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To cite this version:

Isabelle I. Bertrand, L.J. Janik, R.E. Holloway, R.D. Armstrong, M.J. Mclaughlin. The rapid assessment of concentrations and solid phase associations of macro- and micronutrients in alkaline soils by mid-infrared diffuse reflectance spectroscopy. Australian Journal of Soil Research, 2002, 40 (8), pp.1339-1356. 10.1071/SR01104 . hal-02681542

HAL Id: hal-02681542
https://hal.inrae.fr/hal-02681542v1

Submitted on 31 May 2020

CSIRO Publishing

Australian *Journal* of Soil Research

VOLUME 40, 2002

An international journal for the publication of original research into all aspects of soil science

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Aust. J. Soil Res., 2002, **40**, 1339–1356

The rapid assessment of concentrations and solid phase associations of macro- and micronutrients in alkaline soils by mid-infrared diffuse reflectance spectroscopy

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Abstract

Chemical analysis is a crucial but often expensive and time consuming step in the characterisation of soils. Mid-infrared diffuse reflectance (MIR-DRIFT) spectroscopy coupled with partial least square (PLS) analysis was used to determine macro- and micronutrient concentrations of a range of alkaline soils from southern Australia. Solid phase associations of macro- and micronutrients were also investigated using the mineralogical information contained in the infrared spectra of soil samples. Results showed that MIR-PLS analysis is a powerful and rapid technique for the accurate prediction of more than 15 chemical properties from each soil sample spectrum. Correlation coefficients for MIR derived concentration *versus* laboratory determined values were greater than $R^2 = 0.80$ for soil moisture, calcium carbonate concentration, total concentration of Mg, K, S, Fe, Al, Mn, Zn, Cu, and oxalate-extractable Al, Fe, Mn, and Si. In calcareous soils, sulfur was associated with carbonate and conversely Mg was more related to the clay concentration of soils. Micronutrients such as Fe, Zn, Mn, and Cu were positively associated with smectite/illite in the clay fraction and negatively with kaolinite. The potential use of these results in partitioning model to assess plant available micronutrients pools is discussed.

Additional keywords: alkaline soils, mid-infrared spectroscopy, carbonates, clays.

Introduction

Alkaline soils represent an important proportion of world soils but are often associated with fertility problems such as sodicity and nutrient deficiencies (Matar *et al.* 1992; Ford *et al.* 1993). Calcarosols, Vertosols, and alkaline Duplex soils, as defined by McKenzie *et al.* (1999), are amongst the most common Australian alkaline soils. These soils represent the majority of soils used for grain production in southern Australia. For example, highly calcareous soils cover an area >1 million hectares and they produce 40% of South Australia's wheat crop (Holloway *et al.* 2001). In Victoria, alkaline sodic soils, i.e. Duplex soils or cracking clays, represent 50% of the total agricultural area (Ford *et al.* 1993; Peverill *et al.* 1999). The major constraints for agricultural productivity associated with alkaline soils include micronutrient deficiencies (Zn, Cu, Mn, Fe) and/or toxicities (e.g. B), a constant need for inputs of N and P, and poor soil physical structure resulting from sodicity.

The agronomic potential of soils can be partly assessed using chemical analyses. However, current methods for the determination of chemical characteristics and nutrient concentrations in soils are both time consuming and costly. Also, chemical extractions, generally performed to assess soil fertility, are often poor predictors of the bioavailability

10.1071/SR01104 0004-9573/02/081339

of many elements (Simpson *et al.* 1997; Saggar *et al.* 1999). Consequently there is an increasing need to develop a rapid method to accurately assess soil chemical characteristics. However, total concentrations may not adequately describe the relationships between macro- or micronutrients and major soil chemistry. It may be more appropriate to model the nutrient and micronutrient concentrations according to their relationships with soil mineralogy, e.g. clay, iron oxides, and with the type of organic matter in order to predict element availability. Soil fractionation procedures and sequential extractions have been developed to address these problems (for example Chang and Jackson 1957, for phosphorus). However, the numerous procedures available in the literature all suffer from a lack of specificity for the extracting solution used (Barbanti *et al.* 1994; Flores-Vélez *et al.* 1996). Consequently, the distribution and binding of chemical elements among different soil mineral phases remains difficult to determine.

Mid-infrared (MIR) spectroscopy offers a potential alternative and a much faster and cheaper method for determining soil macro- and micronutrient concentrations. MIR has been widely used in soil chemistry to separate and identify soil organic compounds (Schnitzer 1965). More recently, partial least square (PLS) regression has been used for the quantitative prediction of organic carbon and nitrogen concentrations in peats (Holmgen and Norden 1988). However, only a few studies have reported the use of MIR-PLS analysis for soil chemical characterisation. Janik *et al.* (1995, 1998) and Janik and Skjemstad (1995) have used MIR diffuse reflectance (DRIFT) spectroscopy coupled with PLS analyses to predict major elemental composition of a large range of Australian soils determined by X-ray fluorescence (XRF), and other common laboratory measurements such as pH, organic carbon, carbonate, and clay concentrations. However, no published report exists on the success of MIR-DRIFT to predict micronutrient concentrations in alkaline soils and on the use of the supplementary mineralogical and organic information offered by MIR to determine the soil constituents with which micronutrients are associated.

The aims of this study were (*i*) to assess the validity of using MIR-DRIFT spectroscopy, coupled with PLS, to determine chemical characteristics, and nutrient and micronutrient concentrations of highly contrasting alkaline soils from southern Australia, and (*ii*) to use MIR-PLS analysis to determine the major mineral phases responsible for retention of nutrients and/or pollutants in alkaline soils.

Materials and methods

Soil samples

Surface soil samples (10 cm depth) from 48 alkaline soils were collected from southern Australia. Soil pH measured in 1 : 5 soil : water extracts according to Rayment and Higginson (1992) had a mean of 8.48 ± 0.41. Most of the soils collected had been cropped for at least 25 years and had received regular applications of macronutrients (especially P and N) and micronutrients (mainly Zn) at variable rates. Sampling was performed mainly in 2 regions, i.e. northern agricultural South Australia (upper Eyre Peninsula) and western Victoria. These regions have a Mediterranean climate with mean annual rainfall ranging from 300 mm/year for upper Eyre Peninsula to 500 mm/year for western Victoria.

Of the 25 soils collected from western Victoria, 6 were from the Wimmera area and classified as Grey and Brown Vertosols (Isbell 1996), 9 were from the southern Mallee and were classified as alkaline Duplex soils, 6 were from the central Mallee and were identified as Sodosols, and 4 were from the northern Mallee and were classified as Vertosols for two of them and as Red Brown Calcareous soils for the two other. According to the classification of Isbell (1996), the 23 soil samples collected from Upper Eyre Peninsula were classified as Supravescent and Hypervescent Calcarosols. The soil samples were air-dried and sieved to <2-mm before storing at room temperature prior to analysis.

Chemical soil analyses

Concentrations of nutrients and micronutrients in soils were determined after extraction and microwave heating following the USEPA SW 3051A method (USEPA 1993). Ca, S, Na, B, Al, Fe, K, Mg, P, Mn, Cu, and Zn were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Oxalate-extractable Al (Al_{ox}), Fe (Fe_{ox}), Mn (Mn_{ox}), and Si (Si_{ox}) were determined according to the method of McKeague and Day (1966). Organic carbon and organic P were measured following the procedures of Heanes (1984) and Walker and Adams (1958), respectively. Analyses of $CaCO_3$ were performed according to the procedure of Martin and Reeve (1955). Air-dry moisture and moisture content at 120 cm water-tension (water holding capacity, WHC) were determined following methods 2A1 and 2C1 respectively by Rayment and Higginson (1992).

Clay fraction extraction and characterisation

The clay fractions (<2 µm) were extracted using a procedure according to Jackson (1956) and the clay concentration of the soils was then deduced from the total amount of clay collected from each soil sample. Iron and aluminium oxy-hydroxides were extracted from the clay fractions when sufficient clay was present (i.e. 32 samples) by using a citrate bicarbonate dithionite (CBD) solution according to McKeague and Day (1966). Fe and Al concentration in the extracts were measured by ICP-AES analysis. Concentrations of nutrients and micronutrients were also determined on the clay fractions using the procedures described above for the whole soil sample.

X-ray diffraction (XRD) analyses were performed on some clay fractions using a Philips PW1800 microprocessor-controlled diffractometer with Co Kα radiation, and graphite monochromator. Quantitative analysis of the XRD data was performed using the commercial software package SIROQUANT from Sietronics Pty Ltd.

Infrared analysis

All spectra were recorded on a rapid scanning Fourier Transform Spectrometer (BioRad FTS-175C) scanning at 1 scan/sec, with an extended range KBr beamsplitter and Peltier-cooled DTGS detector, and with a full spectral range of 8300–470 cm^{-1} at 8 cm^{-1} resolution. Sampling was by diffuse reflectance from the powdered sample surface using an off-axis diffuse reflectance accessory (Harrick DRS-3SO). Spectral frequencies were referenced against an internal He-Ne laser to give a precision of 0.01 cm^{-1}. A KBr blank was used to test spectrometer performance and as a reference for the sample spectra. Acquisition and processing of each spectrum took about 1 min per sample over 60 co-added scans. The sample absorbance spectra were directly acquired in IBM-PC Grams-32 format (Galactic NH).

Subsamples of soils used for chemical analysis were ground in an orbital mill with a stainless steel ball (Siebtechniqe) to obtain a minimum particle size of 100 µm for MIR analysis. A comparison of 2 methods was then used for MIR: (*i*) after 1 min of grounding, soil samples were directly scanned by MIR as neat powders using the diffuse reflectance infrared method outlined by Janik *et al.* (1995), or (*ii*) 0.1 g of soil samples was diluted with 1 g powdered KBr (10% w/w) and ground for 1 min. All samples were then immediately transferred to a sample holder and the surfaces of the powders were levelled. Spectra of all clay fractions were determined only on neat samples.

The specific software used for both principal component analysis (PCA) and partial least squares (PLS) was PLSplus/IQ V4.05 (Galactic) within Grams-32 (Galactic NH). The spectra were averaged over successive 3 points segments, in order to reduce computation time. The optimum frequency range (4000–1030 cm^{-1}) and number of PLS terms (factors) were determined empirically to give maximum cross-validation R^2 values which corresponded to the minimum standard error of cross-validation (SECV). In this paper, all references to regression coefficients (R^2) were determined following cross-validation. Spectra were baseline corrected and mean centered.

Partial least squares and principal component analysis

The procedure for PLS analysis was adapted from the PLS1 method of Haaland and Thomas (1988). Essentially, an X data variable array and corresponding properties are transformed into a smaller set of mutually orthogonal factors, which are used as subsequent predictor variables. These factors are characterised by loading vectors which include a loading for each reflectance value (eigenspectra), loading weights which represent the importance in the spectra with respect to concentration, and scaling terms for the loading called scores. The original spectrum for each sample in the X array can be reconstructed from a linear combination of loadings and scores. Most of the spectral and property information is represented by the first 2 loadings. The scores can be used to provide scatter plots maps of the sample variability or combined with the PLS regression coefficients to yield predictions, whilst loading weights give qualitative information on the correlation between the spectra and sample properties or concentrations. Although the first loading weight is in essence a spectrum of the 'pure' soil components correlating most strongly with the soil properties, subsequent loading weights show variation within this 'pure' component spectrum, i.e. minor components or frequency shifts and aberrations.

A PCA using the Grams PLSplus-IQ self-prediction option for a maximum of 23 factors was performed for the 48 neat soil samples (no outliers removed). The 4000–1030 cm^{-1} portion of the spectra was used and only 2 principal components were needed to account for 90.4% of the variance.

Calibration for the determination of soil properties by PLS were carried out by means of the 'leave-one-out' cross-validation procedure, a method based on the algorithm developed by Haaland and Thomas (1988).

Six different types of calibration were performed. The first type was a calibration between the laboratory-determined analyses and the analyses derived from MIR spectra of the whole soils (Table 1). The same types of calibrations were then performed for samples with and without carbonate (Table 2). The third type of calibration was performed between the laboratory-determined analyses of the clay fraction and the MIR-derived analyses from the spectrum of the clay fraction (Table 3). A calibration was then set up with measured laboratory analyses of the whole soil and the analyses derived from MIR of the clay fraction (Table 3). The 2 last calibrations were performed between the measured laboratory analyses of the whole soil and the MIR derived analyses from the spectrum of the clay fraction without carbonate and after a CBD extraction, respectively (Table 3).

Results and discussion

Assessing a grouping of the soil samples with common mineralogy

PCA was carried out using the PLSplus/IQ software so that sample variability according to their spectra could be assessed. The results of the PCA are depicted in Fig. 1, which shows a plot of scores for the principle component PC1 *versus* PC2 for the full set of neat soil spectra. PC1 was characterised by strong peaks at 2600–2520 and 1800 cm^{-1} due to carbonates (data not shown) and PC2 by positives peaks at 2000–1860 cm^{-1}, which can be associated with quartz (Nguyen *et al.* 1991). Peaks due to clay minerals were also observed at 3620, 3450, 3300, and 1200 cm^{-1} (data not shown) (Fig. 1). In spite of the relative small number of samples used in the training set, the PCA analyses demonstrated that only 2 factors would adequately describe over 90% of the variance. For the present study, fewer than 11 factors were usually sufficient to describe the model (Table 1).

The laboratory data from the 48 soil samples used in this study showed a wide distribution of physical and chemical properties (Fig. 1 and Table 1). Samples from the central Mallee exhibited the highest amount of sand, whereas those from the Eyre Peninsula were the most calcareous, and Wimmera and southern Mallee soils had high clay concentrations (Fig. 1). These results agree well with the proportions of the major phases (clay and carbonate concentrations) of the soils (Table 1). PCA coupled with near-infrared (NIR) spectrum has been used by Stenberg *et al.* (1995) to improve field-sampling protocols. They concluded that this method could reduce by up to 70% of the cost associated with specific soil analyses and was a useful tool for the selection of field sites. However, these authors made their evaluation with the emphasis on 5 specific soil properties important for soil fertility, i.e. clay concentration, soil organic matter, CEC, pH, and base saturation. Their results revealed that none of the methods tested were ideal for all 5 parameters. They finally proposed a peripheral selection from a 2-dimensional PCA plot and pH data. In the present study, the use of PCA loadings allowed the determination of the major mineral or organic constituents of the soil, together with a grouping of the soils as a function of their major mineralogical characteristics. The method improves the accuracy of

Table 1. Soil properties and MIR-PLS parameters for neat and KBr dilute samples

Range of concentration, MIR-PLS regression coefficients (R^2), standard errors on the cross validation (SECV), and number of factors for the neat and KBr dilute samples. All regressions were significant at $P \leq 0.01$. Statistical differences (F value) at 0.05 (*) were performed between the regressions obtained for neat and dilute samples assuming a normal distribution of the error. Moisture (Moist), organic carbon (Org. C), calcium carbonate ($CaCO_3$), clay concentration (Clay), water holding capacity (WHC), and organic P (Org. P)

	Moist	Org. C	$CaCO_3$	Clay	WHC	Org. P	Mg^A	P^A	K^A	S^A	Al_{ox}^B	Fe_{ox}^B	Mn_{ox}^B	Si_{ox}^B	Al^A	Fe^A	Mn^A	Zn^A	Cu^A
			(%)									(mg/kg)							
									Range of concentrations										
Minimum	0.4	0.3	0	2	4	23	410	33	630	41	119	68	11	43	4600	3100	12	4	3
Maximum	12	4.7	87	42	52	243	15530	761	14320	1246	1756	1418	356	1083	55800	37900	506	41	22
									Neat samples										
R^2	0.91	0.51	0.98	0.74	0.92*	0.58	0.84	0.60	0.87	0.86	0.88	0.86	0.85	0.95	0.93	0.93	0.80	0.88	0.82
SECV	0.9	0.5	4	8	4	30	1211	101	1499	134	165	152	41	69	4708	2991	66	4	2
Factors	13	5	7	8	12	2	15	3	9	3	7	6	6	11	11	11	6	8	13
									KBr dilute samples										
R^2	0.86	0.66	0.97	0.67	0.84*	0.56	0.82	0.54	0.91	0.91	0.84	0.85	0.90	0.94	0.93	0.94	0.87	0.91	0.86
SECV	1.2	0.4	5	7	5	30	1274	105	1241	129	189	160	33	82	4924	2825	50	3	2
Factors	14	9	8	3	8	4	12	3	12	14	5	7	7	11	20	13	7	11	12

[A] Total concentrations.

[B] Oxalate-extractable.

Table 2. **Range of concentration and MIR-PLS parameters of neat samples with more (n = 25) or less (n = 23) than 2% $CaCO_3$**

Regressions were all significant at $P \leq 0.01$. Statistical differences (F value) at 0.05 (*) were performed between the regressions obtained for samples with > and <2% $CaCO_3$ assuming a normal distribution of the error

	Moist	Org. C	$CaCO_3$	Clay	WHC	Org. P	Mg	P	K	S	Al_{ox}	Fe_{ox}	Mn_{ox}	Si_{ox}	Al	Fe	Mn	Zn	Cu
			(%)									(mg/kg)							
Range of concentrations for samples with $CaCO_3$ >2%																			
Minimum	1	0.7	3	3	11	67	1290	129	630	117	119	68	17	43	4600	3200	58	5	4
Maximum	12	3.3	87	40	36	243	15530	761	12100	1246	1756	1100	214	1074	55800	37900	377	36	19
Range of concentrations for samples with $CaCO_3$ <2%																			
Minimum	0.4	0.3	0	2	4	23	410	33	780	41	200	150	11	104	5700	3100	12	4	3
Maximum	11	4.7	1	42	52	173	8020	352	14320	212	1694	1418	356	1083	58300	36800	506	41	22
$CaCO_3$ > 2%																			
R^2	0.68	n.r.	0.94*	0.53	0.74	0.40*	0.47*	0.59	0.94*	0.71*	0.92*	0.91	0.82	0.94	0.94	0.95	0.58	0.72	0.74
SECV	1.5		7	9	5	37	2284	112	836	179	117	86	38	64	3468	3057	61	4	2
$CaCO_3$ < 2%																			
R^2	0.91	0.62	0.56*	0.74	0.95	0.75*	0.93*	0.39	0.85*	0.50*	0.69*	0.79	0.83	0.91	0.94	0.92	0.88	0.91	0.84
SECV	1	0.6	0.4	7	4	19	633	80	1694	42	256	188	48	90	4493	3248	57	3	3

n.r., no regression possible with the present data set.

Table 3. MIR-PLS parameters of the clay fraction

Means ± standard deviation of the percentage of the chemical elements lost during the clay fraction extraction. MIR-PLS regression coefficients (R^2) performed with (*i*) measured laboratory clay analyses and clay spectra, (*ii*) laboratory whole soil analyses and the clay spectra, (*iii*) laboratory whole soil analyses and the clay spectra without carbonates, and (*iv*) laboratory whole soil analyses and the CBD-clay spectra. Regressions were all significant at $P \leq 0.01$

	Org. C	$CaCO_3$	Org. P	Mg	P	K	S	Al_{ox}	Fe_{ox}	Mn_{ox}	Si_{ox}	Al	Fe	Mn	Zn	Cu
% element lost																
				36 ± 25	32 ± 11	38 ± 12	40 ± 29					17 ± 12	32 ± 14	33 ± 12	18 ± 7	37 ± 13
Cross validation of clay laboratory analysis and clay spectra (48 samples)																
R^2				0.64	n.r.	0.83	0.40					0.96	0.94	n.r.	0.48	0.49
SECV				1421		1927	459					2610	3145		11	9
Cross validation of whole soil laboratory analysis and clay spectra (48 samples)																
R^2	n.r.	0.90	0.36	0.32	0.37	0.69	0.91	0.71	0.63	0.59	0.77	0.69	0.73	0.51	0.70	0.64
SECV		9	38	2509	125	2315	105	260	242	67	152	8973	5892	97	6	3
Cross validation of whole soil laboratory analysis and clay spectra without carbonates (23 samples)																
R^2		n.r.	0.43	0.68	0.36	0.59	0.43	0.48	0.49	0.47	0.60	0.61	0.68	0.54	0.66	0.64
SECV			29	15	96	2854	52	349	283	80	199	11619	6627	111	7	4
Cross validation of whole soil laboratory analysis and clay spectra after CBD extraction (32 samples)																
R^2	n.r.	0.95	n.r.	n.r.	0.28	0.47	0.74	0.57	0.50	0.43	0.66	0.58	0.57	n.r.	0.55	0.40
SECV		5			89	2975	152	305	296	83	181	11464	7496		7	4

n.r., no regression possible with the present data set.

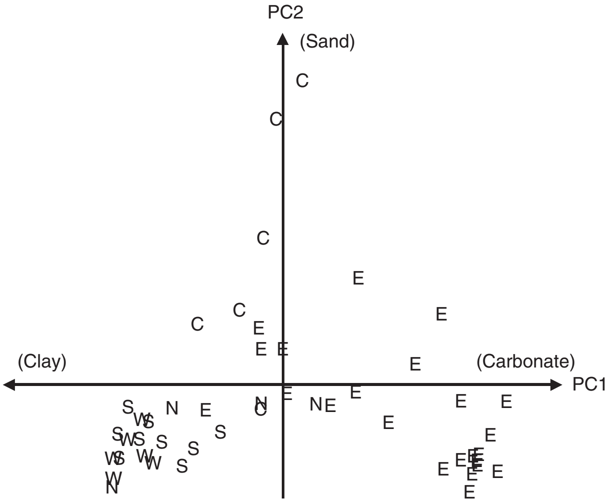

Fig. 1. Plot of the principal component analyses (PCA) score 2 *v.* score 1, where carbonate and clay peaks are strong in score 1 and sand in score 2. The full soil spectra set, i.e. 48 samples, was considered. The letters indicate the region of sampling: (E) Eyre Peninsula; (W) Wimmera; (S) Southern Mallee; (C) Central Mallee; and (N) Northern Mallee.

the sampling technique, by an objective selection of the soil samples directly from the mineralogical information contained in the IR spectrum.

Effect of sample preparation techniques on PLS quantification

Regression coefficients for PLS cross-validation (R^2) are presented in Table 1 for the neat and KBr dilute samples. All samples were considered for PLS analysis and no outliers were identified or omitted. Of the 19 laboratory-determined soil characteristics presented in Table 1, only 4 relationships had R^2 values <0.80 for the neat and dilute samples. Differences in regression coefficients between dilute and neat samples were generally low as indicated by the F-test values (Table 1), with only 1 analysis exhibiting a statistical difference at $P \leq 0.05$. Janik *et al.* (1995, 1998) and Nguyen *et al.* (1991) have stressed the advantages of analysing neat samples by MIR as it reduces sample preparation time, and eliminates weighing errors. However, to our knowledge no comparison of neat or KBr incorporated (dilute) soil samples has ever been published for the determination of soil properties by MIR-PLS. Our results prove that MIR of neat samples correlates well with a wide range of chemical analyses except for the determination of water holding capacity in soils (Table 1). However, even if the MIR-PLS regression coefficient, using the dilute method, was better in this case than for neat samples, there are several problems using the dilute method. The dilute method may have interferences that influence the regression coefficients, such as matrix effects that cause ion exchange (Piccolo and Stevenson 1982) or adsorption of water onto the particles used for the dilution, i.e. KBr. Consequently, taking into account the reduced sample preparation time and the elimination of possible artefacts resulting from the addition of KBr to the sample, there are significant advantages in utilising the neat sample method.

PLS quantification of macro- and micronutrient concentrations

Regression coefficients (R^2) for nutrients such as Mg, K, and S were >0.80 (Table 1). In contrast, the R^2 for P, one of the more important nutrients, was only 0.60. Likewise, regression coefficients for organic carbon and organic phosphorus were <0.60. However, Janik *et al.* (1995, 1998) found a good correlation (R^2 = 0.92–0.93) for the determination of organic carbon in soils by MIR-PLS analyses. The reasons for the poor regression coefficients for organic C and P in these alkaline soils are unclear. It is known that carbonates adsorbed strongly near 2900 and 1450 cm^{-1}, a similar region to that of organic C. It is not unreasonable, therefore, that there might be significant interferences in these spectral regions leading to a decrease in the predictions accuracy for organic C. In the case of organic and mineral P, the range of concentrations studied was wide. Consequently, due to the variable nature of P associations in soils, such as Ca-P, Fe-P, Al-P compounds, there are few uniform phases which can be identified by MIR within this soil set.

Regressions obtained in this study are limited to alkaline soils. As shown in Table 1, the values of standard errors of cross validation (SECV) are generally larger than the minimum concentrations, so predictions for unknown samples at low concentrations should be interpreted with caution.

Micronutrient concentrations correlated highly with spectral features determined by MIR-PLS (Table 1). Janik *et al.* (1998) reported that DTPA-extractable Fe, Mn, Zn, and Cu were difficult to predict by MIR-PLS with regression coefficients (R^2) of 0.55, 0.57, 0.24, and 0.20, respectively. They concluded that MIR was unlikely to provide quantitative data when (*i*) the soil property being predicted was not related to the major constituent of the soil, or (*ii*) the soil solution concentrations were too low, or not in equilibrium, with the solid phases. DTPA extractions were probably less related to the soil constituents than those using stronger extractants such as oxalate. In addition, oxalate extractions are well known as extractants for the amorphous fraction of iron and aluminium oxides in soil and consequently are directly related to soil mineralogy (Schwertmann 1964).

The correlations of spectral features with micronutrient concentrations were surprisingly good, considering the low elemental concentrations (Table 1). For example, Cu and Zn concentrations ranged from 3 to 22 and 4 to 41 mg/kg, respectively. Such small changes in concentration over a wide range of alkaline soils cannot be measured directly by MIR, and the correlations are probably related to other soil properties involving the major soil components. Malley *et al.* (1999) have shown that NIR was able to predict Mn concentration in 28 Canadian soil samples from 3 boreholes down to a depth of 10 m. However, all their soils were from one soil type and one location and it was concluded that their results could not be used for prediction in other soil types or location.

Compounds consisting of metal cationic species such as Mn, Cu, Zn, and to a lesser extent Al and Fe can absorb strongly in the mid- and near-infrared wavelength bands. Their direct detection at such low concentrations (<100 mg/kg), however, is probably not possible. The good regressions obtained may be due to the association of these metals with strongly O-H absorbing groups, such as those present at the surface of clays or organic matter (Krischenko *et al.* 1992), or to their association with CO_3^{2-} groups (Ben-Dor and Banin 1990). Nevertheless, Fig. 2 shows a linear plot of the data along the regression line for Fe, Cu, Zn, and Mn, and a similar relationship was obtained for Al, Fe_{ox}, Al_{ox}, and Mn_{ox}. The SECV values (Table 1) were generally lower than the minimum measured concentrations for Mn, Zn, and Cu, which indicates the high quality of the regressions over the range of concentrations studied.

Figure 3*a* depicts the first loading weight for Fe. This loading weight is characterised by the spectral signatures of soil components correlating with Fe concentration, e.g. Fe-oxy-hydroxides and Fe substitution within carbonates and clays. This loading weight was also characteristic for the other trace elements (Cu, Zn, Mn), which are apparently associated with similar soil mineralogy. As already shown by Janik *et al.* (1995), generally the first few PLS loading weights are sufficient to describe the main relationships between soil mineral phases and measured chemical properties. The first weight spectrum for Fe,

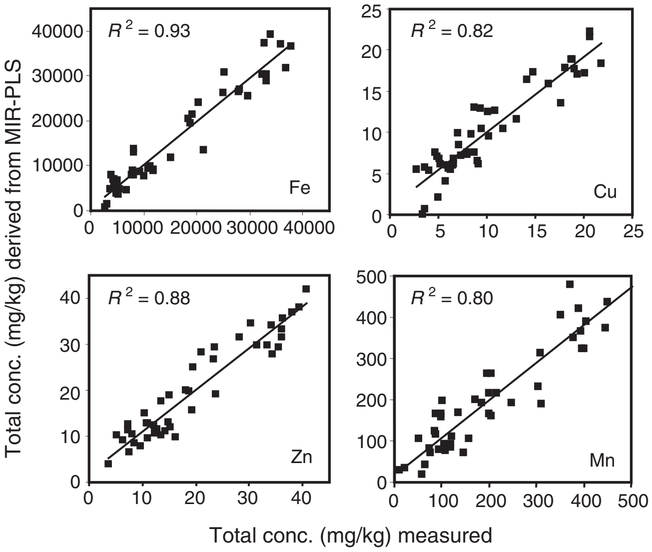

Fig. 2. Calibration relationships between concentrations derived from MIR-PLS analyses *v.* concentrations measured by microwave extraction for iron (Fe), copper (Cu), zinc (Zn), and manganese (Mn). Analyses were performed from the full soil spectra set ($n = 48$) obtained from the neat sample.

typical of those for the other metal concentrations in soils (Fig. 3*a*), showed strong positive peaks, which after comparison with standard materials (Fig. 4) were attributed to 2 : 1 layer alumino-silicate clay minerals such as smectites, illites, and interstratified illite/smectites and kaolin/smectites. These clay phases are characterised by broad bands near 3632 cm^{-1}, between 3500 and 3200 cm^{-1}, and near 1260–1191 cm^{-1}, and a small but sharp peak due to kaolinite at 3698 cm^{-1} (Fig. 3*a*). Dominant negative peaks in the first loading weight spectrum were assigned, according to Fig. 4, to lime (calcium carbonate), with peaks at 2875 cm^{-1}, 2590–2516 cm^{-1}, 1795 cm^{-1}, and 1494 cm^{-1}.

To confirm the correlation effect of high carbonate concentrations on the loading weight of some of the samples, an additional PLS analysis was performed using only those samples with no detected carbonate (Fig. 3*a*2). The first loading weight for Fe, depicted in Fig. 3*a*2 and also typical of the first loading weights for the other trace metals, was now dominated by positive peaks due to clay minerals at 3641–3597 cm^{-1}, 1630 cm^{-1}, and at 1194 cm^{-1}, and according to Fig. 4 negative peaks due to quartz (sand) near 2238 cm^{-1} and 1993–1791 cm^{-1} (Nguyen *et al.* 1991). Minor negative peaks characteristic of alkyl species for organic matter were observed near 2925–2856 cm^{-1}, and near 3711–3700 cm^{-1} and 3625 cm^{-1} for kaolinite. The clay mineral peak at 3597 cm^{-1} was near 3605 cm^{-1} for the Fe-rich Mulloorina illite illustrated in Fig. 4. This result suggested that trace metal concentrations were positively correlated with clay minerals, most probably smectite and Fe-rich illite, and inversely correlated with quartz, carbonate when present, and organic matter.

The second loading weights for Fe, Mn, Cu, and Zn are illustrated in Fig. 3*b*. These are characterised by strong positive peaks at 1993–1812 cm^{-1} due to quartz and weaker peaks near 3700 cm^{-1} and 3600 cm^{-1} due to kaolin and illite, respectively. The kaolin peak is particularly strong for Mn and Cu, and almost absent for Zn, suggesting a slightly different relationship with soil clay. The appearance of positive quartz peaks may be explained by an attempt by the PLS procedure to account for non-linearity in the intensity of the mid-infrared diffuse reflectance spectra due to quartz of varying particle size, but this explanation is purely conjecture. As for the first loading weight, negative organic alkyl peaks can be observed for all metals.

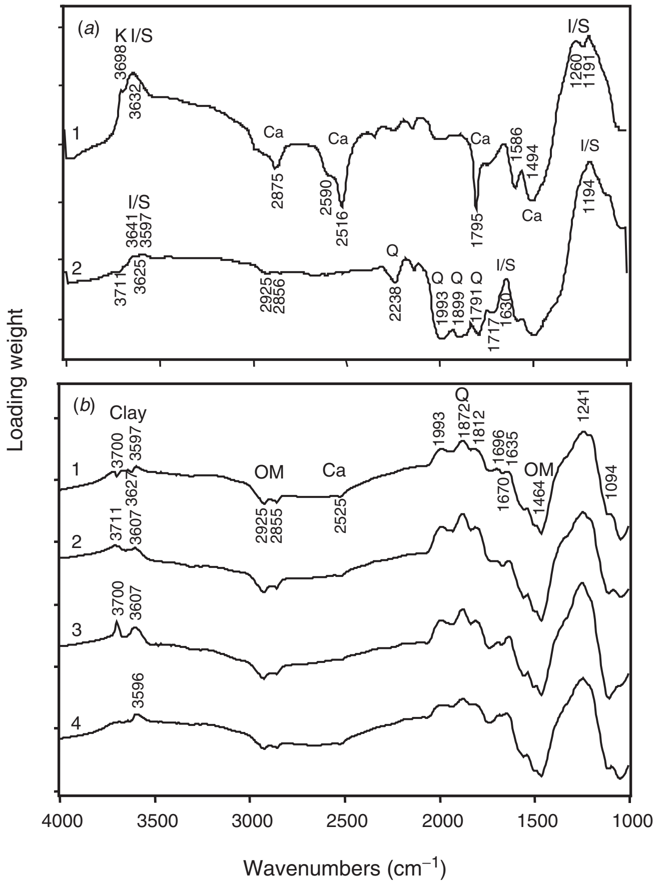

Fig. 3. (*a*) First weight loadings for iron: (*a*1) in all 48 samples and (*a*2) in samples without carbonates; and (*b*) the second weight loading for: (*b*1) iron, (*b*2) manganese, (*b*3) copper, and (*b*4) zinc obtained from the PLS analyses of all 48 neat soil samples. Minerals were identified as illite (I), smectite (S), kaolinite (K), calcite (Ca), quartz (Q); organic matter (OM) was also identified.

Effect of $CaCO_3$ concentrations on PLS quantification

The regression relationships for micronutrients may have been affected by a dilution effect due to the quartz, carbonate, and clay concentrations of the sample. Soils having a low concentration of clay were also those with the lower total micronutrient concentrations (Fig. 5). In addition, samples with the highest amount of sand also contained the lowest amount of clay and, to a lesser extent, carbonate (Fig. 1). Consequently, the dilution effect by sand and/or carbonate could possibly explain the resulting regressions. To test this hypothesis, the MIR-PLS relationships were split on the basis of the carbonate concentrations of the samples. The median value of 2% $CaCO_3$ was chosen arbitrarily to split the data set into 2 portions, as it allowed for a similar number of samples in the 2 new data subsets (Table 2). For neat samples with <2% $CaCO_3$, the regression relationships were significantly better for organic carbon, organic phosphorus and magnesium, and conversely poorer for potassium, sulfur, oxalate extractable Al and, as expected, $CaCO_3$. Thus, the presence of $CaCO_3$ adversely affected the relationship between spectral data and organic carbon regressions. The large difference obtained for the regression coefficients of organic carbon (Table 2) may be explained by a lack of specificity of organic carbon peaks in the presence of high levels of $CaCO_3$. The poor R^2 value for sulfur in less calcareous soils, and inspection of the first and second weight loading for S regression coefficients (data not shown), indicated that S was mainly correlated with $CaCO_3$. Since the regression for S,

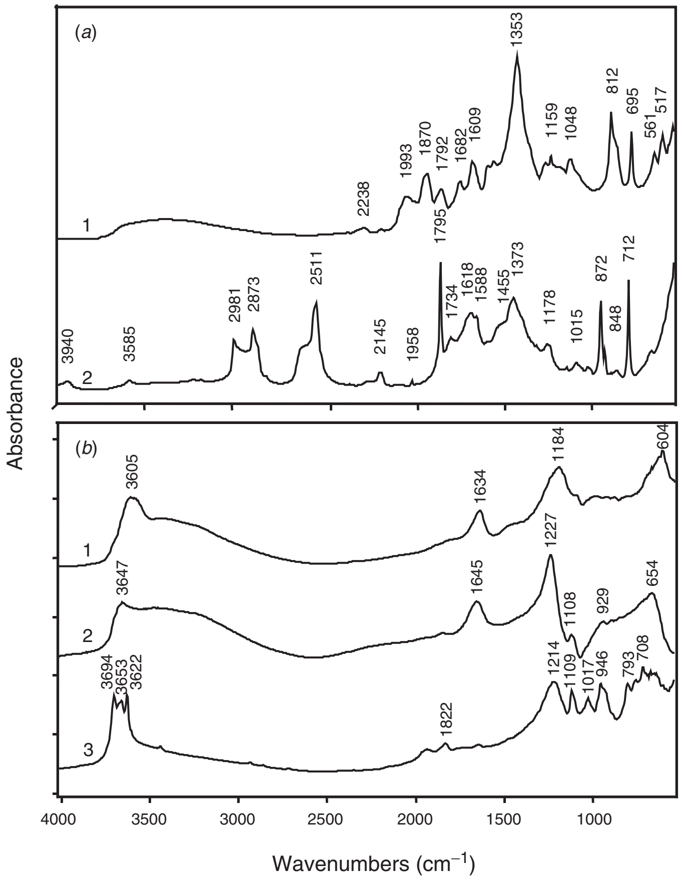

Fig. 4. Infrared spectra of neat standards of (*a*1) pure ignited quartz sand, finely ground (*a*2) pure calcium carbonate (Merck) and (*b*1) Muloorina illite, (*b*2) Andamooka-Ca saturated smectite, and (*b*3) poorly crystalline Georgia kaolinite.

Al_{ox}, and P in samples with >2% $CaCO_3$ (Table 2) was better than that for calcium carbonate-poor soils (Table 2), this confirmed the important role of $CaCO_3$ concentration on these regressions. For P, higher regression coefficients could be obtained using a more appropriate calibration set. Effectively, at high concentrations of P and in presence of calcium carbonate such as in calcareous soil, the formation of Ca-P compounds is likely (Freeman and Rowell 1981). These precipitations may cause the MIR spectra to become atypical of the remaining calibration set leading to difficulties in predictions. The regression coefficients for metals such as Cu, Zn, Al, and Fe were statistically independent of the $CaCO_3$ concentration. For Mn, the R^2 was only 0.58 for samples with >2% $CaCO_3$ compared with 0.88 for samples with <2% $CaCO_3$. Consequently, the high Mn correlation may have resulted from a dilution effect of carbonate on quartz, i.e. when the $CaCO_3$ concentration increases, the quartz and clay concentrations decrease. Another possible explanation was that Mn could be occluded in calcium carbonates particles and just not seen by MIR in calcareous soils. However, these explanations are inconclusive, as the differences between regression coefficients for Mn were not statistically significant

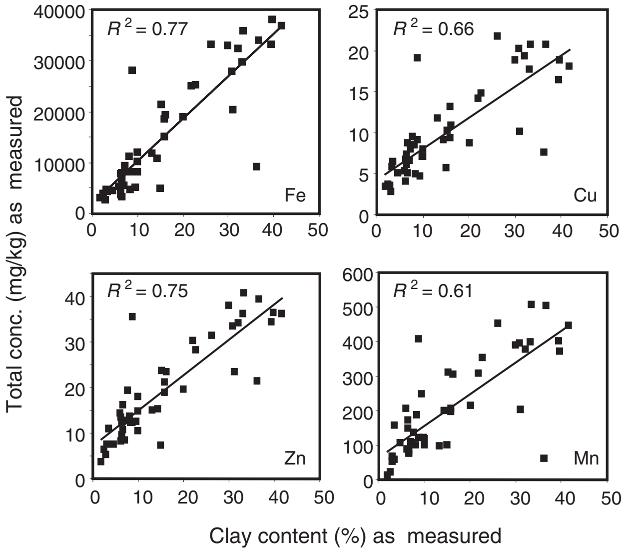

Fig. 5. Regression between clay concentration and total concentration (as measured in laboratory) for iron (Fe), copper (Cu), zinc (Zn), and manganese (Mn). The whole soil set was considered, i.e. 48 soils.

(Table 2). Even if the regression coefficients for Zn, Cu, Al, and Fe were not influenced by the carbonate, dilution by quartz remains one possible explanation for the good regressions obtained. In addition, trace metal concentration was mainly related to the clay concentration of the soils (Fig. 3). However, as the correlation between laboratory-determined clay concentration and laboratory-determined metal concentrations for the 48 soils (Fig. 5) was lower than the regression coefficients determined between MIR-PLS derived metal concentrations and laboratory-determined metal concentrations (Fig. 2), we can thus conclude that clay concentration was not the only property which influenced the relationship. It appears from Figs 3 and 5 that the type of clay, e.g. smectite, illite, or kaolinite, also plays an important role in the determination of metal concentrations in alkaline soils.

Assessing solid phase associations of nutrient and micronutrient

Table 3 represent the regression coefficients obtained from the regression of (*i*) measured laboratory concentrations of the clay fraction correlated with the MIR-derived concentrations from the spectra of the clay fraction, (*ii*) laboratory analyses of the whole soil with the analyses derived from MIR of the clay fraction, (*iii*) measured laboratory analyses of the whole soil with the analyses derived from the MIR spectra of the clay fraction without carbonates and after a CBD extraction, respectively. The observation of the clay fraction spectra (data not shown) indicates that only 23 clay samples were totally free of $CaCO_3$ after extraction.

A large part of the chemical elements was removed during extraction of the clay fraction (Table 3). In most cases >30% of the trace elements were lost probably by an exchange process with the concentrated NaCl and $CaCl_2$ solutions used during extraction. In addition, successive extractions were performed leading to desorption of exchangeable ions. This may also explain the high losses of chemical elements observed. The regressions obtained from MIR-PLS analysis performed between clay fractions and chemical analysis of the clay fraction were high for all the elements that are typical of the clay structure such as Fe, Al, and to a lesser extent K and Mg (Table 3). In the case of Zn, Cu, and Mn, the regression coefficients were poorer when the MIR-PLS analyses were performed between the clay spectra and laboratory clay analyses rather than the clay spectra and the laboratory whole soil analyses (Table 3). However, considering the fact that even when the regressions were performed between the clay spectra and the laboratory whole soil analyses, the R^2 values were always >0.50, it was thus concluded, as expected, that the clay fractions played a major role in the retention of Zn, Cu, Al, and Fe in these soils.

For calcareous samples, regression relationships for S, Al_{ox}, Fe_{ox}, Mn_{ox}, Si_{ox}, and Fe_{ox} (Table 3) with infrared spectral characteristics of the clay fraction were 10–53% better than the regressions for the clay spectra without carbonate and laboratory determined whole soil analyses (Table 3). These data confirmed the role of $CaCO_3$ in the retention of these elements in soil. For sulfur (S), for example, the regression coefficient (R^2) was 53% better in the samples containing $CaCO_3$, thus confirming the association of S with $CaCO_3$ as previously suggested. The most likely form of S in these soils is gypsum, co-precipitated with the $CaCO_3$. Conversely, the regression for Mg was 53% better when performed from the clay fraction spectra without carbonate (Table 3), thus confirming the same tendency already observed in Table 2. The large difference between regressions performed between clay spectra and whole soil analysis and CDB-clay spectra (Table 3) with laboratory-determined whole soil analysis strongly suggests that a substantial proportion of Mg was associated with iron or aluminium oxides possibly as well as within clay minerals. All the regressions performed with oxalate-extractable elements improved by 20–30% in soils containing $CaCO_3$ compared with soils without (Table 3).

The presence of carbonate did not affect regressions from the MIR-PLS analyses performed between the clay spectra and the laboratory whole soil analysis for Mn, Cu, and Zn (Table 3). The weight loadings of these micronutrients (Fig. 6) confirm that they were mainly associated with clay minerals. The first weight loading for Fe, depicted in Fig. 6, was similar to that of Mn, Cu, and Zn (not shown) and showed positive peaks due to an

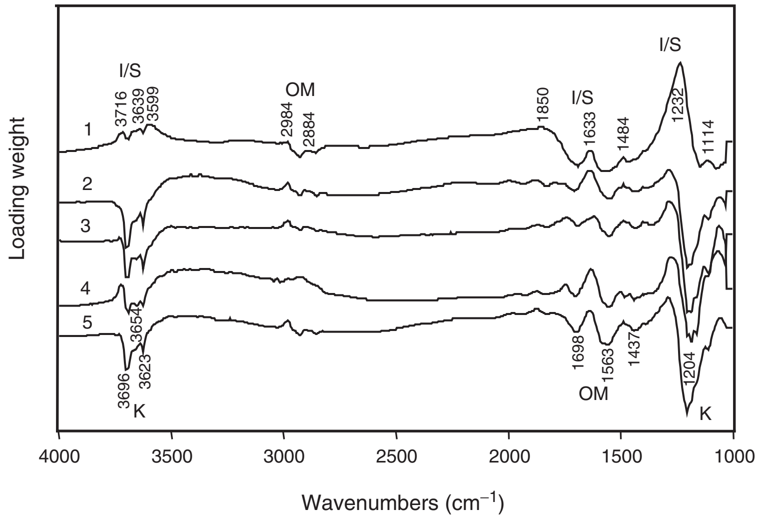

Fig. 6. First weight loadings for (1) iron and second weight loading for (2) iron, (3) copper, (4) zinc, and (5) manganese obtained from the PLS analyses of the clay fraction without carbonates and soil data. Minerals were identified as illite (I), smectite (S), kaolinite (K), calcite (C), quartz (Q), and iron oxide (Fe-O).

Fe-rich 2:1 layer alumino-silicate clay mineral indicated by peaks near 3600 cm^{-1}, 1633 cm^{-1}, and near 1232 cm^{-1}. In the second loading weight, negative peaks, suggesting a negative correlation with metal, were observed at 3696 and 3623 cm^{-1} for kaolinite and 2930 and 2860 cm^{-1} for organic matter. Sharp, strong negative peaks were observed in the second loading weight for all metals at 3696 and 3623 cm^{-1} due to kaolinite, near 1698 and 1563 cm^{-1} due to organic matter, and near 1204 cm^{-1} due to kaolinite. Additional positive peaks at 2984 and 2884 cm^{-1} suggested some contamination by acetate used in the preparation of the clay fractions.

XRD (data not shown) of the clay fractions showed that samples with high concentrations of metals, such as Mn, Cu, and Zn, had a low concentration of kaolinite and a higher concentration of smectite. This is consistent with the infrared results, which suggested a positive relationship with smectite/illite and negative relationship with kaolinite. Traces of hematite were identified by XRD, but not in sufficient amounts to be quantified. Essentially, the XRD results confirmed the spectra observed in Fig. 6.

In this study, there appeared to be no association between micronutrients, and Cu and organic matter. Previous studies have reported that organic matter, and its differing constituents (humic and fulvic acids), have been found to strongly bind Cu, and consequently influence Cu availability for plants (Petruzzelli and Buidi 1976; Peverill *et al.* 1999). However, most of the work previously performed on the dynamics of copper in soils was focussed on the available, or exchangeable, pool of Cu. This pool represents only a very small fraction of the total copper in soils. As IR peaks corresponding to organic matter were very small, they were considered to have an insignificant influence on the PLS analyses for the regressions for Cu. It was therefore concluded that the clay concentration, and particularly the type of clay, has more influence on the distribution of Cu concentrations in these alkaline soils than organic matter.

The regressions obtained from the laboratory-determined whole soil analysis and MIR spectra of the clay fraction after CDB extraction (Table 3) were considerably poorer for Cu, Zn, and particularly Mn after removal of the iron and aluminium oxides. Even if these elements were mainly associated with the clay mineral as interlayer cations (smectites) or with the clay mineral lattice, iron and/or aluminium oxides in the clay fraction also play an important role in the retention of micronutrients and especially Mn. The CBD extraction does not completely remove all the Fe and Al present (analyses not shown); a portion of these elements appears to be incorporated within the clay structure. Consequently, in the clay fraction, the relationships between the major structural elements such as Fe, Al, and Si remained; however, the regression coefficients were poorer as expected.

Use of a partitioning model to predict metal availability

The regression relationships determined by MIR-PLS allows the rapid analysis of soils to determine total concentrations of several micronutrients. In terms of soil fertility, total concentrations are not sufficient in themselves, but combined with models of metal availability (Sauvé *et al.* 2000), the technique offers the possibility of rapidly determining concentrations of available micronutrients or contaminants in soil solution. The model proposed by Sauvé *et al.* (2000) uses the total concentration of elements in soils, pH, and soil organic matter in the Eqns 1 and 2 for Zn and Cu, respectively:

$$\log_{10}(\mathrm{Zn_s}) = -0.55 \pm 0.04 * \mathrm{pH} + 0.94 \pm 0.08 * \log_{10}(\text{total Zn}) - 0.34 \pm 0.12 * \log_{10}(\mathrm{SOM}) + 3.68 \pm 0.31 \quad (1)$$

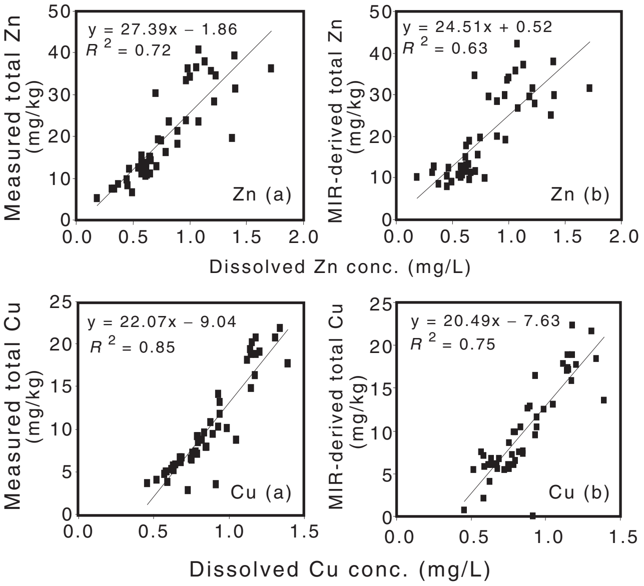

Fig. 7. Linear regressions of dissolved metal (Zn and Cu) concentrations (mg/L) deduced from the model of Sauvé *et al.* (2000) as a function of total concentration (*a*) as measured, and (*b*) as derived from MIR-PLS analyses.

$$\log_{10}(\mathrm{Cu_s}) = -0.21 \pm 0.02 * \mathrm{pH} + 0.93 \pm 0.05 * \log_{10}(\text{total Cu}) - 0.21 \pm 0.02 * \log_{10}(\mathrm{SOM}) + 1.37 \pm 0.14 \qquad (2)$$

with soil organic matter (SOM) expressed as %C, and total element concentration (total) expressed as mg/kg of dry soil (from Sauvé *et al.* 2000). $\mathrm{Zn_s}$ and $\mathrm{Cu_s}$ are the concentrations of Zn and Cu in solution as mg/L, respectively.

Figure 7 shows the relationships of MIR-derived total concentrations of Cu and Zn versus dissolved Cu and Zn as deduced from the Eqns 1 and 2. The same relationships with laboratory-measured concentrations are also reported. In both cases, the regression coefficients (R^2) were reduced by using the MIR-derived total concentration values instead of the measured concentration. However, even with the reduced R^2, the relationships between MIR derived total concentration and dissolved concentration in soils remains good (Fig. 7) and constitutes a convenient and practical rapid means of evaluating the mobile pools of metals or nutrients.

Conclusions

This study demonstrated that MIR-PLS analysis is a powerful and rapid technique to assess the grouping of soil samples on the basis of their common mineralogy. In addition, in alkaline soils from southern Australia, with the exception of mineral and organic P and C, the regression relationships of the macro- and micronutrient concentrations could be correctly predicted by this technique. The loading weight indicated that micronutrients were associated with the clay fraction and dependent on the type of clay present. A positive correlation was found between micronutrients, such as Cu, Zn, Mn, Fe, and smectite/illite, and conversely, a negative relation with kaolinite. Manganese was exclusively related to the content of iron and aluminium oxides, whereas Cu and Zn were related to these to a lesser extent. Inspection of the PLS weight loadings enabled us to conclude that, in calcareous soils, sulfur (S) was associated with carbonate and conversely that Mg was more related to the clay concentration of soils. Taking into account that soil sample preparation with

MIR-PLS analysis takes only about 2 min for scanning and predictions of ground samples, and that more than15 chemical properties can be predicted using this technique, MIR-PLS analysis provides a rapid and inexpensive technique for the assessment of several key soil characteristics. In addition, by using MIR-PLS and a partitioning model such as the one described by Sauvé *et al.* (2000) for metals, the potential bioavailability of several metal micronutrients could be rapidly determined. For the present study, the relatively small numbers of samples used to model the PLS analyses was clearly sufficient as a research or pilot study on Australian alkaline soils. However, many more samples, including a larger variety of soil types, would obviously have to be included for use as an established analytical technique.

Acknowledgments

The authors thank the Grains Research and Development Corporation (Project No. CSO200) for providing funding support for this research program. We wish also to thank Dr J. Churchman, Mr R. Merry, Dr W. Gates, and Dr R. Correll for valuable discussion and helpful comments on the manuscript.

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Manuscript received 21 November 2001, accepted 24 June 2002