



RICE CRC

FINAL RESEARCH REPORT

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Research Organisation Name :	NSW Agriculture
Principal Investigator Details :	
Names :	Brian Dunn and Geoff Beecher
Address :	Yanco Agricultural Institute Private Mail Bag Yanco NSW 2703
Telephone contact :	(02) 6951 2621

THE ESTIMATION OF SOIL SODICITY AND pH USING NIR SPECTROSCOPY

Brian Dunn ^{1,2} and Geoff Beecher ^{1,2}

¹Cooperative Research Centre for Sustainable Rice Production
C/- Yanco Agricultural Institute
PMB Yanco 2703
Email: brian.dunn@agric.nsw.gov.au
<http://www.ricecrc.org>

²NSW Agriculture
Yanco Agricultural Institute
PMB Yanco 2703
Email: brian.dunn@agric.nsw.gov.au

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SUMMARY

Surface soil sodicity is a major cause of reduced rice grain yields in the Western Murray Valley rice growing areas of New South Wales. Rice soils can have a large range of surface sodicity within the same field. Although gypsum applications can reduce the problem of high surface soil sodicity, gypsum has the disadvantage of increasing potential recharge to the watertable by increasing infiltration. Therefore it is extremely important that gypsum only be applied where necessary.

Low soil pH and variations in soil pH across rice fields has been identified and could be best managed by differential lime applications. In irrigated agricultural systems, lower soil pH results in poor plant growth and reduced yield especially for plant species sensitive to acid soils. If the within field variability of soil sodicity or pH can be easily evaluated then it may be economic to apply gypsum or lime at variable rates across the field.

Near-infrared reflectance spectroscopy (NIRS) technology has the potential to provide a rapid, low cost analysis enabling within field variability to be identified. NIRS was evaluated for its ability to predict a range of soil properties in the Riverine Plain soils of southern NSW.

The results demonstrated that NIRS can successfully determine some soil properties in both the topsoil and subsoil. The large range of samples obtained from many soil types, combined with the method used in this study, gives us confidence that the results achieved would be commercially applicable in the Riverine Plain soils of southern NSW. The results achieved would be suitable for use in site specific agriculture where the aim is to divide a field into a number of management zones. In the topsoil, CEC, exchangeable Ca and Mg, pH, Ca:Mg ratio and possibly OC, ESP and Al% were all adequately predicted by NIRS for use in site specific agriculture. Whilst in the subsoil, CEC, exchangeable Na, Ca, Mg, ESP, pH and Ca:Mg ratio were all adequately predicted for use in site specific agriculture.

Soil samples are normally air dried and crushed to pass a 2mm sieve before being scanned by NIRS. Experiments identified that further processing of samples to decrease their particle size does not improve and in the case of CEC reduces their predicability using NIRS. It is recommended that normal soil preparation is adequate.

The predictive ability of NIRS for many soil constituents makes it suitable for use in agricultural soil assessment for site specific agriculture in the Riverine Plain soils of southern NSW.

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1. BACKGROUND

Surface soil sodicity has been identified as a major cause of lower rice grain yields in the Western Murray Valley rice growing areas of New South Wales (Beale 1998). Rice soils can have surface sodicity ranging from 7 to 29 within the same field (P. Beale. pers. comm.) and although gypsum applications can reduce the problem, gypsum increases potential groundwater recharge by increasing infiltration (Slavich and Petterson 1992).

In irrigated agricultural systems, low soil pH results in poor plant growth and reduced yield especially for acid soil sensitive plant species. The environmental implications of past irrigation practices is increasing the awareness that irrigated cropping systems need to be managed so as to reduce groundwater accessions and increase water-use efficiency. Dunn and Beecher (2001) have identified low soil pH values and variations in soil pH levels with depth across rice fields, which could be best managed by differential lime applications. If the within field variability of soil sodicity or pH can be easily identified then it may be economic to apply gypsum or lime at variable rates across the field.

Implementation of precision (site specific) agriculture requires extensive spatial information on soil properties and conventional laboratory systems are too costly and labour intensive for generating the necessary data. The benefits of NIRS analysis fit in well with the requirements of soil analysis in precision agriculture. Soils are rarely homogeneous, Viscarra Rossel and McBratney (1998) suggest that accurate, rapid and economical methods are needed to obtain information on the fine-scale spatial variability of soil. Analysis of soil using NIRS could make the testing of many sites within a field economically viable, compared to the current practices of combining many samples to form a composite field sample, this would allow assessment and subsequent management/treatment of smaller zones within a field.

NIRS is accepted world-wide as a method for the analysis of many constituents in various tissues of many plant species (Batten 1998). The reasons for NIRS being adopted as a preferred analytical method include: minimal sample preparation, fast analysis, cost effective to analyse a single or batch of samples, several constituents can be determined simultaneously, non destruction of samples, no hazardous chemical used, and results can be very accurate (Batten 1998).

Analysis of soil using NIRS has been investigated for the determination of soil moisture, organic carbon (OC), electrical conductivity (EC), cation exchange capacity (CEC), pH, N, C, P, S, Ca, Mg, Na, K, Fe and Mn (Dalal and Henry 1986; Morra et al. 1991; Ben-Dor and Banin; 1995; Malley *et al.* 1999a; Malley *et al.* 1999b; Reeves *et al.* 1999, Chang *et al.* 2001). Some of the results achieved appear promising, but importantly many of the investigations involved either a limited number of samples, or the samples came from a limited number of

sites of similar soil type. To have widespread commercial usefulness NIRS must be a reliable analytical technique across a range of soil types where variations in the inorganic and organic components of soil are present.

2. OBJECTIVES

The objective of this work was to investigate the usefulness of NIRS in estimating various soil chemical properties, in soils of the Riverine Plain of South Eastern Australia. The aim was to then develop calibrations for ESP, pH, CEC and other soil constituents specifically for ricegrowing soils of the Riverine plain and test the prediction accuracy of the calibrations. Calibrations with suitable accuracy of prediction would have potential as quick, inexpensive commercial soil tests to farmers, agronomists, land managers and regulators.

3. INTRODUCTION

The Western Murray Valley yield lift project (Beale, 1998) identified poor rice crop establishment on dispersive sodic soils as a major cause of lower yields in the Western Murray Valley. In this area, 50 to 60% of rice soils have surface sodicity ranging from 7 to 29 often within the same field (Beale. pers. com.). Sodic soils slake producing fine particles which suspend in the flood water making it muddy in aerial sown rice crops, the field is flooded and pre-germinated seed dropped into the flooded bays. The muddy water reduces temperature and light levels at the seed and combined with seed burial and the loss of root grip for the young seedling, leads to poor establishment.

Gypsum application is the main soil amelioration technique utilised to date and when combined with reduced cultivation and shallow water management can reduce the problems associated with seedling establishment on sodic soils. Gypsum application rates need to be kept to a minimum because gypsum increases potential recharge to the watertable by increasing infiltration (Slavich and Petterson, 1992). Humphreys and Barrs (1998) reported that gypsum broadcast at 1.25 t/ha increased infiltration by 0.6 ML/ha, while 2.5 t/ha increased it by 0.9 ML/ha.

A low cost, quick sodicity test could be used to explore sodicity variation across rice fields and this could be used to decide between parts of a field which require gypsum or not. This would reduce recharge from areas within fields under a uniform application approach where gypsum would otherwise have been applied. No method is available which enables an accurate prediction of the most effective rate of gypsum application to ameliorate sodicity (Rengasamy and Churchman, 1999). Rates of gypsum application are generally limited by application costs and concern that higher rates increase infiltration.

A quick, inexpensive NIR based soil test would enable widespread field sampling at known locations (using Global Positioning System) to produce a surface soil sodicity map of the field. The current practice of applying an even rate (1.5 to 2.5 t/ha) over the entire field would cease and gypsum would only be applied to the areas within a field where it is required. Humphreys and Barrs (1998) stressed the importance of restricting gypsum use to problem areas only. The benefits would include reduced costs for gypsum and its application, reduced

recharge from excess gypsum applications and increased rice yields due to more uniform crop establishment.

An NIR soil sodicity calibration has considerable potential in precision farming. A quick, reliable NIR analysis, combined with GPS, has potential to assess sodicity across a field to much greater accuracy than the traditional test applied to bulk sampled soils. This precision farming system also offers an affordable solution to the monitoring of reclamation of sodicity over several years.

Soil sustainability is a major objective of the CRC for Sustainable Rice Production with soil acidity identified as a significant problem. The potential early identification of soil acidity issues using NIRS, at limited additional cost to the farmer, would be a major step forward in awareness and action on the problem.

4. METHODOLOGY

This project was made possible by the large archive of soils covering the full range of soil types in the ricegrowing and irrigation areas of the Murrumbidgee and Murray Valleys held at Yanco Agricultural Institute. These soils and their associated physical and chemical analyses were utilised in the project, making the NIRS soil calibrations obtained ready for use in these areas.

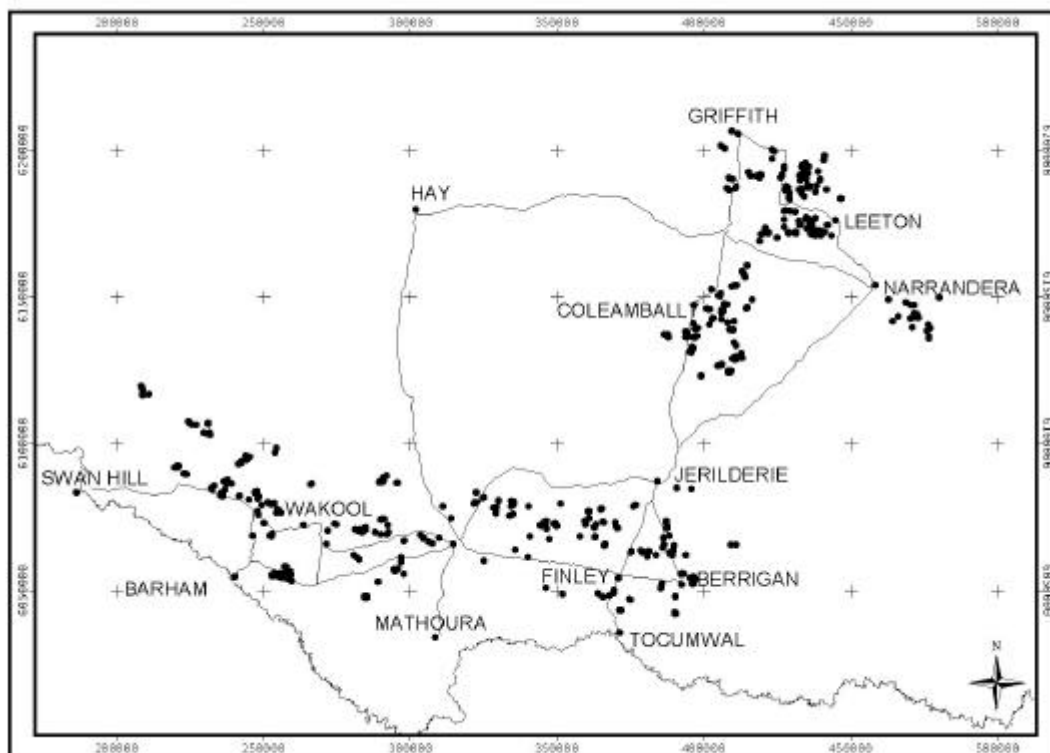
4.1 Collection of samples

Soil samples collected from over 550 sites covering the Murrumbidgee Irrigation Area, Coleambally Irrigation Area, Eastern Murray Valley and Western Murray Valley in southern NSW were used in this study. The distribution of sampling sites is shown in Figure 1. Sample sites covered all local major soil groups and a range of cropping histories. The majority of soil sampling sites had some history of irrigation and included horticultural, rice growing, mixed farming and grazing/dairying enterprises.

Samples were collected by 2 methods:

- A) 10 sites along a 100 m transect were sampled in 10 cm intervals to 50 cm, with equivalent depths bulked together (only 0-10 and 40-50 cm samples used in this study) or
- B) 12 to 15 samples, 0-10 cm deep from an area 6 m by 6 m square combined into a composite sample.

Figure 1: Map illustrating the distribution of sites where soil samples were collected. The x and y axis coordinates are Australian Map Grid, zone 55, in metres.



4.2 *Sample preparation*

The soil samples were air dried before being passed through a jaw crusher (Van Gelder Crushers Pty Ltd, Sydney). The samples were fed through the crusher a number of times until they passed a 2 mm sieve. Two sub samples were taken, one sample was analysed using standard methodologies by a commercial soil testing laboratory and the second sample was ground through a Glen Creston cross beater mill with a 2 mm screen. After passing through the cross beater mill 97% of the sample was less than 0.5 mm in size. This sample was scanned by NIRS spectroscopy. Batten (1987) reported that particle size has a significant influence on the absorbance of plant samples scanned by NIRS, but little research has been conducted on particle size for soil samples, so all samples were finely ground to overcome any such potential problems. During the project, research was conducted on the effect of soil particle size on the predicability of CEC, ESP and pH using NIRS (Section 7).

4.3 *Chemical analysis*

Chemical analysis of the samples was performed by Pivot Laboratories (Geelong, Australia). Exchangeable cations were determined by 0.1 M barium chloride combined with 0.1M ammonium chloride with no pretreatment for soluble salts, based on Gilman and Sumpter, 1986 (Rayment and Higginson 1992). The effective cation exchange capacity (CEC) was calculated on the sum of the exchangeable cations. Electrical conductivity (EC) from a 1:5 soil/water extract (Rayment and Higginson 1992) and pH was determined from a 1:5 soil/0.01M calcium chloride extract (Rayment and Higginson 1992).

Phosphorus was measured by the bicarbonate-extractable phosphorus method (Colwell 1963) with automated colorimetric finish based on Murphy and Riley (1962) (Rayment and Higginson 1992). The Walkley and Black method was used to determine organic carbon (Rayment and Higginson 1992). Mean, standard deviation, ranges and the number of soil samples for each chemical parameter are given in Table 1.

4.4 *Scanning by near infrared spectroscopy*

The air dried, crushed and milled soil samples were scanned with a NIRSystems model 6500 scanning spectrophotometer (Foss-NIRSystems, Silver Spring, MD, USA). Using the Near-infrared Spectral Analysis Software (NSAS), samples were scanned (32 scans per sample) from 400 to 2498 nm using a standard 50mm sample cup. Data was collected every 2 nm giving 1050 data points per spectrum. The spectra of 6 samples selected to cover the spectral range of soil samples used in this study are shown in Figure 2.

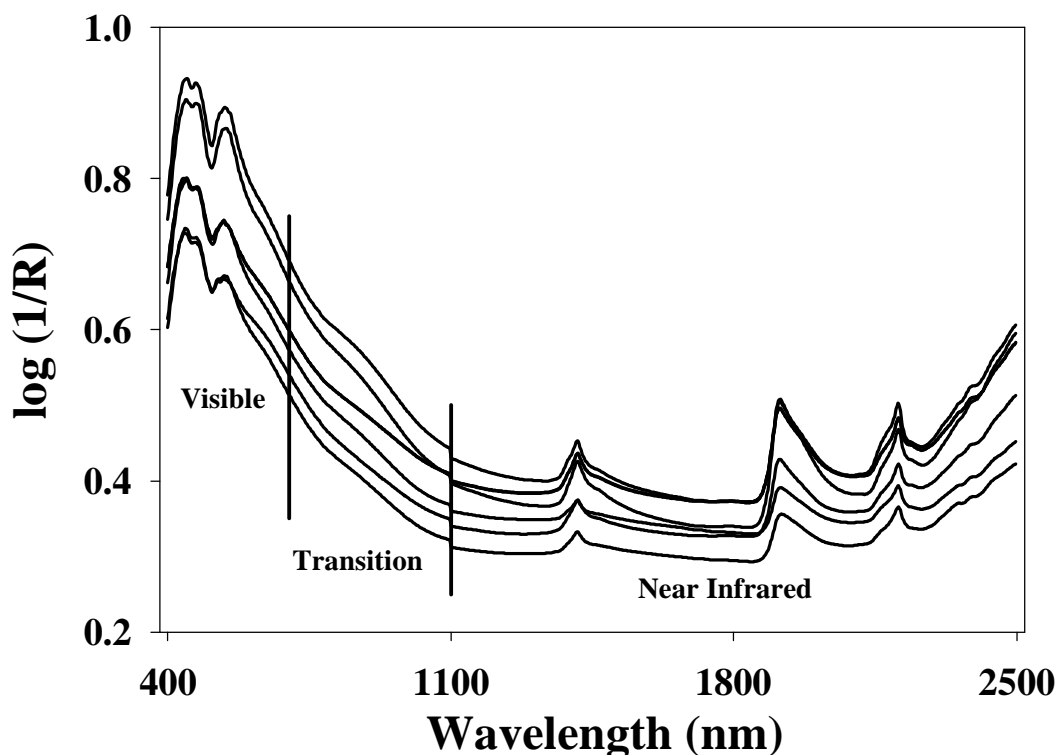
4.5 *Development of NIRS calibrations*

The Partial Least Squares (PLS) regression procedure was used to determine the best correlation (i.e. calibration) between the chemical reference data and the spectral data. The software WinISI II – version 1.02A (Infrasoft International LLC, Port Matilda, PA, USA) was used to develop the calibrations and test their validity. Not all samples were used for each calibration as concentration outliers that were very different from the general range of the samples were removed. No spectral outliers were removed from the 0-10 cm sample set. In the 40-50 cm sample set, 10 spectral outliers were identified using principle component analysis (WinISI II). The samples were a large spectral distance from the population mean and were very distinct outliers from the sample cloud. All 10 samples were found to have a

very low CEC (most below 4) and were deleted from the sample set before calibrations were developed.

For each constituent, the samples' chemical reference data was sorted from lowest to highest concentration. Every fourth sample and its data was moved to a separate file for use as a validation set. Calibrations were developed on the remaining samples. Organic carbon results were only available for 360 samples in the 0-10 cm depth.

Figure 2: Near-infrared spectra for 6 soil samples chosen to illustrate the variation in reflectance across the range of samples.



A combination of raw optical data, first and second derivatives combined with wavelength groups using the entire spectrum (400-2498 nm) and the NIR portion only (1100-2498 nm) and 2, 4 and 8 nm intervals were tested for each soil chemical property. The number of PLS terms suggested by the software were used, being 16 (0-10 cm) and 13 (40-50 cm) for all calibrations except organic carbon and Al which had less samples. A 4 nm gap (the gap over which the derivative is calculated) and 4 nm smoothing (small amount of smoothing of points) and “SNV and Detrend” scatter correction (software default conditions) were used for all calibrations. SNV scales each spectrum to have a standard deviation of 1 to help reduce particle size effects and Detrend removes the linear and quadratic curvature of each spectrum.

For all variables except P and exchangeable K the first derivative treatment using 1100 – 2498 nm wavelengths with a 2 nm interval gave the calibration with the best predictive ability. Using the second derivative with the same wavelengths gave the best results for exchangeable K, while normal spectra over 400-2500 nm wavelengths and 2 nm interval gave the most predictive calibration for P. The calibration results presented were obtained using no elimination passes in developing the calibrations.

The values of the various chemical constituents for which NIRS calibrations were developed are presented for the surface soil (0-10 cm) in Table 1 and the subsoil (40-50 cm) in Table 2. The samples used in the surface soil calibrations were collected using both sampling methods, whereas the samples used in the subsoil calibrations were the 40-50 cm samples taken by method 1. Overall, a wide range of values for most constituents were available, which is excellent for development of NIRS calibrations. Some data sets were skewed in their distribution. Exchangeable Al and Al% were severely skewed in the subsoil set with almost all the samples below the detectable limit of the laboratory chemistry (data not presented). Exchangeable Na, ESP and EC data sets were skewed in the topsoil but not in the subsoil sample set.

Table 1. Chemical characteristics of the 0-10 cm soil samples used in this study.

Variable	No. of samples	Mean \pm SD	Range
PH	555	5.21 \pm 0.73	3.8 – 7.3
EC, dS/m	555	0.13 \pm 0.07	0.01 – 0.51
P, Colwell, mg/kg	557	33 \pm 19	5 – 110
% Organic C	360	1.46 \pm 0.42	0.64 – 3.00
CEC, cmol(+)/kg	562	15.2 \pm 6.2	2.70 – 33.60
exch. Ca, cmol(+)/kg	562	7.20 \pm 3.45	0.90 – 21.00
exch. Mg, cmol(+)/kg	558	5.72 \pm 2.86	0.53 – 13.17
exch. Na, cmol(+)/kg	550	0.98 \pm 0.81	0.04 – 3.91
exch. K, cmol(+)/kg	559	0.91 \pm 0.31	0.20 – 2.10
exch. Al, cmol(+)/kg	220	0.41 \pm 0.35	0.1 – 1.50
% ESP	551	6.80 \pm 4.91	0.08 – 24.00
% Al	220	4.61 \pm 4.75	0.40 – 22.80
Ca:Mg ratio	551	1.39 \pm 0.58	0.42 – 3.51

Table 2. Chemical characteristics of the 40-50 cm soil samples used in this study.

Variable	No. of samples	Mean \pm SD	Range
PH	314	7.53 \pm 0.71	5.30 – 8.80
EC, dS/m	315	0.27 \pm 0.26	0.02 – 1.81
CEC, cmol(+)/kg	317	25.22 \pm 6.16	5.18 – 42.44
exch. Ca, cmol(+)/kg	317	10.55 \pm 3.52	2.39 – 20.21
exch. Mg, cmol(+)/kg	318	10.62 \pm 3.06	1.11 – 18.50
exch. Na, cmol(+)/kg	316	3.24 \pm 2.69	0.13 – 15.01
exch. K, cmol(+)/kg	318	0.74 \pm 0.27	0.22 – 1.77
% ESP	317	12.49 \pm 9.22	0.98 – 42.32
Ca:Mg ratio	316	1.03 \pm 0.36	0.35 – 2.23

4.6 Validation of Calibrations

In many NIRS studies with a limited number of samples, cross-validation [Standard Error of Cross-Validation (SECV)] is used to determine the predictive ability of a calibration. Cross validation is a method where each sample in the calibration is predicted to give an estimate of the prediction accuracy of the calibration and generally gives an over-optimistic idea of the actual performance of the model (Dardenne *et al.* 2000). In this experiment there were a large number of samples, so independent validation sets with samples unknown to the calibration were used to test the predictive ability of the calibrations.

All samples in the validation data set were used when testing the predictive ability of each calibration. As the soil samples were analysed by a commercial laboratory over three years with no duplication of samples to check accuracy, it is probable that there is error in the laboratory measurements. To check if outliers identified in the prediction process may have had incorrect analysis results, samples with the largest residuals from each soil variable prediction were re-analysed. Any samples with large differences in the replicated chemical analysis were removed from the validation set.

The best calibration is one with the highest coefficient of determination r^2 , and the lowest Standard Error of Performance (SEP), the standard deviation in the difference between the reference and the NIRS estimated values for samples in the validation set. But it is difficult to compare calibrations with different ranges for a constituent using only r^2 and SEP. For the value of a calibration to be put in perspective, comparing the SEP with the range and the standard deviation of the population is useful (Batten 1998). Two statistics often used for this purpose are the ratio of the standard deviation of values in the validation set to the SEP (known as RPD) and the ratio of the range in the validation set to the SEP (known as RER) (Williams 1987).

5. RESULTS

5.1 0-10 cm samples

For the surface soils the best predictive ability was achieved for CEC, with an RPD of 3.3, $r^2 = 0.90$ and SEP of 1.9 cmol(+)/kg (Table 3). pH (CaCl₂), exchangeable Ca and Mg and Ca:Mg ratio were also predicted well by the NIRS with RPD ≥ 2.2 , $r^2 \geq 0.79$ and SEPs of 0.31 pH units, 1.3 and 1.1 cmol(+)/kg and 0.26 respectively (Table 3). Other soil constituent predictions were ESP, OC%, Na and Al% with RPD ≥ 1.7 , and exchangeable K and Al with RPD ≥ 1.5 . EC and P were very poorly predicted with RPD < 1.3 (Table 3). Figure 3 provides an appreciation of the range and accuracy of many of these predictions.

Table 3: Calibration and prediction results for the 0-10 cm soil properties

Variable	Calib. R ²	SECa	No. Calib. Samples	Pred. r ²	SEPB	No. Pred. Samples	RPDc	RERd
pH	0.83	0.30	417	0.80	0.32	138	2.3	10.3
EC, dS/m	0.49	0.05	417	0.37	0.06	138	1.2	5.7
P, Colwell, mg/kg	0.27	16.1	418	0.18	18.0	139	1.1	5.8
% Organic C	0.62	0.26	270	0.66	0.25	90	1.7	8.8
CEC, cmol(+)/kg	0.88	2.19	422	0.90	1.88	139	3.3	14.8
Exch. Ca, cmol(+)/kg	0.87	1.23	422	0.86	1.26	139	2.7	13.7
Exch. Mg, cmol(+)/kg	0.91	0.88	419	0.85	1.05	139	2.7	10.3
Exch. Na, cmol(+)/kg	0.69	0.45	413	0.64	0.48	137	1.7	7.5
Exch. K, cmol(+)/kg	0.67	0.18	420	0.61	0.19	139	1.6	8.7
Exch. Al, cmol(+)/kg	0.60	0.22	165	0.58	0.23	55	1.5	5.9
% ESP	0.69	2.55	414	0.68	2.69	135	1.8	7.9
% Al	0.62	2.90	164	0.69	2.85	56	1.7	6.9
Ca:Mg ratio	0.87	0.21	414	0.79	0.26	136	2.2	11.1

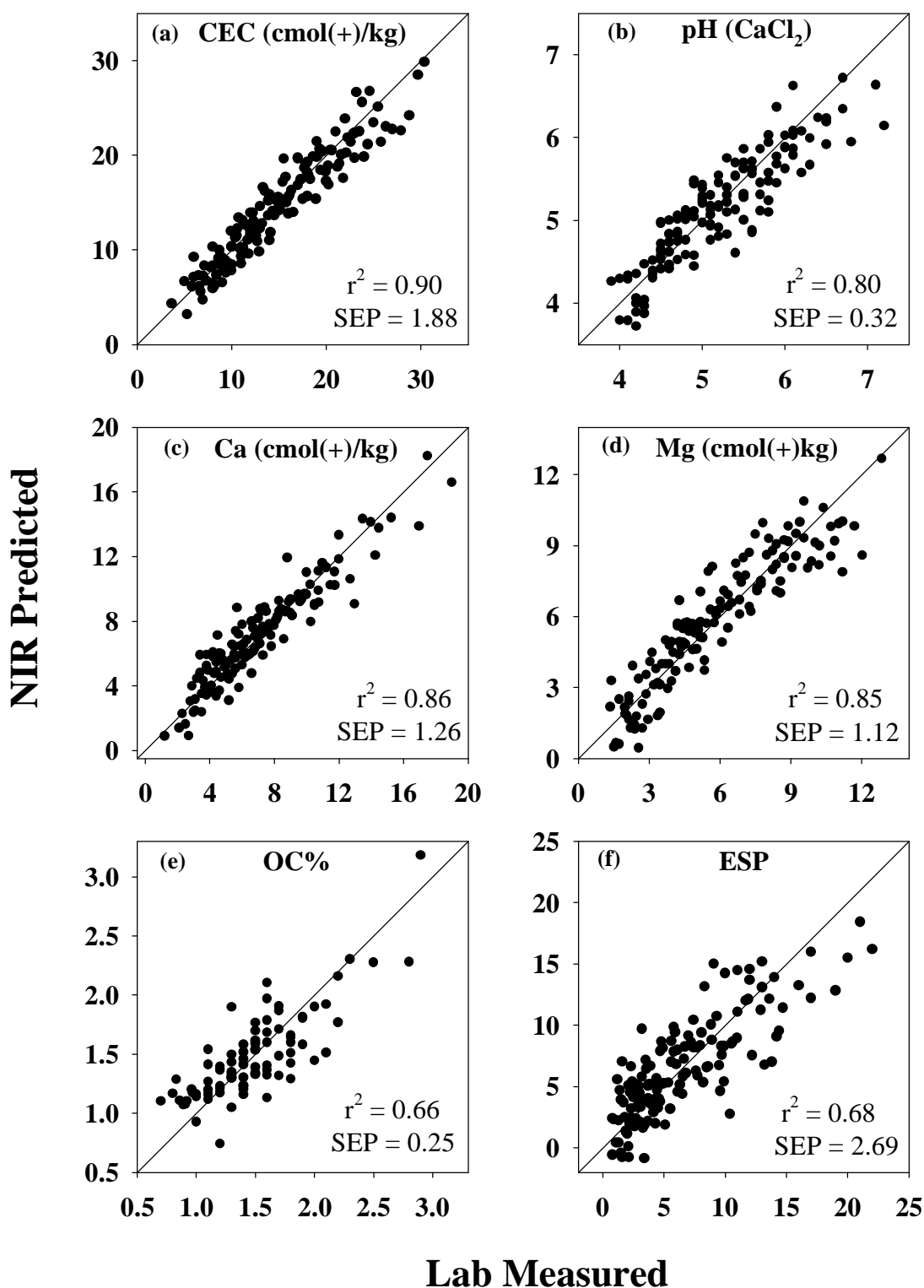
a. SEC is the standard error of calibration

b. SEP is the standard error of performance

c. RPD is the ratio of standard deviation of the validation set to SEP

d. RER is the ratio of the range of the validation set to the SEP

Figure 3: NIRS predicted values of topsoil (0-10 cm) (a) CEC, (b) pH, (c) Ca, (d) Mg, (e) OC% and (f) ESP plotted against values measured by conventional laboratory methods.



5.2 40-50 cm samples

For the subsoils the best predictive ability was achieved for exchangeable Na, CEC and ESP with RPD > 2.2, $r^2 \geq 0.80$, and SEP of 1.13 cmol(+)/kg, 2.74 cmol(+)/kg and 4.28 respectively (Table 4 and Figure 4). Ca:Mg ratio, pH (CaCl₂) and exchangeable Mg and Ca were also predicted well by the NIRS with RPD > 1.9, $r^2 \geq 0.68$ (Table 4 and Figure 4). Other soil variable predictions were EC and exchangeable K with RPD of 1.6 and 1.4 respectively.

Table 4: Calibration and prediction results for the 40-50 cm soil properties

Variable	Calib. R ²	SEC ^a	No. Calib. Samples	Pred. r ²	SEP ^b	No.Pred. samples	RPD ^c	RER ^d
pH	0.80	0.31	232	0.71	0.35	77	2.0	9.1
EC, dS/m	0.77	0.12	236	0.63	0.17	79	1.6	10.1
CEC, cmol(+)/kg	0.71	3.27	237	0.80	2.74	79	2.3	12.1
exch. Ca, cmol(+)/kg	0.80	1.59	237	0.68	2.06	79	1.9	14.9
exch. Mg, cmol(+)/kg	0.65	1.80	237	0.74	1.51	79	2.0	10.0
exch. Na, cmol(+)/kg	0.85	1.00	238	0.82	1.13	77	2.3	10.5
exch. K, cmol(+)/kg	0.68	0.15	238	0.72	0.15	79	1.4	8.9
% ESP	0.83	3.80	237	0.80	4.28	79	2.2	9.5
Ca:Mg ratio	0.67	0.20	234	0.79	0.18	81	2.1	10.7

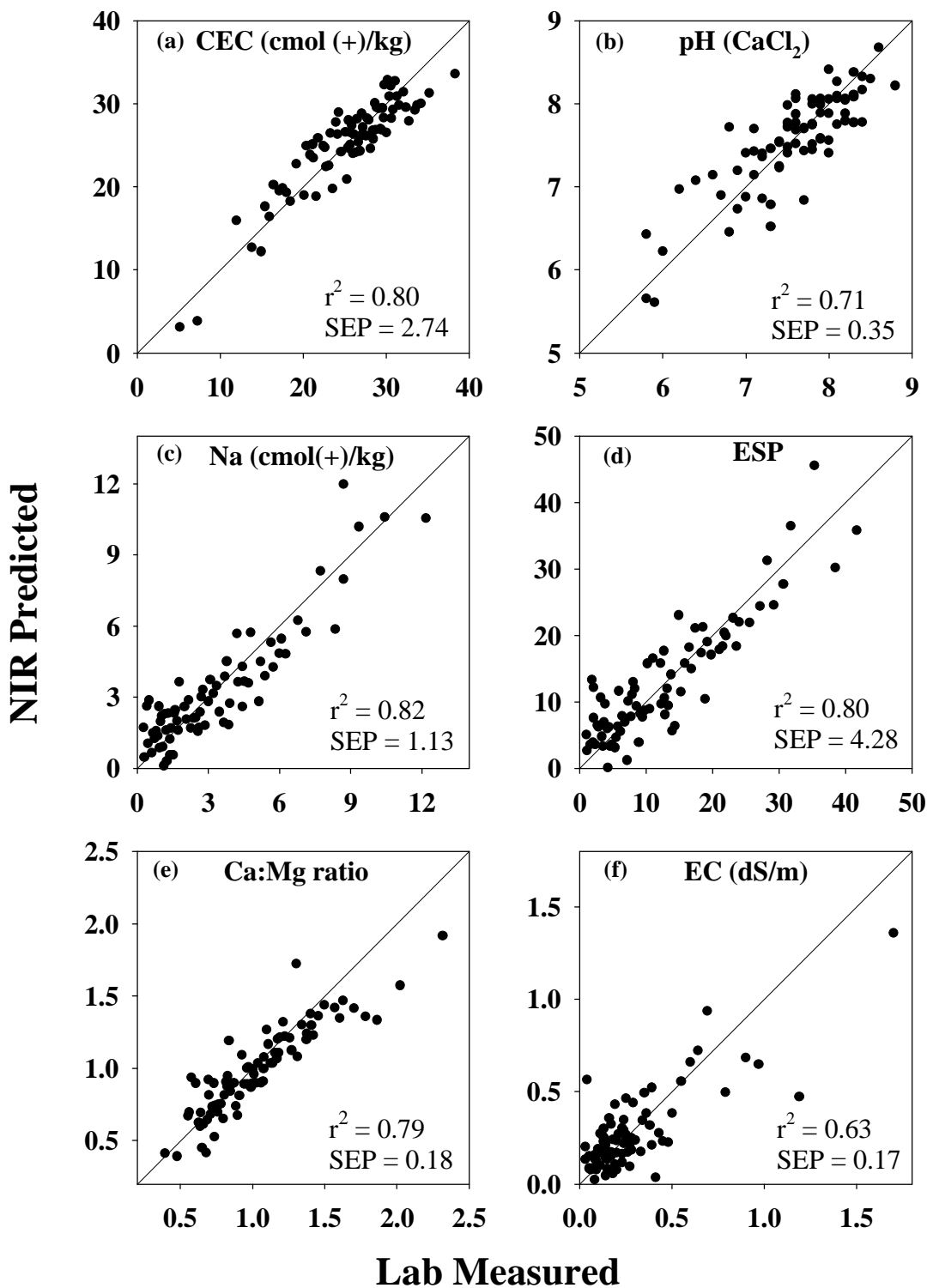
a. SEC is the standard error of calibration

b. SEP is the standard error of performance

c. RPD is the ratio of standard deviation of the validation set to SEP

d. RER is the ratio of the range of the validation set to the SEP

Figure 4: NIRS predicted values of subsoil (40-50 cm) (a) CEC, (b) pH, (c) Ca, (d) Mg, (e) OC% and (f) ESP plotted against values measured by conventional laboratory methods.



6. DISCUSSION

A role exists for NIRS analysis of soils in site specific agriculture, where the aim is to divide a field into a number of management zones. Viscarra Rossel and McBratney (1998) suggest that spatial variability of soil properties is relevant to direct or indirect effects on crop yield and to site specific resource application. In this role a slight decrease in individual sample analysis accuracy is far outweighed by the speed and cost efficiency of NIRS analysis enabling a range of chemical properties to be determined for many samples within individual fields.

It is often difficult to compare results from different calibrations and it can be quite misleading if only the r^2 or SEP values are used. For example ESP in the topsoil and subsoil have r^2 of 0.68 and 0.80 respectively, leading us to conclude that the subsoil calibration is superior, but the SEP values are 2.69 and 4.28 respectively which suggests that the topsoil calibration is superior. The major difference between these two calibrations is the range of ESP values in each set, the topsoil validation set range is 0.8 to 22.0 whereas the subsoil range is 1.0 to 41.7. The much larger range of the subsoil set gives a higher r^2 but the SEP is also larger.

In order to overcome these discrepancies RPD and RER have been calculated for the topsoil (Table 3) and subsoil (Table 4) predictions in this study. In agricultural commodity applications where, RPD and RER were developed it is suggested an $RPD > 3$ is considered acceptable and $RPD > 5$ excellent (Malley *et al.* 1999a). RER should be above 10 (Williams 1987) and is often above 20 (Malley *et al.* 1999a). While no critical levels of RPD and RER have been set for the NIRS analysis of soils, acceptable values depend on the intended application of the predicted values.

Chang *et al.* (2001) reported that NIRS had the ability to predict values of soil properties and used 3 categories based on RPD in the ranges > 2 , 1.4-2.0 and < 1.4 to indicate decreasing reliability of prediction using NIRS. Chang *et al.* (2001) believed that the prediction of soil properties in the middle category could be improved by using different calibration strategies, while properties in the lower category may not be reliably predicted using NIRS.

We suggest that when using NIRS for the analysis of soils for site specific agriculture that suitable limits may be RPD: < 1.6 is poor, 1.6 - 2.0 is acceptable and > 2.0 is excellent. RPD values of 1.6 to 1.7 for soil properties may still be marginal in their usefulness for site specific agriculture allowing the division of a soil property into possibly only 3 categories, for example OC% in Figure 2 which has a RPD of 1.6.

NIRS soil analysis reported by Chang *et al.* (2001) have similar RPD values to this study for CEC and exchangeable Ca, but lower values for pH and exchangeable Mg and much lower values for exchangeable Na. Chang *et al.* (2001) reported exchangeable Na to be poorly predicted by NIRS with r^2 of 0.09 and RPD of 0.92. Evidence suggests that this poor prediction may result from a poorly distributed sample set with a small range, rather than the inability of NIRS to predict exchangeable Na. A poorer predictive ability was achieved for exchangeable Na in the topsoil where the sample set was skewed in distribution. Chang *et al.* (2001) reported 439 samples for exchangeable Na with a minimum 0.1, maximum 1.8 and mean 0.2 cmol kg^{-1} , illustrating a data set skewed in distribution to the lower values. Our research also achieved poor predictions for surface soil EC with a similar skewed distribution.

CEC was very accurately predicted in both the topsoil and subsoil sample depths in this study and similar results have been reported in other studies (Chang *et al.* 2001 and Malley *et al.* 1999b). Exchangeable Ca and Mg are also accurately predicted and it was expected this may have been due to their correlation with CEC, but the Ca:Mg ratio is predicted with a reasonable level of accuracy it suggests that they are being predicted independently.

The accurate prediction of pH achieved in this research confirms findings by Reeves *et al.* (1999) who used a limited range of sampling sites and soil types and maximum sample depth of 20 cm. However Chang *et al.* (2001) reported a less accurate predictive ability for pH with $r^2 = 0.56$ and RPD = 1.47 for a 743 sample set obtained from 4 regions at a range of depths to 30 cm. Malley *et al.* (1999a) reported $r^2 = 0.56$, a RPD of 1.72 and RER of 5.43 for pH from a small sample set over a range of depths to 10 m. One explanation for the variable reports of NIRS prediction for pH may be the range of depths that are included in many sample sets. In all other reported sample sets except possibly Reeves *et al.* (1999), a combination of topsoil and subsoil samples were included in the calibrations.

CEC, pH and many other soil constituents do not have a primary response to the near-infrared region but their correlation to clay content and soil organic matter (Chang *et al.* 2001) may explain how they are predicted. There are strong correlations between CEC and exchangeable Mg, $R = 0.91$, exchangeable Ca, $R = 0.85$ and pH, $R = 0.65$, in the topsoil samples and these relationships may explain how they are being predicted by NIRS.

The ability of NIRS to predict OC in this study was not as accurate as other research reported in the literature. Sudduth and Hummel (1993) reported predicted versus measured OC content for 30 soils with $r^2 = 0.89$ and SEP = 0.23. In their study, OC was determined by dry combustion, which is considered a more reliable method for the determination of OC than the Walkley and Black method used for the analysis of our samples.

There was little difference between the predictive ability of NIRS for the topsoil compared to the subsoil. Any differences that occurred between predictive ability can be attributed to a better distribution of sample constituents (eg EC in subsoil) rather than the effect of higher organic matter levels in the topsoil.

The large range of samples from many soil types, combined with the separate validation sample set method used in this study, gives us confidence that the results achieved could be commercially applicable in the Riverine Plain soils of southern NSW. The results achieved would be suitable for use in site specific agriculture where the aim is to divide a field into a number of management zones. In the topsoil, CEC, exchangeable Ca and Mg, pH, Ca:Mg ratio and possibly OC, ESP and Al% were all adequately predicted by NIRS for use in site specific agriculture. Whilst in the subsoil, CEC, exchangeable Na, Ca, Mg, ESP, pH and Ca:Mg ratio were all adequately predicted for use in site specific agriculture.

7. EFFECT OF SOIL PARTICLE SIZE ON NIRS CALIBRATIONS

7.1 Methodology

From the large soils database, 112 topsoil (0-10cm) samples were selected to cover the range of CEC, ESP and pH(CaCl₂) found in soils from the Riverine Plain (Table 5). These samples covered most soil types, farming enterprises and pasture/cropping histories. The soil samples were air dried after collection before being passed through a jaw crusher (Van Gelder Crushers Pty Ltd, Sydney). The samples were fed through the crusher a number of times until they passed a 2mm sieve.

Table 5. Chemical characteristics of 112 soil samples used in the particle size study.

Variable	No. of samples	Mean \pm SD	Range
PH	112	5.24 \pm 0.8	3.8 – 7.3
CEC, cmol(+)/kg	112	13.8 \pm 5.8	2.7 – 25.9
% ESP	112	7.98 \pm 5.6	0.8 – 22.3

The crushed and sieved soil samples were scanned with a NIRSystems model 6500 scanning spectrophotometer (Foss-NIRSystems, Silver Spring, MD, USA). Using the Near-infrared Spectral Analysis Software (NSAS) samples were scanned (32 scans per sample) from 400 to 2498 nm using a standard sample cup. Data was collected every 2 nm giving 1050 data points per spectrum.

After scanning, each sample was passed through a “Fritsch Analysette 3” automatic sieve shaker set on vibration amplitude = 8 for 5 minutes. The shaker was fitted with five 200mm-diameter sieves with aperture sizes of 1.0mm, 500 μ m, 250 μ m, 125 μ m, 63 μ m and a base. The soil remaining in each sieve and at the base was weighed, then re-combined and mixed thoroughly.

The same soil samples were then ground in a “Glen Creston Cross Beater Mill” with a 2mm round hole sieve. All samples were again scanned by NIR as described previously and then put through the sieve shaker and the weight of soil remaining in each sieve was recorded. The soil from the sieves was then combined and mixed.

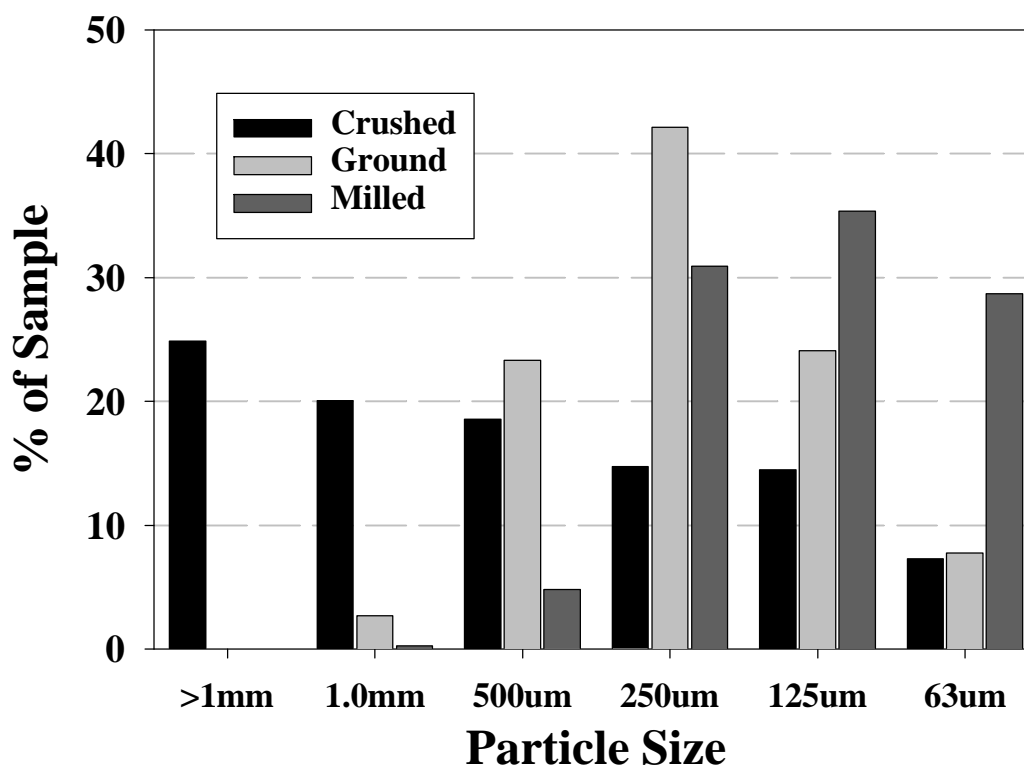
A “Rocklabs” Puck and Ring mill was then used to further decrease the size of the soil particles. Each sample was placed in the ring with the puck inside and milled for 3 minutes. The samples were again scanned and put through the sieve shaker as previously described and weights recorded.

7.2 Results

7.2.1 Particle Size

The particle size distributions of the processed samples are shown in Figure 5. After being crushed and put through the 2mm sieve the samples have a large range of particle sizes with almost 25% of the sample being particles larger than 1mm, but there were also many very small particles with 7% smaller than 63um. As the grinding process becomes more aggressive, the particles become smaller and the range of distribution of particle size becomes smaller.

Figure 5: The particle size distribution of the samples after being crushed, ground and milled.



7.2.2 Calibrations

The Partial Least Squares (PLS) regression procedure was used to determine the best correlation (i.e. calibration) between the chemical reference data and spectral data. For each constituent, the samples' chemical reference data was sorted from lowest to highest. Every fourth sample and its data were moved to a separate file for use as a validation set. Calibrations were developed using the remaining samples

A combination of raw optical data, first and second derivatives combined with wavelength groups using the entire spectrum (400-2498 nm) and the NIR portion only (1100-2498 nm) and 2, 4 and 8 nm intervals were tested for each soil chemical property.

For all constituents the samples crushed and put through a 2mm sieve gave as good as or better predictive calibrations than the samples put through further processing. There was little difference in the NIRS ability to predict pH or ESP regardless of sample preparation and

subsequent particle size. Increased sample processing and reduced particle size appeared to reduce the predictive ability for CEC. When the sample is loaded into the NIR scanning cell, it was observed that even with the 2mm sieved sample, the face of the cell was covered with very small particles. The results are presented in Table 6.

Table 6. Comparison of soil constituent calibrations and predictive ability with grinder type used for CEC, pH and ESP.

Grinder	Constit.	Derivative	Wavelengths	R ² Calib	SEC	R ² Verif	SEP
2mm	CEC	1	1100-2500, 2nm	0.85	2.22	0.92	1.82
Fine	CEC	1	1100-2500, 2nm	0.82	2.45	0.87	2.25
Rocklab	CEC	1	1100-2500, 2nm	0.89	1.89	0.86	2.45
2mm	PH	1	400-2500, 2nm	0.79	0.38	0.62	0.50
Fine	PH	1	400-2500, 2nm	0.65	0.50	0.58	0.55
Rocklab	PH	2	1100-2500, 2nm	0.62	0.52	0.59	0.50
2mm	ESP	2	1100-2500, 4nm	0.75	2.71	0.61	4.06
Fine	ESP	2	1100-2500, 4nm	0.72	2.88	0.47	4.40
Rocklab	ESP	1	1100-2500, 4nm	0.50	3.87	0.57	4.26

7.3 Conclusion

Processing of samples to decrease particle/aggregate size does not improve their predictive ability using NIRS and in the case of CEC it is reduced by further sample processing. It is concluded that soil crushing to pass a 2 mm sieve is adequate for NIRS analysis and calibration.

8. IMPLICATIONS AND RECOMMENDATIONS

NIRS scanning of soils has proved suitable for the estimation of many soil constituents. With increasing awareness of within field variability affecting rice grain yields (Pringle 2003) and the use of site specific agriculture, there is interest for a quick inexpensive soil analysis. Many ricegrowers have EM31 surveys of rice fields and increasingly are accessing yield maps. Both of these mapping techniques identify within field variability in soil or yield respectively, but need targeted soil analysis to help identify possible causes of the observed differences. NIRS could provide the inexpensive rapid soil analysis for some important constituents to facilitate explanation and uptake of site specific agriculture.

Promote soil sampling on the basis of EM31 maps with soil analysis by NIRS using the relationship developed in this project to further explore the basis for within field crop yield variability.

It is recommended that CRC Rice negotiate with potential commercial NIRS service providers (Sunrice, Prime Wheat, CSU, NSW Agriculture, Incitec/Pivot) to develop and promote acceptance and adoption of NIRS based soil analysis.

9. Intellectual Property and commercially significant developments arising from the Project.

No commercial developments have arisen from the project. The demand for a commercial NIRS soil testing service is growing, but a commercial company interested in providing the service is required. There are suitable NIRS machines in the region undertaking plant analysis, it would not be difficult or expensive for them to create the calibrations and provide a soil analysis service.

As the transfer of plant or soil calibrations from one NIRS to another NIRS machine is not accurate, soil samples with relevant chemical analysis can be provided to a potential commercial service provider allowing calibrations to be easily and economically developed for commercial use. We hold an existing soil sample database appropriate for irrigated Riverina soils, which would be suitable for this purpose.

During the project, discussions between ourselves and “Integrated Spectronics”, a Sydney company who produce a portable NIR (PIMA) which scans in the 1300 to 2500 nm wavelengths, took place. The instrument can produce good predictions for many soil constituents from air dried and crushed soil (Russell 2002) but research would need to be undertaken to determine the effects of field particle size and soil moisture on its ability to predict soil constituents in the field.

10. Recommendations on the activities or other steps that may be taken to further develop, disseminate, or to commercially exploit the results of the project.

10.1 Further development and commercial exploitation

Portable NIRS

A logical progression to further develop the technology would be to look at portable NIRS instruments that could scan soil in the field. This would remove the laborious and expensive soil sampling and sample preparation parts of the process. Connected to a GPS a portable NIR could take many scans from a field and potentially produce a map of soil constituent levels across the field in a near kinematic approach.

During the project discussions were held between ourselves and a Sydney company “Integrated Spectronics” who produce a portable NIR which scans in the 1300 to 2500 nm wavelengths range. The instrument could produce good predictions for many soil constituents from air dried and crushed soil, but research would need to be undertaken to determine the effects of field particle size and soil moisture on its ability to predict soil constituents in the field.

Development of a commercial NIRS soil testing service

The demand for a commercial NIRS soil testing service is growing, what is needed is a commercial company interested in providing the service. There are suitable NIRS machines in the region undertaking plant analysis, it would not be very difficult or expensive for them to create the calibrations and provide a soil analysis service.

Use of NIRS based soil assessment within ongoing research projects

Within research projects targeting rice plant NIR analysis via airborne remote sensing, soil sampling and analysis as a co-variate may allow development of a more integrated and appropriate approach. Pringle (2003) has used the approach of electromagnetic surveying with limited soil sampling and analysis. Use of NIRS soil analysis using the existing relationships (ie NIRS used at YAI) within these commercial investigations could prove beneficial. NIRS was not investigated for the prediction of soil EC due to a poor range of EC in the samples. If a satisfactory calibration could be developed for EC the analysis method would be particularly useful in the Land and Water Management plans where soil pH, ESP and EC need to continually monitored.

10.2 Dissemination

Presentation of the work in this project has to date been essentially within the scientific community with the exception of a brief article within “The Graingrower” magazine. We should present material in the IREC Farmers Newsletter, Agriculture Today, and make presentations at more grower focussed meetings.

11. A technical summary of all information developed as a part of the Project, including discoveries in methodology and equipment design.

The project demonstrated that NIRS can successfully determine some soil properties in both the topsoil and subsoil. The large range of samples obtained from many soil types combined with the method used in this study, gives us confidence that the results achieved would be commercially applicable in the Riverine Plain soils of southern NSW. The relations/predictions developed would be suitable for use in site specific agriculture where the aim is to divide a field into a number of management zones. In the topsoil, CEC, exchangeable Ca and Mg, pH, Ca:Mg ratio and possibly OC, ESP and Al% were all adequately predicted by NIRS for use in site specific agriculture. Whilst in the subsoil, CEC, exchangeable Na, Ca, Mg, ESP, pH and Ca:Mg ratio were all adequately predicted for use in site specific agriculture.

Table 7. Calibration and prediction results for the 0-10 cm soil properties.

Variable	Calib. R ²	SECa	No. Calib. Samples	Pred. r ²	SEPB	No. Pred. Samples	RPDc	RERd
PH	0.83	0.30	417	0.80	0.32	138	2.3	10.3
EC, dS/m	0.49	0.05	417	0.37	0.06	138	1.2	5.7
P, Colwell, mg/kg	0.27	16.1	418	0.18	18.0	139	1.1	5.8
% Organic C	0.62	0.26	270	0.66	0.25	90	1.7	8.8
CEC, cmol(+)/kg	0.88	2.19	422	0.90	1.88	139	3.3	14.8
Exch. Ca, cmol(+)/kg	0.87	1.23	422	0.86	1.26	139	2.7	13.7
Exch. Mg, cmol(+)/kg	0.91	0.88	419	0.85	1.05	139	2.7	10.3
Exch. Na, cmol(+)/kg	0.69	0.45	413	0.64	0.48	137	1.7	7.5
Exch. K, cmol(+)/kg	0.67	0.18	420	0.61	0.19	139	1.6	8.7
Exch. Al, cmol(+)/kg	0.60	0.22	165	0.58	0.23	55	1.5	5.9
% ESP	0.69	2.55	414	0.68	2.69	135	1.8	7.9
% Al	0.62	2.90	164	0.69	2.85	56	1.7	6.9
Ca:Mg ratio	0.87	0.21	414	0.79	0.26	136	2.2	11.1

Table 8. Calibration and prediction results for the 40-50 cm soil properties.

Variable	Calib. R ²	SECa	No. Calib. Samples	Pred. r ²	SEPB	No. Pred. samples	RPDc	RERd
PH	0.80	0.31	232	0.71	0.35	77	2.0	9.1
EC, dS/m	0.77	0.12	236	0.63	0.17	79	1.6	10.1
CEC, cmol(+)/kg	0.71	3.27	237	0.80	2.74	79	2.3	12.1
exch. Ca, cmol(+)/kg	0.80	1.59	237	0.68	2.06	79	1.9	14.9
exch. Mg, cmol(+)/kg	0.65	1.80	237	0.74	1.51	79	2.0	10.0
exch. Na, cmol(+)/kg	0.85	1.00	238	0.82	1.13	77	2.3	10.5
exch. K, cmol(+)/kg	0.68	0.15	238	0.72	0.15	79	1.4	8.9
% ESP	0.83	3.80	237	0.80	4.28	79	2.2	9.5
Ca:Mg ratio	0.67	0.20	234	0.79	0.18	81	2.1	10.7

a. SEC is the standard error of calibration

b. SEP is the standard error of performance

c. RPD is the ratio of standard deviation of the validation set to SEP

d. RER is the ratio of the range of the validation set to the SEP

Examination of the effect of soil grinding intensity on the relationships developed above found that for CEC, pH and ESP, the samples crushed and put through a 2mm sieve gave as good as or better predictive calibrations than the samples put through further processing. There was little difference in predicability for pH and ESP regardless of sample preparation and subsequent particle size. Increased sample processing and reduced particle size appeared to reduce the ability of NIRS to predict CEC.

Table 9. Comparison of soil constituent calibrations and predictive ability with grinder type used for CEC, pH and ESP.

Grinder	Constit.	Derivative	Wavelengths	R ² Calib	SEC	R ² Verif	SEP
2mm	CEC	1	1100-2500, 2nm	0.85	2.22	0.92	1.82
Fine	CEC	1	1100-2500, 2nm	0.82	2.45	0.87	2.25
Rocklab	CEC	1	1100-2500, 2nm	0.89	1.89	0.86	2.45
2mm	PH	1	400-2500, 2nm	0.79	0.38	0.62	0.50
Fine	PH	1	400-2500, 2nm	0.65	0.50	0.58	0.55
Rocklab	PH	2	1100-2500, 2nm	0.62	0.52	0.59	0.50
2mm	ESP	2	1100-2500, 4nm	0.75	2.71	0.61	4.06
Fine	ESP	2	1100-2500, 4nm	0.72	2.88	0.47	4.40
Rocklab	ESP	1	1100-2500, 4nm	0.50	3.87	0.57	4.26

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