QUANTITATIVE ASSESSMENT OF SOIL CHEMICAL PROPERTIES USING VISIBLE (VIS) AND NEAR-INFRARED (NIR) PROXIMAL HYPERSPECTRAL DATA

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ABSTRACT

Techniques capable of capturing variability of soil properties evolved understanding the importance for wider range of applicability in diverse fields. In this study, we evaluated the ability of hyperspectral data in visible (VIS) and near infrared (NIR) region for prediction of nutrient related soil properties by stepwise regression in soil samples collected from farmer's fields of Jalandhar, Punjab in India. The soil properties evaluated were mineralizable nitrogen (N), available phosphorous (P) and potassium (K), extractable manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), $CaCO_3$, soil organic carbon (SOC), electrical conductivity (EC) and soil reaction (pH). Visible and near-infrared (350-2500 nm) reflectance spectra of 85 processed soil samples were obtained from a portable spectroradiometer (ASD, FS3) in the laboratory conditions. Reflectance, derived absorbance and their first & second derivatives were used for model development with stepwise regression approach. Models developed using derivatives of the spectral data were able to predict some properties with a reasonably higher accuracy. R^2 values indicated that first derivative of absorbance best for nitrogen and second derivative for Mn, Fe, and Zn prediction. Second derivative of reflectance was found best for P and Cu and first derivative for K prediction. The highest predictability (adjusted R^2) was 0.93 recorded for $CaCO_3$ while lowest 0.68 was obtained for N. Prediction evaluation indices (Ratio Prediction Deviation and Range Error Ratio) confirmed that hyperspectral derived models were predicted well except Zn, Cu and pH.

KEYWORDS: Soil Chemical Properties, Hyperspectral, Spectroradiometer, Stepwise Regression

INTRODUCTION

Techniques capable of capturing variability of soil properties evolved understanding the importance for a wider range of applicability in diverse fields. Usually the nutrients content are determined through laboratory analysis; however, many of the existing methods of soil analysis are resource intensive, and do not lend themselves to the use of large number of samples (Ludwig *et al.,* 2002). Geostatistical approaches based on spatial dependency have been extensively studied for parameter prediction beyond sampling locations (Kozar *et al.,* 2002; Brodsky *et al.,* 2004). But the accuracy depends on the number of sampling locations and at least 100 observations have been recommended as a minimum to calculate a reliable variogram (Webster and Oliver, 1992).

Spectroscopy is the study of radiation as a function of wavelength that has been emitted, reflected, or scattered from a solid, liquid, or gas (Clark, 1999). Spectroscopy which deals with huge volume of few nano meters wide bands (Hyperspectral) in the visible and infra-red region (400-2500nm) has been aptly used in soil studies for decades and still advancing in many aspects. Spectroscopic applications in soil science are progressing at field and laboratory level with hand held spectroradiometers. Reflectance responses have been investigated by many scientists for several soil chemical properties with different approaches. Some of the researchers investigated the applicability of data derived from hyperspectral reflectance for fertility studies. They developed hyperspectral band ratios and indices (Liu *et al.*, 2008), absorbance derived from reflectance data (Russell, 2003; Wetterlind, *et al.*, 2008), continuum removed spectra (Gaffey, 1986; Lagacherie, *et al.*, 2008) and diffuse reflectance spectroscopy with good predictability (Couillard *et al.,* 1997; Udelhoven *et al.,* 2003; Waiser, *et al.*, 2007). Many have comprehensively studied spectroscopy for prediction of soil properties using laboratory and field spectroradiometers and were able to correlate spectral properties with soil moisture, organic carbon, total nitrogen, and other chemical properties for their predictions under laboratory conditions (Baumgardner *et al.,* 1985; Dalal and Henry, 1986; Shonk *et al.,* 1991; Ben-Dor and Banin, 1995).

VIS and NIR reflectance spectroscopy has advantages over some of the conventional techniques of soil analysis, in that, they are rapid, timely, less expensive and hence, are more efficient when a large number of analyses and samples are required (McCarty and Reeves, 2006; Nanni and Dematte, 2006).

Moreover, spectroscopic techniques do not require expensive and time-consuming sample preprocessing or the use of (environmentally harmful) chemical extractants. Spectroscopy may, on instances, be more straightforward and accurate than conventional soil analysis (Viscarra Rossel *et al.,* 2006). For example, McCauley *et al.* (1993) suggested that infrared spectroscopy may be more accurate than dichromate digestions for analysis of soil organic carbon and Viscarra Rossel and McBratney (2001) suggested that the precision of the mid-infrared (MIR)-partial least square (PLS) technique better than conventional analysis for quantifying soil pH. Another advantage is the potential adaptability of the technique for *insitu* field use (Viscarra Rossel and McBratney, 1998). The ability of hyperspectral techniques for many soil properties are still to be evaluated.

In this study, the ability of hyperspectral data in visible (VIS) and near infrared (NIR) region was evaluated for prediction of nutrient related soil properties by stepwise regression.

MATERIALS AND METHODS

Study area and soil sampling

Soil sampling was done in a strip of 7.5 x 106 km^2 (30°45' to 31°45'N latitude and 76°25' to 76°45'E longitude) in the middle of Jalandhar District, Punjab, India. The major land use is agriculture and dominant cropping system is rice-potato and rice-wheat. Soil type is alluvial covering only two soil orders (Entisols and Inceptisols). Soil samples from 85 farmers fields were collected during May 2008.

Laboratory analysis

Soils were air-dried, ground and passed through a 2 mm sieve. Chemical properties were determined using standard methods. Walkley and Black (1934) method was used for estimation of soil organic carbon (SOC). Mineralizable nitrogen (N) was estimated using Kjeldahl distillation method (Subbiah and Asija, 1956). Ascorbic acid method (Watanabe and Olsen, 1965) was used with spectrophotometer for estimation of available Phosphorous (P). Ammonium acetate method (Hanway and Heidal, 1952) with flame photometer has been adopted for estimation of available potassium (K). Calcium carbonate ($CaCO_3$) was estimated using rapid manometric method using Calcimeter (Williams, 1949). Zinc (Zn), copper (Cu), iron (Fe) and manganese (Mn) were estimated using Diethylene Triamine Penta Acetic acid (DTPA) with atomic absorption spectrophotometer (AAS) (Baker and Suhr, 1982). Soil reaction (pH) was been determined in 1:2.5 soil-water suspensions using standard pH meter. Same suspension was also used for determination of electrical conductivity (EC) with a standard Electrical Conductivity Meter (Jackson, 1973).

Spectral data

Air-dried (36 hours), crushed and sieved (2 mm) soil samples (2 cm thick) were scanned using Field-Spec3 Analytical Spectral Device (ASD; Boulder, CO, USA) covering wavelength ranging from 350 to 2500nm in the laboratory condition (Liu *et al.*, 2002). Reflectance spectra were measured under two calibrated halogen lamps (1000 W) situated at 0.70 m with zenith angle of 30° in a dark room after calibration of sensor using a white spectral panel. Mean of the 50 spectra was taken as the final reflectance spectra for each of soil sample. The ASD software of the instrument has been set to process reflectance at 1 nm interval. Spectral reflectance was derived as the ratio of reflected radiance to incident radiance estimated by a calibrated white reference. All the recorded soil spectral signatures were converted into Tab delimited text file format using the ViewSpec Pro (Version 4.05) software to facilitate data sharing with other software.

Model development

ViewSpec Pro (Version 4.05) and 'Spectral analysis' a free software (Space Application Centre, India) was also used for spectral re-sampling of spectral data into 10nm wave length interval. Statistical analysis and model development were done using SAS and SPSS statistical software.

Reflectance data were transformed to absorbance through the expression, $\log_{10}$ (1/reflectance). The derivative spectra for reflectance and absorbance was computed using finite approximation to calculate the change in reflectance over a bandwidth $\Delta\lambda$, defined as $\Delta\lambda = \lambda_j - \lambda_i$, where $\lambda_j > \lambda_i$ (Equation 1 and 2; Tsai, 1998).

$$\left.\frac{ds}{d\lambda}\right|_{i} \approx \frac{s(\lambda_i) - s(\lambda_j)}{\Delta\lambda} \quad \text{............(1)}$$

$$\left.\frac{d^n s}{d\lambda^n}\right|_{j} = \frac{d}{d\lambda}\left(\frac{d^{(n-1)} s}{d\lambda^{(n-1)}}\right) \quad \text{............(2)}$$

Where, $s(\lambda_i)$ is spectral reflectance/absorbance at λ_i^{th} wavelength/band.

Correlation analysis in SPSS software was performed between each soil property and each 10nm band reflectance and best correlated 30 bands from each reflectance related data sets were selected for each soil property. During models development adjusted R^2 was used for selecting the model and the optimum number of independent variables (10nm spectral bands) in each model for each soil property. Stepwise regression procedure in SAS software was used for development of parameter prediction models. However, randomly selected two third of 85 soil sample data was used form development of spectral prediction model for different soil properties. Rest data records were used for model validation.

Validation of prediction model

Three statistical indices were used for validation of developed prediction models and were the Standard Error of Prediction (SEP), Ratio Prediction Deviation (RPD) and Range Error Ratio (RER). SEP (Equation 3) gives the standard deviation of the predicted values about the 1:1 line the. The SEP was calculated as the root mean square of residuals using the difference between laboratory measured and model predicted values for independent validation data sets (Davis and Grant, 1987).

$$SEP = \sqrt{\frac{\sum_{i=1}^{n}(y_{pred,i} - y_{act,i})^2}{n-1}} \quad \text{...............(3)}$$

Where n denotes the number of samples in the validation set, $Y_{pred,i}$ is the value of predicted parameter for sample i and $Y_{ref,i}$ is the associated measured value. Higher predictability of models associates with lower SEP values.

Ratio Prediction Deviation (RPD) is defined as the ratio of standard deviation (S.D.) of measured values of soil properties in the validation set to the standard error of prediction (SEP) and is expressed as given in the equation 4. Range Error Ratio (RER) is the ratio of range of measured values of soil properties in the prediction set to SEP (equation 5; Islam *et al.*, 2003).

$$RPD = \frac{S.D.}{SEP} \quad \text{.....................(4)}$$

$$RER = \frac{(Y_{max} - Y_{min})}{SEP} \quad \text{.....................(5)}$$

Where, S.D. is standard deviation, Y_{max} and Y_{min} is maximum and minimum values of soil property in the validation dataset. The higher values of RPD and RER indicate the better models.

The evaluation of the model predictability for different soil properties was done using the plot RPD and RER against coefficient of determination (R^2) of prediction and measured values (Islam *et al.*, 2003).

RESULTS AND DISCUSSION

Soil properties

The summary statistics of each soil property are given in Table 1. Some properties like N, P K, Mn, etc showed skewed distribution due to high values in some locations and the other properties followed the normal distribution.

Table 1. Description of soil chemical composition of physicochemical properties of study area (85 soil samples)

Parameter	Min	Max	Mean	Std. Dev
1. Mineralizable Nitrogen (mg kg^{-1}) N	69.0	207.0	122.3	28.8
2. Available Phosphorous (mg kg^{-1}) P	1.8	104.4	12.6	14.3
3. Available Potassium (mg kg^{-1}) K	4.1	143.1	22.4	17.2
4. Extractable Manganese (mg kg^{-1}) Mn	0.8	43.3	6.2	6.3
5. Extractable Zinc (mg kg^{-1}) Zn	0.8	10.5	3.3	2.0
6. Extractable Copper (mg kg^{-1}) Cu	0.8	5.7	2.8	1.4
7. Extractable Iron (mg kg^{-1}) Fe	3.0	194.5	28.9	27.6
8. Soil Organic Carbon (%) SOC	0.1	1.2	0.7	0.24
9. $CaCO_3$ (mg kg^{-1})	0.05	10.8	2.1	3.04
10. Soil reaction pH (1:2.5)	5.3	8.5	7.3	0.75
11. EC (dS m^{-1}) (1:2.5)	0.06	1.0	0.2	0.15

Effect of spectral data enhancement

Comparison of normalised reflectance (R) to absorption (A), spectral derivatives of reflectance (first and second) and absorption (R′, R″ and A′, A″) was adopted as shown in Figure 1. It is apparent that the conversion of reflectance data into absorbance does not affect the original spectral features. The absorbance curve can be characterized as a "decreasing monotonic function" (Figure 1.A). As a result, its first derivative yielded negative values in most of the spectral region.

All the six spectral data sets with each soil property were evaluated for developing prediction models for considered soil properties and coefficient of determination (R^2) was computed and plotted as shown in Figure 2. It was revealed that original spectrum i.e. reflectance (R) and derived absorption (A) have very low R^2 values and first and second derivatives of R and A have comparatively higher values for different soil properties. It is clearly observed that the first derivative manipulation greatly enhanced some of the spectral features and the second derivative enhanced them even more. The second derivative technique has the capability to increase even small changes by eliminating the effect of particle size and is widely reported as the preferred technique for analyzing spectra (Norris and Williams, 1984). The derivation technique enhances small spectral features within the relatively "uniform" spectra of the soils. Based on R^2 value, the different spectral parameters were chosen for different soil properties for development of prediction model.

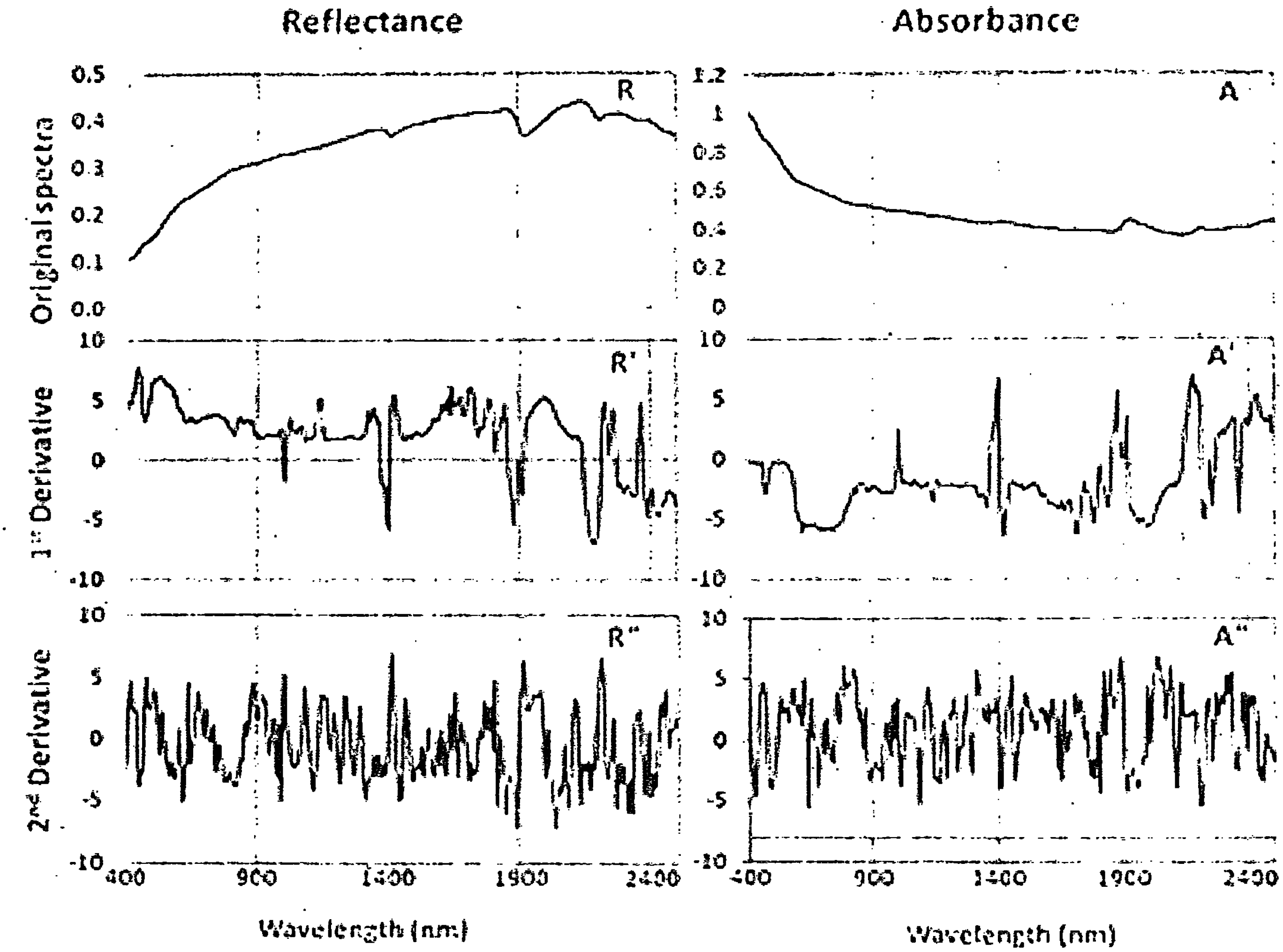

Figure 1. The effect of the mathematical transformation [Absorbance (A) and reflectance (R), their First (R′ & A′) and second (R″ & A″) derivatives] on the original spectrum.

Model development

Model predictability (R^2) for each soil property and each spectral data set (reflectance, absorbance and their derivatives (R, R′, R″, A, A′ and A″) is shown in the Figure 2. Derivative spectral data of both reflectance and absorbance in VIS and NIR region yielded better predictability for all soil properties than the reflectance or absorbance without enhancement and the results agreed with finding of many scientists involved in soil property predictions research (Norris & Williams, 1984: Davis and Grant, 1987; Ben-Dor *et al.*, 1991).

Based on the rank of R^2,for N and K, first derivative of A and R were considered, where as second derivative of reflectance (R″) was used for P and $CaCO_3$ and A″ for SOC. Prediction models of Mn, Zn, Fe and EC were developed using its A″ and for Cu and pH, R″ was yielded as the best.

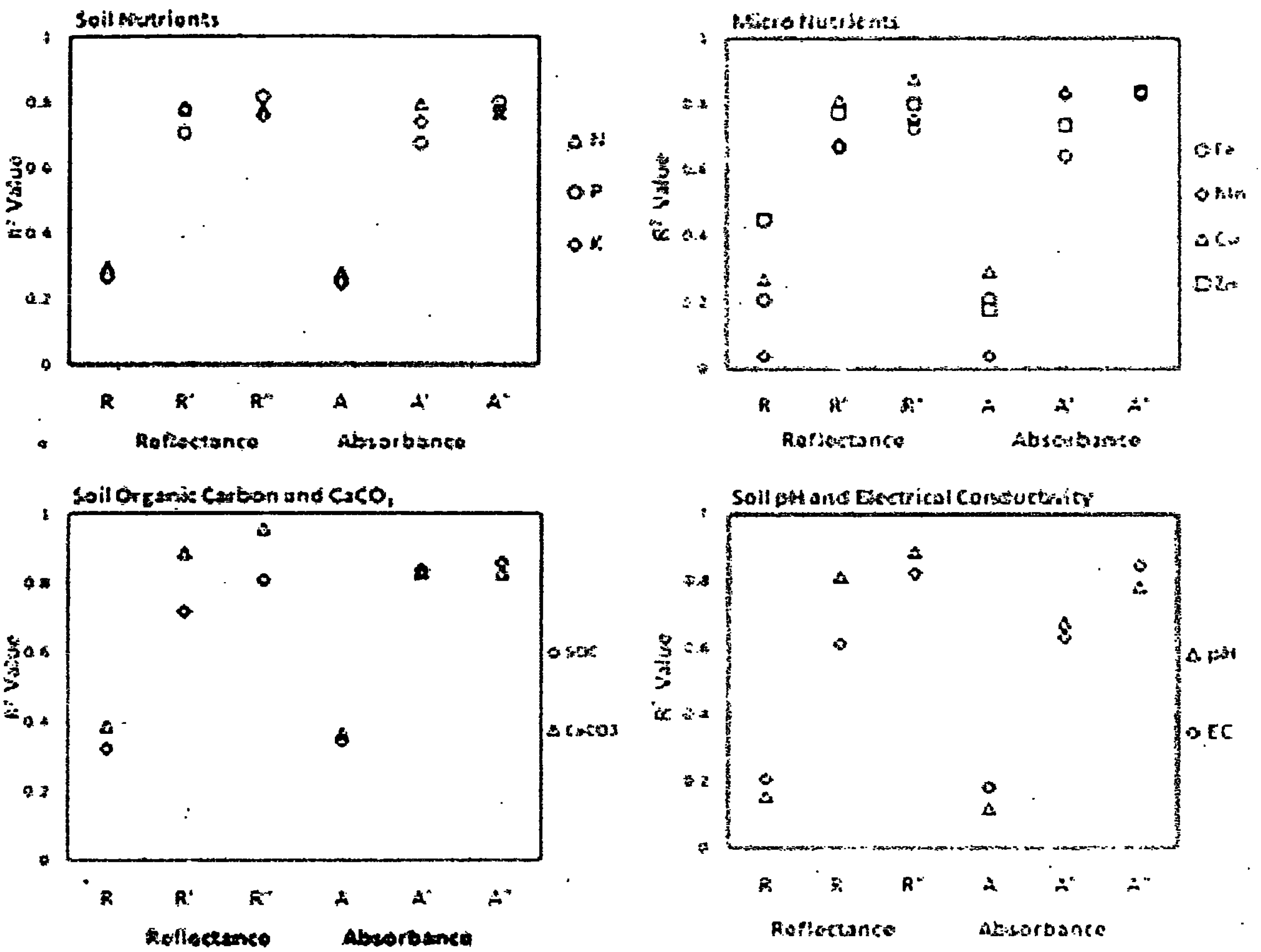

Figure 2. Coefficient of determination (R^2) of multivariate regression models for different spectral data sets (R , R′, R” and A, A′ and A”) for each soil property.

Table 2. Best spectral models, number of bands and predictability for each soil property.

Property[a]	Regression model[b]	Bands	Adj. R^2
N	Y=133.314+2.267A' +8.839A' +21.313A' -24103.206A' -21.607A' +37.334A' +3.674A' -1.103A' +37.586A' + 14.808A' + 1.007A' +4.414A' -1.362A' -19.292A' -3.651A' +12.069A' -50.876A' -25.837A' (1415, 2475, 1865, 1895, 1935, 1945, 1385, 1825, 2145, 2435, 2355, 975, 1775, 2485, 2265, 1955)	18	0.68
P	Y=18.363+0.981R" +1.761R" -2.063R" +1.732R" + 0.22R" +1.121R" -0.188R" -0.14R" -1.758R" + 1.939R" -0.299R" + 0.957R" (1985, 1345, 785, 485, 1835, 1885, 2445, 1095, 1765, 1845)	12	0.75
K	Y=12.388-18.682R' -19.326R' +77.218R' + 16.903R' -48.561R' -15.656R' -2.05R' -18.7R' +8.26R' -7.241R' + 1.494R' -16.422R' -1.626R' -1.937R' + 0.767R' -1.675R' + 16.823R' +1.582R' -0.766R' (2445, 2435, 1975, 2405, 1985, 1965, 1765, 2005, 2185, 2015, 1925, 2215, 1415, 2455, 2265, 1595)	19	0.66
$CaCO_3$	Y=-1.306-0.296R"$_{1375}$ +0.078R"$_{2335}$ -0.479R"$_{1855}$ -0.047R"$_{555}$ + 0.186R"$_{805}$ - 0.166R"$_{2185}$ -0.147R"$_{995}$ + 0.395R"$_{1395}$ +0.459R"$_{1715}$ + 0.763R"$_{2215}$ - 0.082R"$_{1075}$ -0.052R"$_{1575}$ +0.151R"$_{1135}$ -0.101R"$_{2275}$ + 0.105R"$_{2005}$	19	0.93
SOC	Y=0.952-0.012A" -0.007A" -0.009A" + 0.019A" - 0.115A" - 0.019A" +0.056A" - 0.008A" +0.021A" -0.015A" -0.047A" + 0.019A" +0.01A" +0.019A" + 0.033A" +0.01A" (1475, 655, 1885, 1875, 2235, 795, 2175, 675, 2225, 1605, 775, 825, 1425, 2015, 2345, 545)	16	0.79
Mn	Y=14.154+0.451A" -0.315A" +1.179A" -0.506A" -0.143A" + 0.463A" -0.427A" + 4.315A" +0.33A" -0.192A" +0.131A" +0.271A" +0.117A" -0.268A" -0.395A" -0.46A" (1935, 1305, 785, 1055, 975, 965, 485, 2175, 1345, 1205, 945, 1945, 1465, 1235, 435, 2105)	16	0.74
Fe	Y=7.569-1.217A" +1.564A" -0.437A" -0.697A" +1.461A" - 0.812A" +1.327A" -6.438A" -7.905A" -1.743A" +1.574A" + 0.862A" +0.642A" -0.439A" -0.497A" -1.035A" -0.895A" -0.318A" +0.627A" -2.339A" (2065, 555, 1595, 755, 2185, 725, 1165, 2235, 2215, 775, 845, 445, 1905, 855, 1175, 835, 705, 1965, 975, 1385)	20	0.69
Cu	Y=3.302-0.572R" +0.116R" +0.02R" -0.1R" +0.137R" - 0.032R" +0.047R" -0.096R" + 0.025R" +0.033R" -0.288R" - 0.125R" -0.076R" +0.096R" -0.369R" + 0.05R" +0.098R" (2235, 1165, 705, 1935, 1595, 1905, 1065, 1355, 545, 735, 375, 1925, 1895, 675, 2215, 555, 945)	17	0.78
Zn	Y=4.659-0.235A" -0.077A" -0.117A" -0.148A" +0.122A" + 0.058A" +0.089A" +0.191A" + 0.102A" -0.053A" + 0.087A" +0.154A" +0.048A" +0.073A" +0.168A" +0.083A" + 0.109A" (1885, 415, 835, 1865, 1665, 1605, 765, 925, 2365, 535, 2025, 965, 2335, 1225, 2105, 1705, 2445)	17	0.75
pH	Y=6.157-0.101R"$_{2325}$ +0.009R"$_{2335}$ -0.123R"$_{995}$ +0.248R"$_{1455}$ -0.073R"$_{1005}$ - 0.039R"$_{835}$ +0.032R"$_{1415}$ -0.023R"$_{865}$ -0.073R"$_{1055}$ -0.027R"$_{1265}$ -0.041R"$_{1345}$ - 0.411R"$_{1395}$ +0.017R"$_{605}$ +0.015R"$_{405}$ -0.029R"$_{2105}$ -0.031R"$_{1685}$ +0.02R"$_{1825}$ + 0.032R"$_{875}$	18	0.82
EC	Y=0.363+0.008A"$_{485}$ -0.012A"$_{655}$ +0.015A"$_{1765}$ +0.008A"$_{2055}$ -0.005A"$_{1695}$ +0.005A"$_{2015}$ +0.012A"$_{765}$ + 0.013A"$_{2085}$ -0.004A"$_{1245}$ -0.006A"$_{1795}$ +0.026A"$_{2275}$ -0.007A"$_{535}$ +0.004A"$_{455}$ -0.005A"$_{2395}$ +0.002A"$_{2445}$ - 0.003A"$_{1345}$ -0.101A"$_{2135}$ +0.006A"$_{1555}$	18	0.75

a: Values in mg kg^{-1} for N=Mneralizable nitrogen, P=available phosphorous;

K=available potassium, $CaCO_3$; SOC = soil organic carbon (%), *Extractable Manganese (Mn), Iron (Fe), Copper (Cu) and, Zinc (Zn), soil reaction (pH), electrical conductivity (EC) dSm^{-1}*
b: Derivative spectral data at 'x' mid wave length; A'_x = first derivative of absorbance, A''_x = second derivative of absorbance, R'_x = first derivative of reflectance,, R''_x = second derivative of reflectance.

Prediction of soil properties and accuracy assessment

Prediction and validation of soil properties was done using 1/3rd of 85 soil samples which were not used for model development. Comparison was made between the predicted and measured values for each soil property drawing 1:1 line as shown in Figures 3 and 4. The values for most of the soil properties appear to fall in the vicinity of 1:1 line. However, in some cases, bias can be observed. To carefully examine this observation, Miller and Miller test (1988) was applied. This method discriminates good models based on R^2 and coefficient values and three other indices. Standard Error of Prediction is also known as major criterion against which to judge the prediction performance of the model. Relatively low SEP values indicate good prediction. The SEP values for each soil property prediction is given in Table 4 and smaller SEP values were resulted implying good prediction accuracy for most of them. However, N was not well predicted. The possible reason may be few samples with extraordinary concentration were in validation data set.

Other evaluation indices used for prediction model were RPD and RER which were summarized in Table 4. In agricultural applications, RPD > 3 is considered acceptable and an RPD > 5 is considered excellent. RER should be greater than 10. However, no critical levels of RPD and RER have been set for the VIS and NIR analysis of soil, acceptable values depend on the intended application of the predicted values (Dunn *et al.*, 2002).

Chang *et al* (2001) reported that the NIR reflectance spectroscopy technique had the ability to predict various properties of soil and they used 3 categories based on RPD in the ranges >2.0, 1.4- 2.0 and <1.4 to indicate decreasing reliability of prediction using this technique. As from Table 3, except for Zn and pH all the soil properties show RPD above 1.4 indicating better predictability.

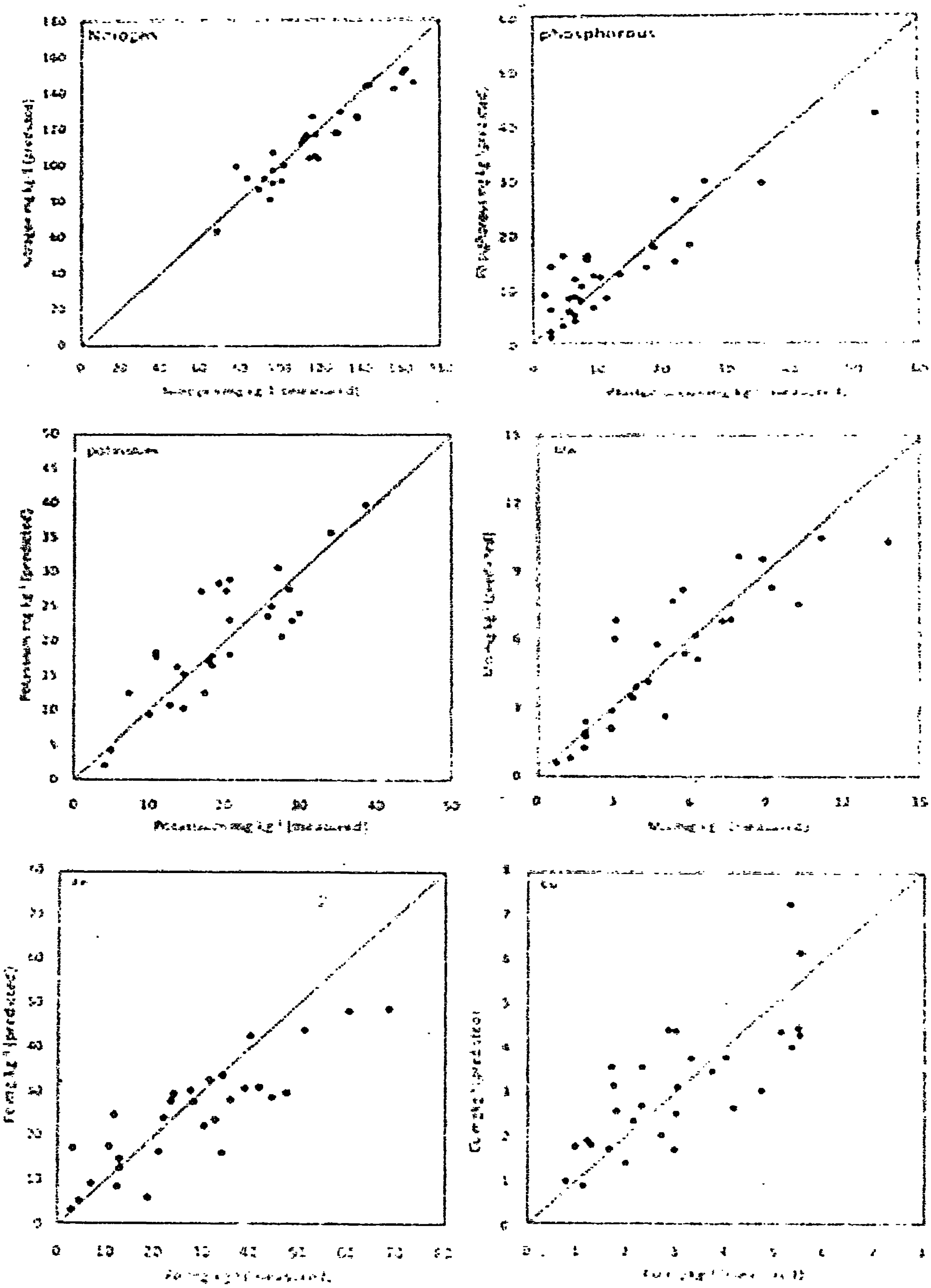

Figure 3. Plot of the predicted vs. measured values for N, P, K, Mn, Fe and Cu

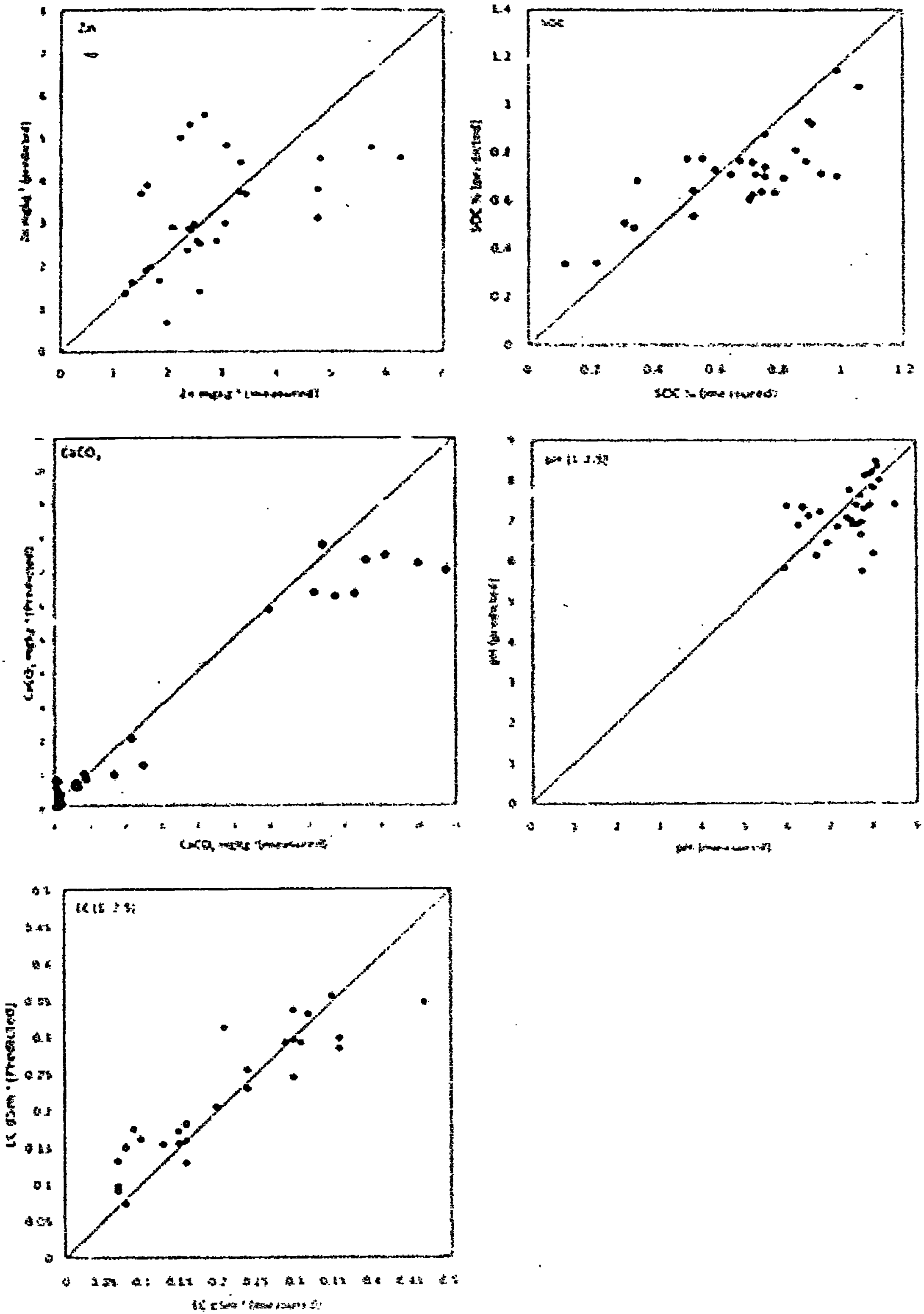

Figure 4. Plot of the predicted vs. measured values for Zn, SOC, $CaCO_3$ pH (1:2.5) and EC (1:2.5)

RPD for pH was 0.89 and was less than 1.4 suggests less reliable prediction for pH. According to suggestions of Dunn *et al.*, 2002, the acceptable RER values for soil properties should be greater than 6 and in this study the models for pH was not qualified as a good model according to this criteria. Figure 5 represents validated R^2 values against (a) RPD and (b) RER. Both the plots indicate low level accuracy for pH and also for Cu and Zn. According to overall assessment, soil property assessment with derivative hyperspectral data for $CaCO_3$, N, P, K, Mn, Fe and EC could be utilized more reliably. Application of hyperspectral data for assessment of pH and Zn was less accurate while accuracy for Cu and SOC assessment was moderate.

Table 3. Listing of spectral parameters, number of bands, SEP, Adj. R^2 RPD and RER for different soil parameters

Soil property	**Spectral parameter**	Bands	SEP	**Adjusted R^2**	**RPD**	**RER**
N (mg kg^{-1})	A′	18	10.7	0.68	2.41	9.16
P (mg kg^{-1})	R″	12	5.6	0.75	2.03	9.18
K (mg kg^{-1})	R′	19	5.3	0.66	2.45	13.13
Mn (mg kg^{-1})	A″	16	1.6	0.74	1.97	8.05
Fe (mg kg^{-1})	A″	20	9.7	0.69	1.72	6.70
Cu (mg kg^{-1})	R″	17	1.1	0.78	1.44	4.46
Zn (mg kg^{-1})	A″	17	1.6	0.75	1.15	5.67
SOC %	A″	16	0.15	0.78	1.56	6.21
$CaCO_3$ (mg kg^{-1})	R″	19	1.1	0.93	3.38	9.66
pH (1:2.5)	R″	18	0.8	0.82	0.89	3.34
EC dS m^{-1} (1:2.5)	A″	18	0.05	0.75	2.19	7.89

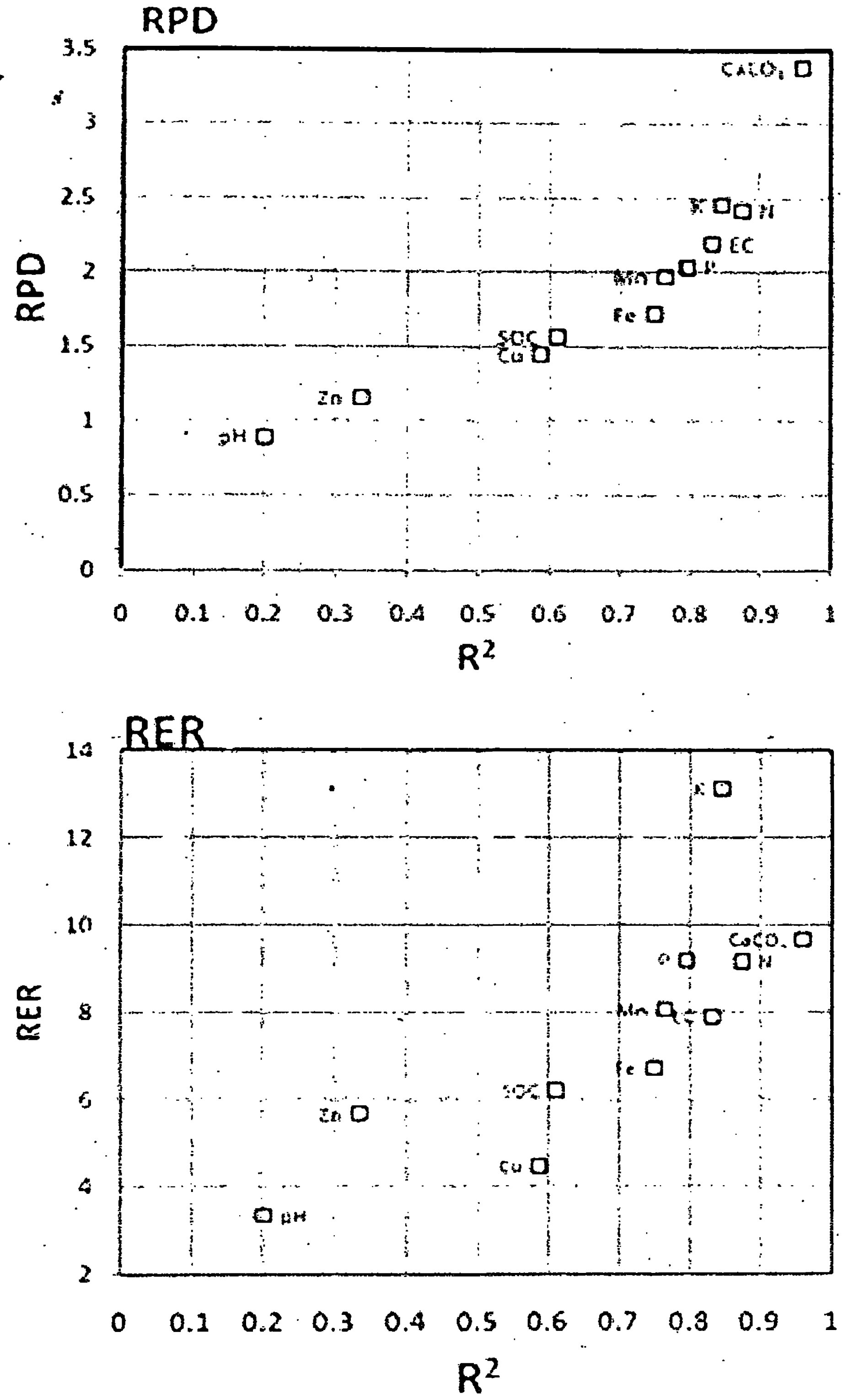

Figure 5. Coefficient of determination (R^2) for measured and predicted values for the prediction data set vs. Ratio Prediction Deviation (above) and Range Error Ratio (below) for different soil properties

CONCLUSIONS

Derivative spectra of 10nm interval Hyperspectral (VIS and NIR region) much better for estimation of range of soil chemical properties and normal spectra when using stepwise regression approach. Prediction models developed with first derivative spectra showed best for prediction of available N and K while other second derivative of spectral data were best for other evaluated soil parameters. Among the soil properties evaluated, prediction models for mineralizable nitrogen, available phosphorous, potassium, extractable manganese, iron, $CaCO_3$ and electrical conductivity show higher RPD values (>2) indicating reliability of prediction using stepwise approach with derivative spectra. RPD for pH and Zn were 0.89 and 1.15 respectively and less than 1.4 suggests less reliable prediction. Predictions for Mn, Fe, Cu and soil organic carbon indicate moderate predictability.

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