample'. Applications of NIR to soil analysis has been less successful than for plant analysis, apparently because the calibrations have been less accurate. Possible roles for NIR spectroscopy for soil tests may be for low-cost screening of several properties or constituents (Dunn et al., 2002; Stenberg et al., 1995), and as an alternative to slow procedures such as incubations, as in this study. In both situations a large number of soil samples is needed for calibration and the samples must span a wide range of values. If ruggedized NIR spectrometers become available, they may even be extended beyond the laboratory to provide analyses of N mineralization *in situ* just before N application. Such a development would overcome the current delays during which soils continue to mineralize between sampling and N application, and would encourage the adoption of new management technologies such as variable-rate fertilizer application.

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