

MULTIVARIATE ANALYSIS OF IR, NIR, AND NMR SPECTRA OF SOIL SAMPLES FROM DIFFERENT LAND USE CONVERSIONS: NATIVE FOREST, PASTURE, AND PLANTATION FOREST

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ABSTRACT

Mid infrared (IR), near infrared (NIR), and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on solid soil samples from three neighbouring sites with similar history but different current land use — namely, native podocarp forest, pasture land cleared from native forest, and exotic softwood plantation converted from improved pasture. Principal component analysis and projection to latent structures regression of the spectra showed changes in carbohydrate and phenolic fractions reflected the current land use, with the introduction of pasture and plantation forest decreasing the aliphatic and increasing the aromatic fractions of the soils. Fractional areas for NMR spectra ranged between 0.16 and 0.34 for aliphatic, 0.33 and 0.50 for carbohydrate, 0.12 and 0.40 for aromatic, 0.04 and 0.11 for phenolic, and 0.01 and 0.17 for carbonyl carbon. High carbon concentrations in native forest micro-sites exhibiting low pH occurred predominantly as aliphatic and carbohydrate fractions, even at depths down to 0.5 m. Soil carbon protection following land use diversification was evident for at least 80 years.

Keywords: podocarp/hardwood forest; pasture land; soil pH; soil organic matter; nuclear magnetic resonance; near infrared; infrared; *Pinus radiata*.

INTRODUCTION

The stability of soil organic matter (SOM) is important when considering sustainable production, particularly in relation to nitrogen availability for plant growth. Interest in carbon sequestration in soil has provided impetus for developing models to

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predict carbon stocks and changes in relation to land use and forestry. New methods are being researched to more readily characterise soil organic matter which consists of a mixture of plant-derived polymers that enter the soil via surface litter, or directly through roots, exudates, and microbial biomass (Kögel-Knabner 2002). Process models predict carbon stock changes from the balance between litter inputs to the soil and its turnover rate. Turnover rates are assigned to various pools differing in decomposability. For example, carbohydrates and proteins are considered readily available, structural components such as cellulose and hemicellulose less available, and lignin is relatively resistant to decomposition (Meentemeyer 1978; van Veen *et al.* 1984; Ryan *et al.* 1990; Hansen *et al.* 1991).

In addition to the characteristics of the organic matter, various physical and biological factors such as temperature, water, and acidity influence microbial activity and hence alter carbon turnover rates. Decomposition is retarded in boreal and peat soils, but carbon accumulation in normal soils involves chemical and physical stabilisation of organic matter (Stevenson & Cole 1999; Baldock & Skjemstad 2000; Krull & Skjemstad 2003). Baldock *et al.* (1992) related the progressive decomposition of soil organic matter to litter disintegration and assimilation by microbes, culminating with physical protection in fine-textured soil aggregates, or as recalcitrant fractions. Recent views suggest the existence of an upper limit to physical carbon protection based on the physicochemical properties of soils, to help explain why soil carbon stocks do not necessarily increase with increasing litter input, as assumed by most soil carbon models (Six *et al.* 2002).

This study extends previous research (Beets & Brownlie 1987; Beets *et al.* 1999, 2002) on the effects of land use on soil carbon in native podocarp/hardwood forest, pasture, and exotic pine forest on pumice soil exhibiting high carbon storage potential. Mineral soil carbon concentrations at 0–0.05 m depth ranged from 4% to 32% in indigenous podocarp/hardwood forest. Chemical stabilisation of organic matter in Andisol is associated with organo-metallic complexes involving aluminium (Beets *et al.* 2002; Parfitt *et al.* 2002). Similarly, Condon & Newman (1998) have investigated soil under grassland and adjacent coniferous forest in the South Island of New Zealand using solid state NMR spectroscopy. In our study, soil carbon fractions were examined in a subset of mineral soil samples selected across a wide range of carbon concentrations, soil depths, and land uses. In addition, sequential soil samples from permanent plots were examined to assess possible effects of tree age after reforestation of pasture with pine.

A wide range of approaches has been used to characterise litter, but no standard methods are generally accepted for characterising soil organic matter fractions. Nuclear magnetic resonance and NIR spectroscopy are increasingly being used to characterise soil samples into biologically meaningful fractions. Near infrared allows rapid compositional analysis, but with mixed success (Krischenko *et al.*

1992; Ben-Dor & Banin 1995; Reeves *et al.* 1999, 2006; Chang *et al.* 2001; Chang & Laird 2002; Madari *et al.* 2006; Terhoeven-Urselmans *et al.* 2006), while NMR appears to be suitable for characterising soil development (Wilson *et al.* 1981; Preston & Ripmeester 1982; Preston 1991, 1996; Newman & Tate 1991; Condon & Newman 1998; Preston *et al.* 2002, 2006; Schöning & Kögel-Knabner 2006; Helfrich *et al.* 2006).

METHODS

Soil Sampling

Soil core samples were collected in 1993 from areas differing in land use within the Purukohukohu Experimental Basin in the central North Island of New Zealand. The geographic history of this site is one of continual volcanic activity. The basin includes three land use catchments — namely, native New Zealand podocarp forest, classified by McKelvey (1963) as containing rimu (*Dacrydium cupressinum* Lamb.) and miro (*Prumnopitys ferruginea* (D. Don) de Laub.); pasture land developed in 1957 after original clearing of the native forest in the 1920s; and pasture land converted to plantation *Pinus radiata* D. Don forest in 1973. Pasture improvement involved multiple applications of fertiliser (mostly superphosphate), sowing of improved grasses, and incorporation of legumes (Beets & Brownlie 1987). A full description of the subcatchments has been published previously (Beets & Brownlie 1987), and the details of the sampling of the cores specific to this study have been given by Beets *et al.* (2002). In summary, 60-mm-diameter cores were taken for surface samples (0–0.05 m) and 98-mm-diameter cores were taken for deeper samples (0.05–0.10 and 0.10–0.50 m), at intervals of 20–30 m along transects. Transects were each 200–300 m long, spanning ridge crest to gully to opposing ridge crest, and encompassing pasture land, *P. radiata* plantation, and native podocarp forest. The 15 samples used in this study represent a subset of the original 120 from the land use transects and supplementary time series samples (0–0.10 m depth) from the *P. radiata* stand, to assess the effect of stand age.

Compositional Analysis

The soil samples were air dried and sieved (<2 mm fraction) prior to chemical analysis. Classical methods of analysis were used to provide calibration data. Total carbon and nitrogen were determined by dry combustion using a Leco CNS-2000 carbon nitrogen analyser (LECO Corp., St Joseph, MI, USA, www.leco.com), phosphorus by Olsen 0.5 M sodium bicarbonate extraction followed by spectrophotometry using the molybdenum blue method. Potassium was determined by atomic absorption spectroscopy after leaching with neutral normal ammonium acetate, and pH was determined in water at a soil:water ratio of 1:2.5.

Spectroscopic Analysis

All spectroscopic analyses were performed on <2-mm-fraction samples that were finely ground by mortar and pestle. Mid infrared spectra were acquired on a Bruker Vector 33 (Bruker Optik, Ettlingen, Germany, www.brukeroptik.com) in the range 4000–500 cm^{-1} at 4 cm^{-1} resolution. Near infrared spectra comprise overtones of the primary, mid infrared, molecular bond vibrational frequencies, and can provide quantitative chemical composition of the sample under study. Near infrared spectra were recorded on the samples using a NIRSystems 6500 NIR system (Foss NIRSystems Inc., Silver Spring, MD, USA, www.nirsystems.com) with static sample cups in a sample transport system. Spectra were acquired between 1100 and 2400 nm at 2 nm resolution and referenced to a white ceramic standard. To remove the effects of baseline offsets, the IR and NIR spectra were converted to their first or second derivative using a Savitzky-Golay (1964) second-order polynomial with 15 smoothing points. Due to noise in the region 2000–2400 nm in the NIR spectra, only the region between 1100 and 2000 nm was used for multivariate analysis.

Carbon-13 CP/MAS NMR spectra of the soils were acquired on a Bruker Avance 200 spectrometer (Bruker BioSpin, Rheinstetten, Germany, www.bruker.de) using a 7-mm MAS probe with zirconia rotor spinning speeds of 5 kHz, a 5 μs preparation pulse, 2 ms contact time, and a relaxation delay time of 500 ms (Preston 2001). No correction for spinning sidebands has been made, as the MAS rotor speed was considered sufficient to reduce sidebands to the level of the noise (Newman *et al.* 1987; Filip *et al.* 1991). More than 80 000 scans were averaged to achieve sufficient signal to noise ratio, and exponential line broadening of 60 Hz was applied prior to Fourier transformation. The spectra were integrated to afford ratios of carbon according to the method outlined by Barron & Wilson (1981) and Newman & Tate (1991) — viz, the regions 0–50 ppm (aliphatic C), 60–110 ppm (carbohydrate related C), 110–160 ppm (aromatic C), 140–160 ppm (oxygenated aromatic C and phenolic C), 160–220 ppm (organic acids and amide C). These regions were used to determine fractions of each type of soil carbon. Additionally, the ratio of phenolic carbon to aromatic carbon ($C_{\text{ArOH}}/C_{\text{Ar}}$) as described by Newman & Tate (1991) was used to determine the overall degree of oxygen substitution of the aromatic rings, while the aromaticity of the soil was taken as the fraction of the NMR signal area in the region 110–160 ppm as described by Hatcher *et al.* (1981) and Wilson *et al.* (1981, 1987). Similar regions were used by Lomax *et al.* (1994) to determine the aromatic content of bark samples. A detailed description of the characterisation of soil NMR spectra can be found in the report by Keeler *et al.* (2006).

Chemometric Analysis

Principal component analysis (PCA) and projection to latent structures regression (PLS) were performed using *The Unscrambler* v9.4 (Camo, Oslo, Norway,

www.camo.no). For principal component analysis, the spectra were analysed to determine the key variance, while for projection to latent structures the spectral data were regressed against the soil chemical data to determine the modelling results. The prediction models were calculated by allowing a set maximum of latent variables (principal components) to be fitted, while the final number of latent variables selected for incorporation into the prediction model was chosen to minimise the residual variance when using full cross-validation (“leave one out” method). The numbers of latent variables used and allowed are reported in the respective tables of results. Thus errors were minimised when using the projection to latent structures model for prediction. The theoretical background to the use of principal component analysis and projection to latent structures can be found elsewhere (Martens & Næs 1991).

Statistical Analysis

The effect of spectral areas of soil organic matter fractions on soil total carbon were examined after accounting for variation in soil pH and sample depth in the analysis, using the GLM procedure in SAS (SAS Institute Inc., Cary, NC, USA, www.sas.com). For analysis purposes, soil depth ranges were recorded as follows: 0–0.05 m (1), 0–0.10 m (1.5), 0.05–0.10 m (2), 0.10–0.50 m (3). We tested the hypothesis that soil organic matter fractions in the indigenous forest would be largely reflected in soils currently under pasture or pine, due to soil carbon protection.

RESULTS

The physical description and chemical characterisation of the soils are presented in Table 1 (for a full description see Beets *et al.* 2002). The integrated areas for the ^{13}C CP/MAS NMR spectra are included for the regions outlined in the experimental section. There was a strong correlation between carbon and nitrogen, phosphorus, and potassium (Table 2). Representative spectra of high carbon content soils from each land-use type for mid IR, NIR, and NMR respectively are shown in Fig. 1–3. Specifically, the ^{13}C CP/MAS NMR spectra of surface soil samples (0–0.05 m depth) for the three land-use types with differing soil development are shown in Fig. 3. All had a high carbon content (> 25%). There was a decrease in the degree of oxygenation of the samples between the native forest soil and the *P. radiata* plantation soil as evidenced by the decrease in the phenolic to aromatic ratio of the soils (ArOH/Ar, Table 1), decreasing in the order native forest (0.61) > pasture (0.31) > 20-year-old *P. radiata* plantation (0.29).

The principal component analysis scores plot for the soil samples based on the mid IR spectra are given in Fig. 4, but the samples do not cluster according to current land use. In contrast, the principal component analysis scores plot for the soil

TABLE 1—Key soil chemical data (g/100 g soil) including fractional areas for NMR spectra (ppm).

Soil ID	Usage	Age* (yr)	Soil depth (m)	pH	C	N	P	K	Aliphatic 0<δ<50	Carbohydrate 60<δ<110	Aromatic 110<δ<160	Phenolic 140<δ<160	Carbonyl 160<δ<220	ArOH/Ar 140<δ<160 110<δ<160
S14365	Pasture		0-0.05	5.11	8.3	0.58	32	0.58	0.24	0.47	0.17	0.08	0.12	0.46
S14368	Pasture		0-0.05	4.64	25	2.07	53	1.64	0.30	0.49	0.12	0.04	0.09	0.31
S14389	Pasture		0.1-0.5	5.12	3.9	0.13	2.66	0.13	0.24	0.42	0.20	0.07	0.14	0.34
S14395	Native		0-0.05	5.87	8.2	0.56	13.5	1.16	0.31	0.37	0.16	0.08	0.17	0.52
S14396	Native		0-0.05	5.18	19	1.16	9.09	1.98	0.32	0.40	0.15	0.09	0.13	0.64
S14400	Native		0-0.05	4.32	32	1.65	45	1.55	0.27	0.50	0.15	0.09	0.08	0.61
S14410	Native		0.05-0.1	3.57	16	0.86	18.6	0.55	0.34	0.47	0.14	0.05	0.05	0.38
S14420	Native		0.1-0.5	4.50	5.8	0.20	5.53	0.32	0.31	0.42	0.25	0.07	0.01	0.28
4035	Pine	5	0-0.1	4.86	9.2	0.57	13.5	0.72	0.23	0.46	0.23	0.07	0.08	0.28
4036	Pine	5	0-0.1	4.94	11	0.66	6.6	1.06	0.29	0.33	0.21	0.09	0.17	0.42
7493	Pine	9	0-0.1	4.94	10	0.63	24	0.87	0.29	0.34	0.21	0.09	0.16	0.41
7494	Pine	9	0-0.1	4.94	10	0.58	7.43	0.91	0.20	0.44	0.27	0.08	0.09	0.29
S14303	Pine	20	0-0.05	4.44	25	1.17	43	0.85	0.16	0.34	0.40	0.11	0.10	0.29
S14301	Pine	20	0-0.05	4.89	8.7	0.55	7.92	0.79	0.23	0.45	0.21	0.07	0.11	0.34
S18395	Pine	23	0-0.1	4.65	9.1	0.55		0.68	0.24	0.43	0.22	0.07	0.11	0.35

* Age since conversion to plantation

TABLE 2—Correlation results for chemical data (g/100 g soil).

	pH	C	N	P	K
pH	1.00	-0.46	-0.33	-0.36	0.13
C		1.00	0.92	0.79	0.70
N			1.00	0.83	0.78
P				1.00	0.41
K					1.00

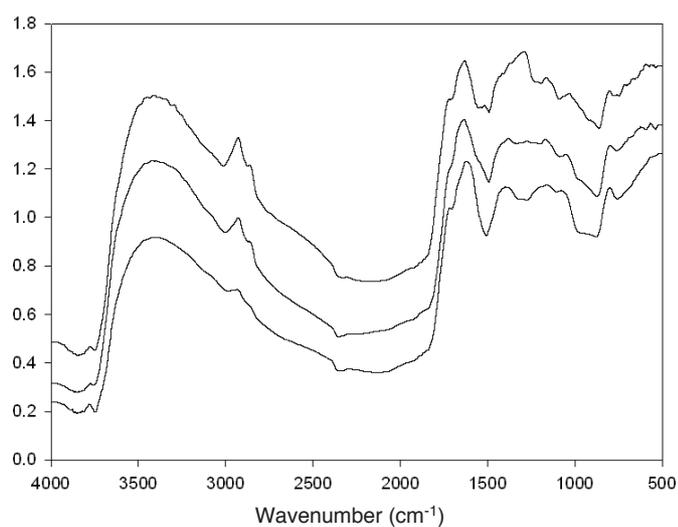


FIG. 1—Mid IR spectra of three high carbon content soils (>25% C) representing the three land uses (top-bottom) native, pasture, and plantation soils (all 0–0.5 m depth).

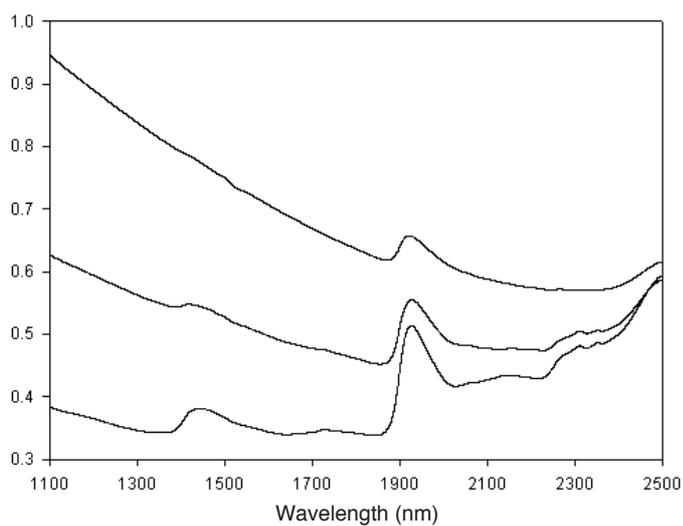


FIG. 2—NIR spectra for high carbon content soils (>25% C) representing the three land uses (top-bottom) plantation, pasture, and native soils (all 0–0.5 m depth).

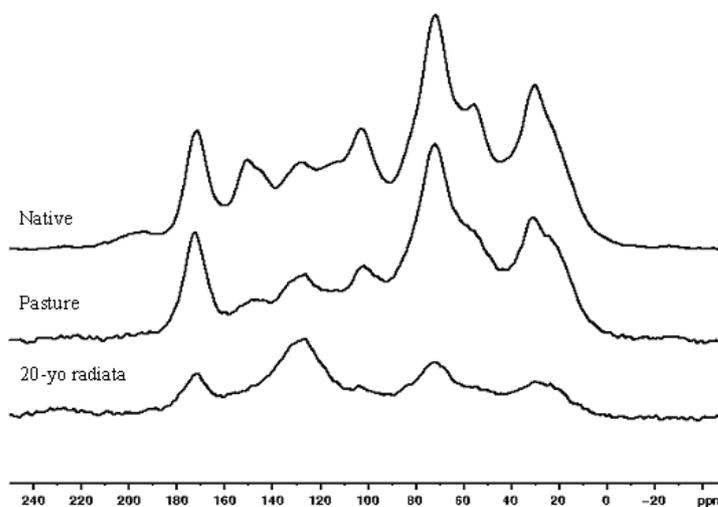


FIG. 3— ^{13}C CP/MAS NMR spectra of three high carbon content soils (>25% C) representing the three land uses (top-bottom) native, pasture, 20-year-old *Pinus radiata* (all 0–0.5 m depth).

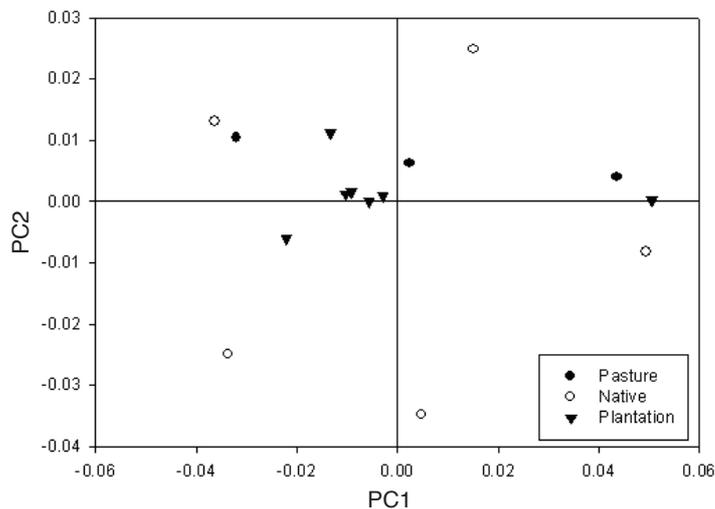


FIG. 4—Principal component analysis scores plot of the 1st derivative IR spectral data for the soil samples showing their separation based on land usage.

samples based on the NIR spectra (Fig. 5) shows segregation of the samples based on their current land usage, particularly the segregation of the native forest soils from the pasture and plantation forest soils. The plantation forest soils were strongly grouped with the exception of one sample, identified as S14303. This sample had a particularly high carbon content compared to the other plantation samples and there was a distinct difference in the intensity of the spectrum in the

vicinity of 1920 nm, attributed to changes in carbonyl content. The pasture soils showed less strong grouping although, in terms of the first principal component, they were grouped between the native forest and plantation forest soils. Principal component analysis of the NMR spectral data (Fig. 6) showed a similar trend. The first principal component again showed separation of the samples based on land use. The carbonyl region of the spectrum between 160 and 190 ppm showed correlation for both the first and second principal components.

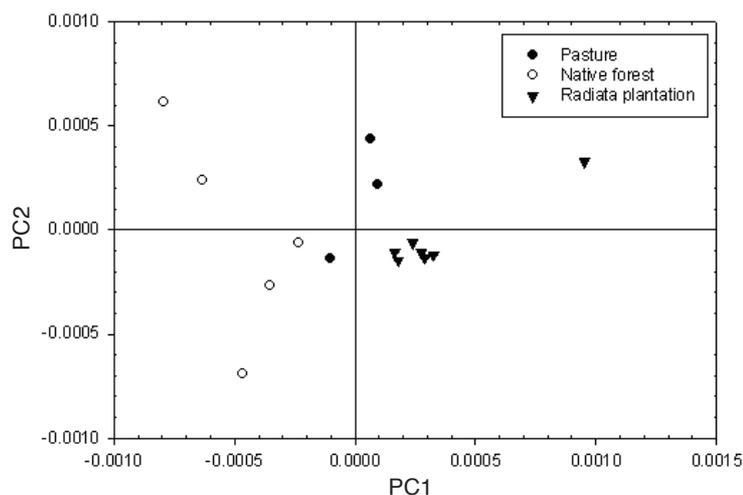


FIG. 5—Principal component analysis scores plot of the 2nd derivative NIR spectral data for the soil samples showing their separation based on land usage.

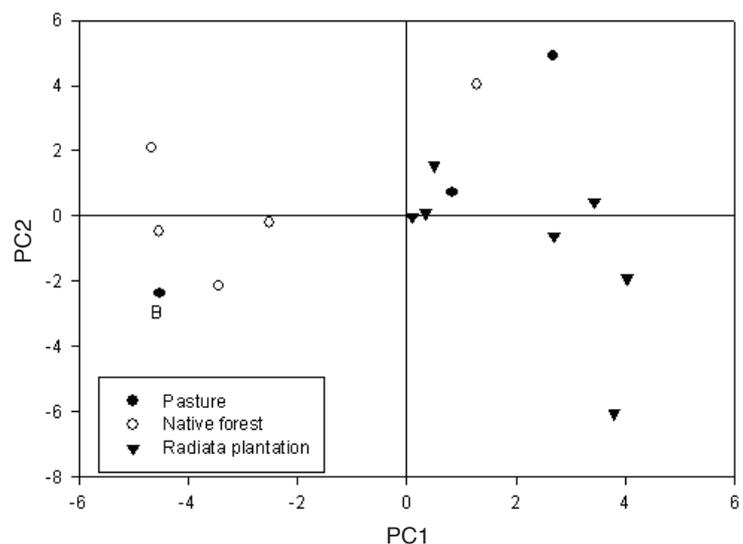


FIG. 6—Principal component analysis scores plot of the NMR spectral data for the soil samples showing their separation based on land usage.

The summary data for the projection to latent structures regression of the mid IR spectra against the chemical data are given in Table 3. Both the calibration and validation data are presented and the error is expressed as a percentage of the range of observed values. The summary data for the projection to latent structures regression of the NIR data are shown in Table 4. While the R^2 values for the calibration data were high for all elements measured and for pH, consistent with results obtained by Reeves *et al.* (1999, 2002) and Chang *et al.* (2001), the poor result for the validation model may be due to the statistically low sample numbers used in this study. The coefficient of determination for NIR prediction of carbon content was 0.91 for the calibration model with an error of prediction of 5.4% C resulting in an error in prediction of 19% of the range. Overall prediction of nitrogen content was poor and is also consistent with previously reported findings (Krischenko *et al.* 1992).

The summary data for the projection to latent structures regression of the NMR spectra against the chemical data are shown in Table 5. Results similar to those for NIR again showed reasonable values for the coefficients of determination (R^2) for the calibration model using four latent variables, but once again the validation values were poor, indicating the effects of low sample numbers. Interestingly, however, the error expressed as a percentage of the mean of the range showed both pH and potassium to be better predicted by NMR than by NIR.

TABLE 3—Results of projection to latent structures regression of chemical data *versus* mid IR spectra (five latent variables, of eight maximum)

	pH	C	N	C:N	P	K
R^2 (calib.)	0.81	0.94	0.92	0.82	0.88	0.81
R^2 (valid.)	0.04	0.53	0.40	0.16	0.13	0.45
RMSEP	0.53	5.6	0.40	7.2	17.1	0.36
Range	2.3	28.3	1.9	17.9	50.5	1.85
%RMSEP	23	20	20	39	34	19

TABLE 4—Results of projection to latent structures regression of chemical data *versus* NIR spectra (five latent variables, of eight maximum)

	pH	C	N	C:N	P	K
R^2 (calib.)	0.74	0.91	0.81	0.86	0.86	0.76
R^2 (valid.)	0.37	0.56	0.45	0.19	0.55	0.26
RMSEP	0.43	5.4	0.39	5.2	14.7	0.55
Range	2.3	28.3	1.9	17.9	50.5	1.85
%RMSEP	18	19	21	29	29	30

TABLE 5—Results of projection to latent structures regression of chemical data *versus* NMR spectra (six latent variables, of eight maximum)

	pH	C	N	C:N	P	K
R ² (calib.)	0.92	0.92	0.92	0.59	0.65	0.90
R ² (valid.)	0.66	0.41	0.40	0.05	0.03	0.67
RMSEP	0.29	6.6	0.40	5.3	22.6	0.28
Range	2.3	28.3	1.9	17.9	50.5	1.85
%RMSEP	13	23	21	30	44	21

The loadings plots for the mid IR, NIR, and NMR spectra resulting from projection to latent structures regression are presented in Fig. 7, 8, and 9 respectively. The loadings represent the regions of the spectra that correlate with the observed variance in the chemical data. The IR loadings (Fig. 7) showed strong correlations for both PC1 and PC2 at 3570 cm⁻¹ (O-H stretch, ArOH), 2970 cm⁻¹ (C-H stretch, -CH₃), 1760 cm⁻¹ (C=O), 1710 cm⁻¹ (C=O, COOH), 1275 cm⁻¹ (N-H amide), 1026 cm⁻¹ (C-O stretch, ArOH; PO₄). The first two principal components accounted for 52% of the spectral variance while accounting for 66% of the variance in the soil chemical data. The NIR loadings (Fig. 8) showed absorbances at 1414 nm (CH, ArOH), 1548 nm (NH, OH), 1732 nm (CH, CH₂), and 1904 nm (H₂O, C=O) which showed the most significant correlation with the chemical data, with 96% of the observed variation in the NIR accounting for only 44% of the variation in the chemical data. The NMR loadings (Fig. 9) exhibiting the greatest correlation showed resonances at δ 180 (C=O), 140 (ArOH), 110 (Ar), and 35 (CH₂), with 85% of the variance in the NMR data accounting for 60% of the variance in the chemical data.

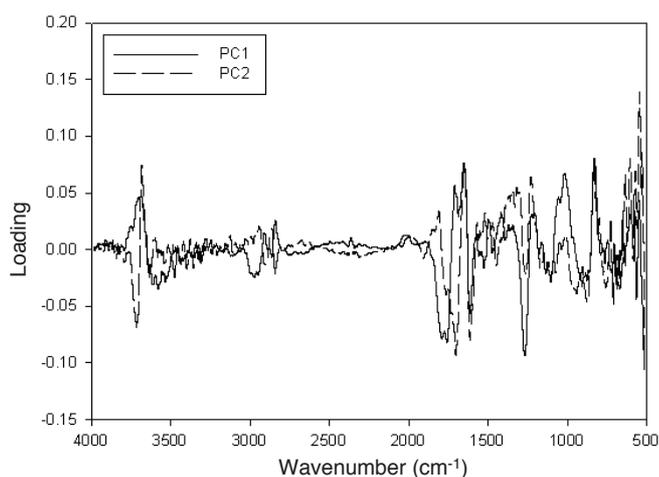


FIG. 7—Loadings plot for the first two latent variables from projection to latent structures regression of mid IR spectra with chemical data.

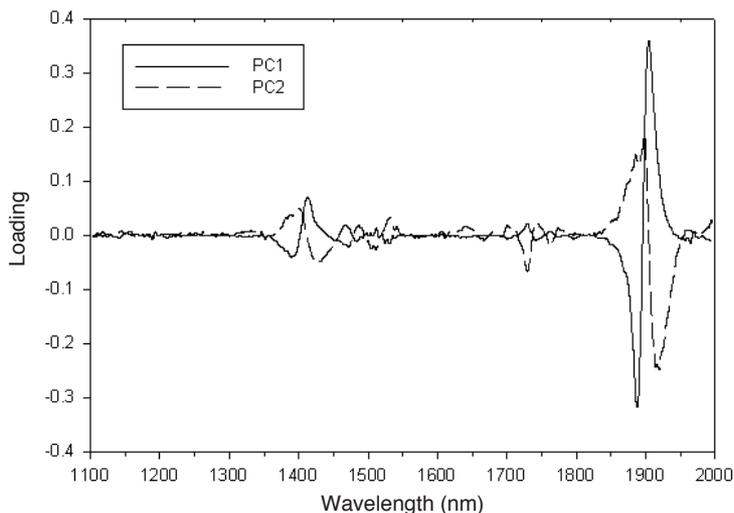


FIG. 8—Loadings plot for the first two latent variables from projection to latent structures regression of NIR spectra with chemical data.

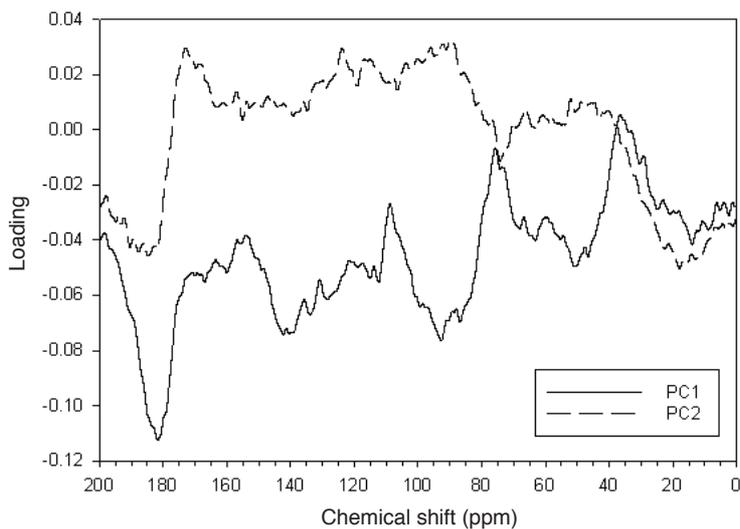


FIG. 9—Loadings plot for the first two latent variables from projection to latent structures regression of NMR spectra with chemical data.

A statistically significant reduction ($p=0.019$) in the aliphatic fraction of the soil was evident following land use change, with fractional areas of 0.31, 0.26, and 0.23 for the native forest, pasture, and *P. radiata* respectively. The aromatic fraction of the soils showed a tendency to increase in the *P. radiata* plantation, which was statistically significant ($p=0.014$) when plantation age was taken into account, and the phenolic/aromatic ratio therefore tended to decrease.

A GLM model that included soil pH, depth, and the aliphatic and aromatic fractional areas (for NMR spectra) jointly accounted for 80% (expressed in natural units) of the variation in soil total carbon (g/100 g soil) (Table 6). Soil carbon decreased as soil pH and sample depth increased, but carbon increased as the aliphatic and aromatic fractional areas increased. For example, at 0–0.05 m depth a doubling in the aliphatic fractional area (from 0.15 to 0.30) increased soil carbon from 7 to 18 at a pH of 3.8, and from 4 to 6 at a pH of 5.5. A small increase in soil carbon was associated with an increase in the aromatic fractional area, when other factors were equal.

TABLE 6—Factors associated with variation in the inverse of soil total carbon (g/100 g soil) from areas under native forest, or converted at least 80 years previously to pasture and *P. radiata*

	DF	MS	F value	Prob.>F
Depth	1	0.0367	113.5	0.0001
pH	1	0.0114	35.3	0.0001
Aliphatic fractional area	1	0.0036	11.2	0.007
Aromatic fractional area	1	0.0021	6.4	0.030

The model explained 80% of the variation in soil total carbon (expressed in natural units)

DISCUSSION

The results of this pilot study of soil organic matter fractions in volcanic soils were consistent with the results from earlier research (Beets *et al.* 2002), which demonstrated the importance of soil acidity as a factor contributing to spatial variation in mineral soil carbon accumulation under indigenous trees. Total carbon concentration decreased with increasing pH and sample depth. Across all land uses the reduction in total carbon with increasing pH was due mostly to a reduction in the aliphatic fraction, which suggests that the more labile pools of soil organic matter decay more slowly in acid microsites within the soil. The correlations between soil carbon and other elements including nitrogen and phosphorus are consistent with protection of organic matter fractions as organo-metallic complexes.

Although previous studies have shown a reduction in the carbohydrate fraction after intensive management of annual crops (Solomon *et al.* 2002), conversion of indigenous forest to pasture or pine involves relatively little cultivation disturbance and this may explain why land use effects were not strong, with only a small but statistically significant decrease in the aliphatic fraction and a gradual increase in the aromatic fraction evident following the land use change to *P. radiata*. Soil pH was less variable after the conversion of native forest to pasture and pine land uses (Beets *et al.* 2002), which may explain why recent organic matter inputs to the soil were not being protected to the same extent as in acidic native forest microsites.

The absence of strong land use effects on soil organic matter fractions suggests that soil carbon levels under pasture and pine largely reflect historical levels under indigenous forest. The pH in some of our subsoil samples was low, and therefore more carbon was protected as aliphatic carbon than in some surface samples, which may explain why an increase in the aromatic fraction with soil depth was not evident in this preliminary study. The initial loss in soil carbon that occurred at Puruki after afforestation of pasture with *P. radiata* (Beets *et al.* 2002) may in future be followed by an increase in soil carbon as the pines gradually acidify the soil.

In this study the results of projection to latent structures regression of spectra against soil chemistry are presented with both the calibration and validation data. This provides a more meaningful analysis of the predictive ability of individual techniques in quantifying soil chemistry.

CONCLUSION

All of the spectroscopic techniques (mid IR, NIR, and NMR) showed ability to establish calibration models for the prediction of soil chemistry, with NIR and solid state NMR spectra in particular showing high R^2 values for the calibration models of carbon, nitrogen, and phosphorus. Their actual predictive ability, however, is not as good, as evidenced by the low R^2 values for the validation set and the high %RMSEP values which showed greater than 10% error in prediction. It is not known whether these results compare favourably with those previously published as the regression data for model validation are seldom presented. Both NIR and NMR, however, did show trends with the origin and age of the land use. The conversion of native forest to pasture and to plantation *P. radiata* showed a decrease in the ratio of phenolic to aromatic carbon, gradually increasing with the age of the plantation as new litter was deposited and accumulated.

High sequestration of soil carbon in this Andisol soil under podocarp / hardwood forest resulted from the protection of the readily decomposable aliphatic fraction at low soil pH. Carbohydrate was the dominant fraction of soil organic matter at all pH values. Nuclear magnetic resonance and NIR spectroscopy of the solid soil fractions provided weak correlations with the current land use of the soil samples, based primarily on variance in the aliphatic and aromatic regions of the spectra, even though indigenous forest clearance had occurred 80 years previously.

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