Diffused Reflectance Spectroscopy for Characterization of Salt-Affected Soil (SAS) Attributes

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Abstract: Identification of soil salinity based on traditional methods (measurement in saturation extract) required time, labour and capital, whereas, ground based non-imaging hyperspectral remote sensing estimates the soil salinity and alkalinity parameters within limited resources and can be used for real time monitoring purpose. Laboratory experiment was conducted to study the spectral properties using VNIR spectroscopy in silt loam and silty clay loam soil saturated with different levels of chloride, sulphate and carbonate of sodium salts. Salinity absorption features were more pronounced around 1900 nm, followed by 1400 and 2200 nm. The salt concentration was inversely related to reflectance values in saline soils. Wavelength was shifted from 1900 nm to higher wavelength value and this shifting feature was also correlated with the increase in salt concentration. Relatively high correlation coefficients of EC_e, saturated extract Na^+ and Cl^- with soil reflectance values were found in between 1420 to 2020 nm than other soil properties. Increased use and application of VNIR for salt-affected soil would help establish a detailed spectral library through captured signature in sodium salt saturated soil.

Key words: *Salt-affected soils, hyperspectral remote sensing, regression model*

Introduction

Soil salinization and alkalinisation are the most common problems of cultivated lands in arid and semi-arid regions of India. Intensive cultivation of land for agricultural production with poor quality of groundwater causes the expansion of area under salt-affected soils (SAS). Increase in the concentrations of carbonate and bicarbonate anions along with sodium cation lead to soil sodicity resulting in yield reduction (Metternicht and Zinck 2003), particularly in the food-growing regions of the Indo-Gangetic plains (IGP).

Timely identification and monitoring of SAS are important for arresting the soil salinization (Sinha *et al.* 2017). The conventional method for identifying SAS is laborious, expensive and require intensive sampling to cover a large area (Shepherd and Walsh 2002), whereas, VNIR spectroscopy is a rapid non-destructive technique, makes easy to cover a wide range of areas.

Reflectance spectroscopy uses the physics of the atomic and molecular vibration process, which causes the absorption features in salts, evaporate minerals and soil spectra (Csillag *et al.* 1993; Metternicht and Zink 1997; Ben-Dor *et al.* 1999). These features are more pronounced in the middle infrared

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bands with water and OH⁻ absorption features which allow distinction of soil surfaces affected by Cl⁻ and SO_4^{2-} salts (Howari *et al*. 2000). This information is used to establish a statistical relationship between spectral properties of salt-affected soils and the various amounts of salts in soil (Farifteh *et al.* 2004). Multiple Linear Regression (Chang *et al.* 2001; Farifteh *et al.* 2007; Volkan *et al*. 2010) model and other data mining techniques (Brown *et al*. 2006) have been applied for interpreting the relationships between soil reflectance spectra and various soil properties including salinity. The MLR technique gives acceptable results between salt concentration and measured reflectance spectra over other complex spectral modelling procedure (Farifteh *et al.* 2007).

However, these statistical relations of salt content with the spectrum is region-specific, discrimination of different degree of salinization can be possible if the spectral characteristics of saline soil's spectrum and the underlying factors are examined based on locally developed hyperspectral models. In this regard, more and more research should be directed towards the analysis of soil reflectance spectra of the major food growing areas suffering from different degree of salinity and sodicity as that of the IGP plains of Haryana. This paper aims to explore the development of a laboratory-based hyperspectral model for soil salinity assessment in the salt-affected soils of IGP areas of Haryana, India using VNIR reflectance spectroscopy through simple MLR technique.

Materials and Methods
Soil sampling

Surface soil samples (0-15 cm) of silty clay loam (Soil-1) with (76°57'04.5" E; 29°42'32.9" N) and silt loam (Soil-2) with (76°09'42.5" E; 28°09'18.8" N) were collected from the research farm of CSSRI, Karnal district of Haryana state just after the harvest of wheat of rice-wheat cropping system. Then a controlled laboratory experiment was used to investigate the relationships between reflectance spectra and soil salinity.

Controlled laboratory experiment

The collected soil samples (reclaimed sodic soil) were air-dried, crushed and sieved through 2-mm sieve by following the procedure described by Van (1993). Subsequently, the soil sample was saturated artificially with three main types of salts, *viz*., chloride, sulphate and carbonate of Sodium (99 % purity) and a mixture of these salts with six levels (percentage by weight), ranging from non-salinity to high salinity (0.2, 0.5, 1, 2, 5 and 10 %). After saturation, excess water was allowed to drain. The treated samples were air-dried and processed. In this way, total 148 samples (soil type–2; salt type–4 (3 types of salts and their mixture); salt level–6; replication–3 and control–4 (2 control from each soil type)) of different levels of soil salinity were artificially created. Before soil analysis, we have taken hyperspectral reflectance by Spectroradiometer. We have considered 98 samples for calibration and 48 samples for validation in MLR analysis.

Soil analysis

A total of 148 samples were air-dried, crushed and passed through a 2 mm sieve and analyzed for EC_e, pH_s, Na⁺, K⁺, Mg^{2+}, Ca^{2+}, CO_3^{2-}, HCO_3^-, Cl⁻ and SO_4^{2-} following standard laboratory techniques (Van 1993). Soil electrical conductivity (EC_e) and pH_s were measured in the saturated soil extract. Exchangeable cations Ca^{2+} and Mg^{2+} (Cheng and Bray 1951), Na⁺, K⁺ and anions CO_3^{2-}, HCO_3^-, Cl⁻ (Richards 1954) and SO_4^{2-} (Chesnin and Yien 1950) were determined in the saturation extract.

Hyperspectral reflectance data acquisition

Soil diffuse reflectance spectra were recorded for each soil sample using a Field Spec Pro FR Spectroradiometer (Analytical Spectral Devices Inc., Boulder, Colorado) at wavelengths ranging from 350 to 2500 nm with a narrow spectral sampling interval of 1 nm. Samples were illuminated from above with two tungsten quartz halogen filament lamps in housings with aluminium reflectors (Lowel pro-lamp, Lowel-Light

Manufacturer Inc., New York, NY) with 50W bulb; 3200 K colour temperature (Welch Allyn, Skaneateles Falls, NY). The reflected light was collected with a 25° field-of-view fore-optic that was kept vertically at a distance of 5 cm above the sample. Air-dried soil samples subjected to a pass-through 2 mm sieve were packed in 23 mm deep, 55-mm diameter black polypropylene dishes. Air-dried soils were used to minimize the effects of variation in soil moisture on reflectance. The over-filled dishes were scrapped-off by a blade to ensure a flat surface flush with the top of the dish. An average of three spectra was recorded for each soil sample to minimize instrument signal to noise ratio. Before recording soil sample reflectance, white reference spectra were recorded using calibrated spectral on (Labsphere, Sutton, NH) placed at the same distance from the fore-optic as those of soil samples for standardization. Reflectance readings for each wavelength band were expressed relative to the average of the spectral on readings. Variation in overall spectral shape among soil samples was studied by plotting the relative reflectance values against different wavebands.

Data processing and transformation

The original spectra consisting of relative reflectance values of 2151 points (at 1 nm interval) between 350 and 2500 nm were weighted averaged at every tenth-nanometer wavelength interval by integration technique as described by Srivastava *et al.* (2015). The integrated value of soil reflectance at every tenth-nanometer wavelength (360, 370, 380,…, 2490 nm) was determined by the following equation:
IR =

$$r^2 = 1 - \left(\frac{\sum_i^n (Y_{pred} - Y_{meas})^2}{\sum_i^n (Y_i - Y_{mean})^2} \right) \quad (1)$$

$$RMSEP = \sqrt{\frac{\sum_i^n (Y_{pred} - Y_{meas})^2}{n-1}} \quad (2)$$

$$RPD = SD_{val.}/RMSEP \quad (3)$$

where: Y_{pred}-predicted values; Y_{mean}-mean of measured values, Y_{meas}-measured values; n number of predicted/measured values with i-1,2,...... n; $SD_{val.}$- standard deviation of measured values in the validation set; and RMSEP=root mean square error of prediction of validation dataset.

Results and Discussion
Chemical composition of salt-affected soils

The statistical parameters of the soil chemical properties of the processed soil samples studied under laboratory conditions are given in table 1. The data indicate that soil pH varies between 6.9 and 10.0 and the majority of the samples (over 75 %) have a soil pH less than 8.0. The EC_e values vary from 0.96 to 130.7 dS m^{-1} and nearly 75 % of the samples have EC_e values of 56.3 dS m^{-1}. This indicates that the majority of the soil samples in this study are of very strong saline. One-fourth of the total samples have EC_e values of 7.1 dS m^{-1} in slightly saline range. Among the cations, average Na$^+$ concentration (1.1 %) is highest, followed by Ca^{2+} (0.05 %), followed by Mg^{2+} (0.03 %); whereas the Cl$^-$ and HCO$_3^-$ (0.80 % and 0.35 %, respectively) dominates over the carbonate and sulphate anions of the total treated the soils.

Soil Spectral Characteristics and its Correlation with Soil Properties

The reflectance spectra showed prominent absorption features around 1400, 1900 and 2200 nm all of which are known to be related to features of free water (~1400 and ~1900 nm) and clay lattice OH features (~1400 and ~2200 nm) (Hunt 1982). Hence, these absorption bands would be more responsive towards the presence of salts in the soils; the sensitivity of which will depend upon the nature and amount of salts present in the soil samples. Farifteh *et al.* (2008) reported an increase in soil salinity induced changes in soil reflectance for wavebands higher than 1300 nm, particularly in the water absorption bands (around 1400 and 1900 nm).

Table 1. Descriptive statistical parameters of soil chemical properties

Soil property	N	Min.	Max.	Mean	SD	Kurt	Skew	Percentile		
								25th	50th	75th
EC_e (mS m^{-1})	148	95.5	13065.0	3396.3	3335.6	0.6	1.1	708.0	1912.8	5633.8
pH_s	148	6.9	10.0	7.9	0.9	0.3	1.2	7.3	7.6	8.0
SE Cl$^-$ (mg L^{-1})	148	82.7	67330.0	8019.2	14832.8	7.1	2.6	454.9	909.9	5955.5
SE HCO$_3^-$ (mg L^{-1})	148	145.2	43118.5	3456.9	8493.6	11.8	3.4	217.8	254.1	1197.7
SE CO$_3^{2-}$ (mg L^{-1})	148	17.9	16493.4	1052.1	3284.8	14.9	3.9	17.9	35.7	196.4
SE SO$_4^{2-}$ (mg L^{-1})	148	14.2	17589.9	1762.8	3638.6	8.1	2.9	45.4	585.3	1047.8
SE Na$^+$ (mg L^{-1})	148	93.5	44000.0	10733.2	13219.5	0.4	1.3	962.5	4125.0	16637.5
SE K$^+$ (mg L^{-1})	148	2.2	300.4	75.7	86.1	0.5	1.3	9.9	29.7	115.3
SE Ca^{2+} (mg L^{-1})	148	22.6	2348.9	500.9	554.2	3.2	2.0	186.8	354.7	498.1
SE Mg^{2+} (mg L^{-1})	148	1.3	1356.9	334.7	348.3	0.7	1.3	85.5	211.3	499.8

SE Saturation extract

Effects of salts mixture (NaCl+Na$_2$CO$_3$+ Na$_2$SO$_4$) on air-dried soil reflectance spectra (Fig. 1)

shows a similar pattern of spectra of a mixture of these three salts but the intensity of absorption peaks near the range of 1850 – 1900 nm wavelengths increase with the level of salinity.
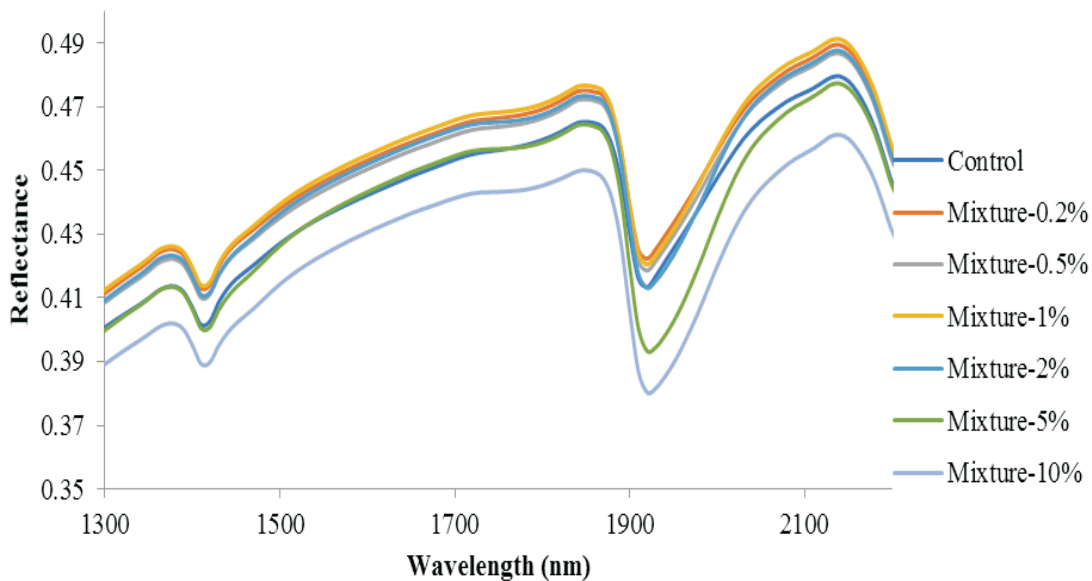
There was also a difference in reflectance of two type soil (Fig. 2). Soil-1 (Silty clay loam) show lower reflectance value than soil-2 (Silt loam). The mean soil reflectance spectra of different salt and soil types exhibited diagnostic absorption features at 1400, 1900, and 2200 nm. A similar result was also reported by Wang *et al.* (2012) with the exception of the behaviour of NaCl spectra from 1300 to 2500 nm.
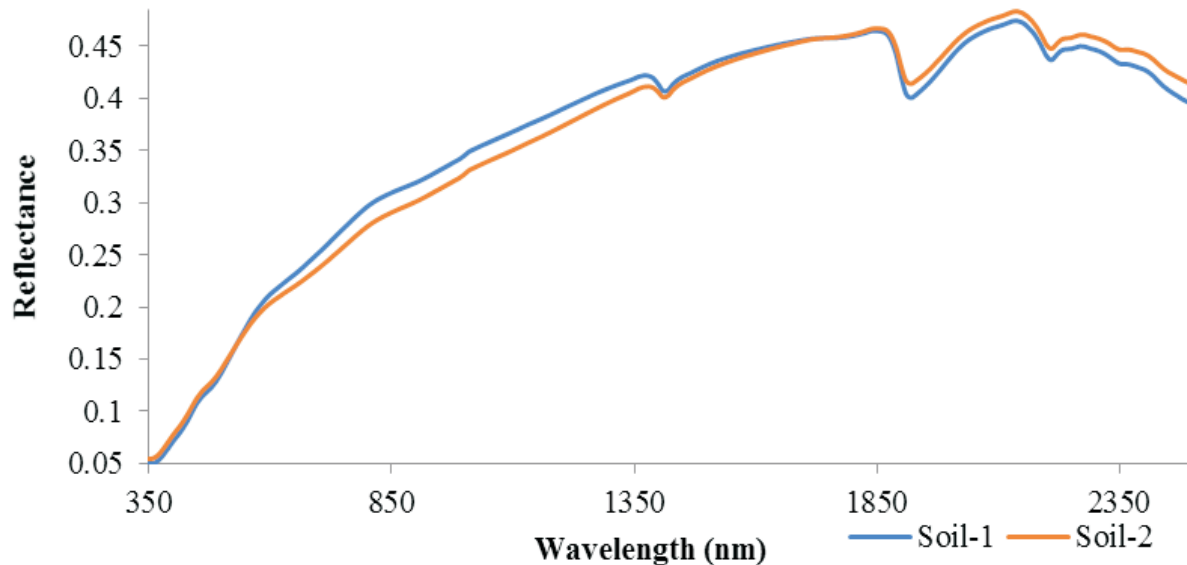
Fig. 2. Effects of soil types on air-dried soil reflectance spectra

The statistical correlation of soil chemical properties with first derivative soil reflectance data shows both positive and negative correlations at various wavelengths across the spectrum (Fig. 3). It indicates that saturated extract cations and anions showed a similar pattern of correlation at different wavelengths with 1st derivative soil reflectance values as EC_e (saturation extract EC). But the relatively high correlation of EC_e with soil reflectance values was found between 1400 to 2220 nm which indicates that this region is highly sensitive to change in salinity levels. Srivastava *et al.* (2017) also reported that region of 1400 to 2450 nm, correlated highly with different soil chemical properties of salt-affected soils of Indo-Gangetic plains of Haryana.

Multiple Linear Regression (MLR) modelling of Hyperspectral Data
Calibration

Salt-affected soil properties *viz*., pH_s (saturation extract pH), EC_e (saturation extract EC) saturated extract cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anions (Cl^- and SO_4^{2-}, CO_3^{2-} and HCO_3^-) were calibrated against the 1st derivatives reflectance wavebands (Table 2). Very good calibrations of MLR models were obtained for EC_e (r^2 - 0.91, RMSE- 8.52), saturation extract HCO_3^- (r^2-0.96, RMSE- 9.54), saturation extract Na^+ (r^2-0.88, RMSE- 21.11), saturation extract Cl^- (r^2 - 0.93, RMSE- 17.16), saturation extract CO_3^{2-} (r^2- 0.98, RMSE- 4.37) and pHs (r^2- 0.95, RMSE- 0.20). Higher regression coefficients (except for sulphate, calcium and magnesium cations) were achieved for all the MLR relations (Table 2). The poor calibration of MLR models for both saturation extract Ca^{2+} and Mg^{2+} may be attributed to the fact that there was no addition of the salt of calcium and magnesium and no replacement of these two divalent cations by monovalent sodium. Hence, the calibrated hyperspectral models for all the salinity and sodicity related parameters showed the good performance except calcium and magnesium cations in this study.
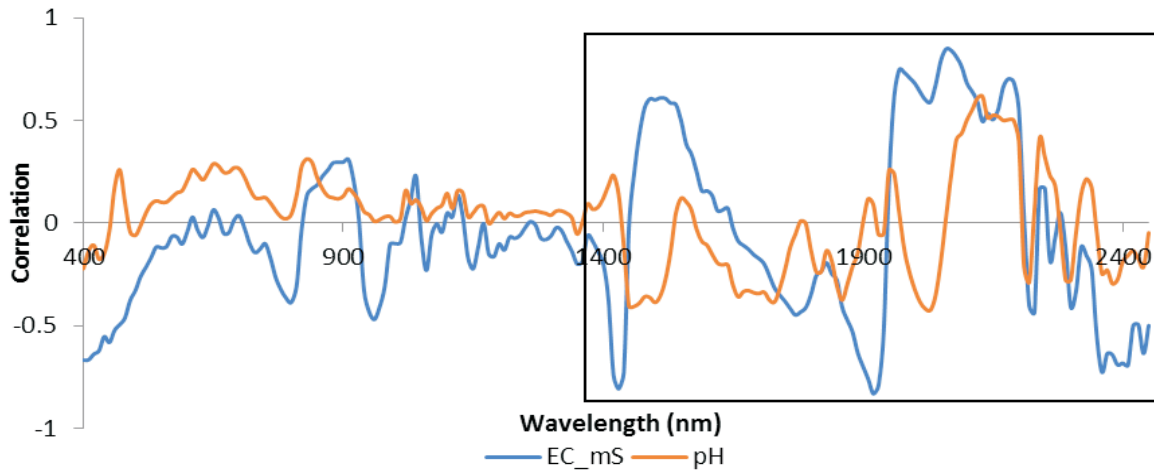
Fig. 3. Correlation of different soil salinity parameters with 1st derivative soil reflectance between
400 and 2450 nm region

Table 2. Summary statistics for the spectral models developed by MLR

Soil parameters*	No. of Factors	Calibration set			Validation set				
		N	R^2	RMSE	N	SD*	R^2	RMSE	RPD
EC_e (mS m^{-1})	05	98	0.91	8.52	50	28.56	0.91	8.89	3.25
pH_s	10	98	0.95	0.20	50	0.87	0.92	0.25	3.44
SE Cl$^-$ (mg L^{-1})	07	98	0.93	17.16	50	63.77	0.90	20.16	3.16
SE HCO$_3^-$ (mg L^{-1})	09	98	0.96	9.54	50	45.58	0.95	10.67	4.27
SE CO$_3^{2-}$ (mg L^{-1})	13	98	0.98	4.37	50	27.98	0.96	5.55	5.04
SE SO$_4^{2-}$ (mg L^{-1})	02	98	0.23	0.75	50	0.85	0.23	0.75	1.14
SE Na$^+$ (mg L^{-1})	03	98	0.88	21.11	50	62.03	0.86	22.97	2.70
SE K$^+$ (mg L^{-1})	06	98	0.86	1.76	50	4.77	0.86	1.85	2.58
SE Ca^{2+} (mg L^{-1})	02	98	0.52	7.24	50	10.77	0.52	7.47	1.44
SE Mg^{2+} (mg L^{-1})	02	98	0.37	7.48	50	9.24	0.26	8.02	1.15

*Square root transformation was applied on all soil parameters except pHs (no transformation) and SO$_4^{2-}$
(Log transformation)

Validation

The validation of the model using the independent dataset for all the parameters was evaluated based on the performance of validation indices of r^2, RMSE and RPD (Table 2). The r^2 indicates the percentage of the variance in the dependent variable that is accounted for by the independent variables. The RMSE estimates the variation of predicted values around observed values, and as it approaches zero, the prediction performance of the equation increases. The

RPD is the factor, by which the prediction accuracy has been increased compared to using the mean composition for all samples. Chang *et al.* (2001) grouped the prediction quality of soil properties using VNIR spectroscopy into three categories based on RPD values in the ranges of >2.0, 1.4–2.0, and <1.4 to indicate excellent, acceptable and poor predictions, respectively. They suggested that the predictions in the middle category could be improved using different calibration strategies, but the properties in the poor category may not be reliably predicted using reflectance spectroscopy.

The application of calibration models for prediction of soil attributes in the independent validation datasets also resulted in high r^2 for all the attributes except soil saturation extract sulphate, calcium and magnesium cation (Table 2). The calibration models obtained for soil sulphate (r^2- 0.23), saturation extract calcium (r^2- 0.52) and magnesium (r^2- 0.37) with 1st derivative soil reflectance data did not show good relationship due to low variability in the datasets. The high RPD values (> 2.0) obtained for EC_e, pHs, saturated extract Na^+, K+, Cl^-, HCO_3^- and CO_3^{2-} indicate that these properties can be reliably predicted from the spectral models (Fig. 5) whereas the spectral model of saturation extract SO_4^{2-} (RPD - 1.14) needs further improvement with larger datasets. The CO_3^{2-} spectral model showed the best performance for all the three validation indices (Fig. 4). Relatively greater variability in prediction at higher concentrations than lower concentrations of different soil salinity variables (Fig. 5) may be because of error in the laboratory analytical methods rather than genuine lack of predictive power of the spectral models. Shepherd and Walsh (2002) observed that increased analytical error at higher concentrations could be expected because of greater variability in amounts of ion extracted and the need for an increasing number of dilutions.

Best regression spectral models of SAS parameters were presented in table 3. Among the cation Na^+ and K^+ models explained the variability more than 85 % with significant water-absorbing central waveband at 2200 and 1900 nm, whereas, among anions carbonate and bicarbonate models contributed more than 95 % variability due to variation among the data set. pH_s and EC_e models significantly ($p<0.05$) fitted with more than 0.91 coefficient of determination value. But other sulphates, calcium and magnesium models fitted with a poor coefficient of determination value (Table 2) due to less replacement from soil solid phase to soil solution by a monovalent sodium ion.

Table 3. Regression spectral models of transformed SAS parameters with their significant waveband

SAS Parameter (Y)	Multiple regression equation	R^2	F
pH_s	$Y = 15.25 + 4.78 (\lambda400) − 12.29 (\lambda1920) − 11.79 (\lambda2040) + 11.11 (\lambda1990) + 8.12 (\lambda1910) + 5.62 (\lambda2400) + 4.25 (\lambda740) - 12.75 (\lambda450) + 8.66 (\lambda540) − 6.16 (\lambda890)$	0.95	154.47**
EC_e (mS m^{-1})	$Y = 49.62 − 11.89 (\lambda1950) + 4.90 (\lambda2350) - 1.19 (\lambda2060) − 3.10 (\lambda2440) + 10.63 (\lambda1940)$	0.91	193.29**
SE HCO_3^- (mg L^{-1})	$Y = 79.45 − 6.44 (\lambda2060) + 7.64 (\lambda2360) − 5.34 (\lambda1450) − 7.86 (\lambda2340) − 11.17 (660) + 3.51 (\lambda2410) + 10.08 (\lambda1480) + 13.06 (\lambda680) − 3.82 (\lambda910)$	0.96	214.20**
SE CO_3^{2-} (mg L^{-1})	$Y = 126.51 + 3.54 (\lambda1890) + 7.82 (\lambda2360) − 4.39 (\lambda1420) − 4.76 (\lambda2340) + 5.99 (\lambda1490) + 1.66 (\lambda2440) − 4.76 (\lambda1820) + 9.23 (\lambda1850) − 6.99 (\lambda1870) − 9.68 (\lambda2110) − 3.08 (\lambda1020) + 3.03 (\lambda1290) + 1.98 (\lambda1690)$	0.98	280.65**
SE Na^+ (mg L^{-1})	$Y = 171.50 + 6.47 (\lambda2350) − 2.75 (\lambda2080) − 4.34 (\lambda2450)$	0.88	224.20**
SE K^+ (mg L^{-1})	$Y = 3.94 − 0.73 (\lambda400) + 3.48 (\lambda2350) − 13.33 (\lambda2170) + 14.69 (\lambda2280) + 3.96 (\lambda1880) − 8.34 (\lambda2220)$	0.86	94.74**

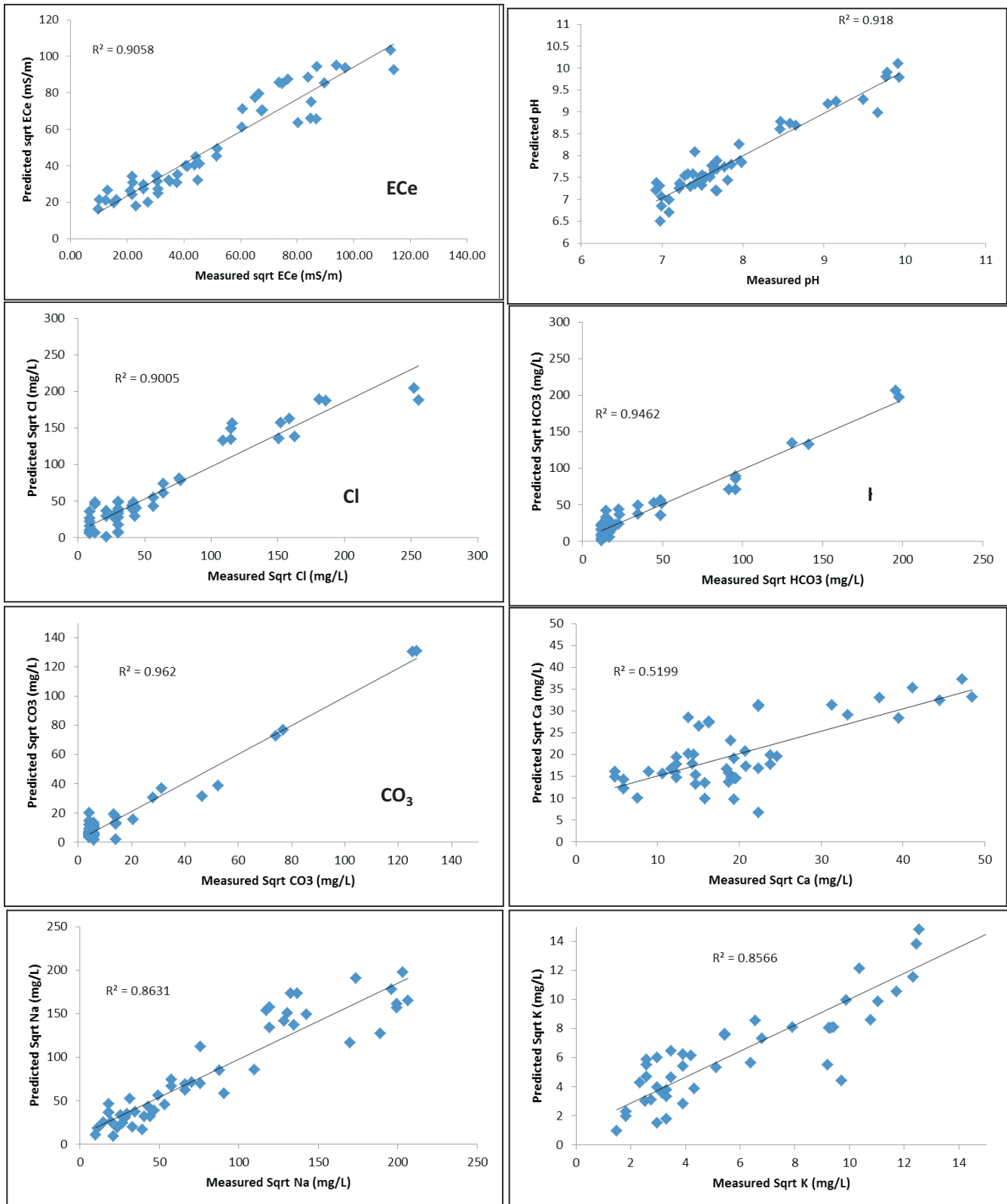*Square root transformation was applied on all soil parameters except pHs

Fig. 4. Scatter plot of measured and predicted values (all in square root transformation except pH$_s$ - no transformation and SO$_4^{2-}$ - Log transformation) of salt-affected properties in validation datasets.

Conclusion

The VNIR spectroscopy can be successfully used for rapid prediction of percentage chloride, carbonate and bicarbonate of sodium salts in saline/sodic soils as well as the type of salt present in the soil. Saline soils have diagnostic absorption features in the VNIR parts of the spectrum that might be attributed to the presence of moisture in the hygroscopic salt minerals. The hyperspectral models of EC_e, pH_s and other salinity related attributes fed with large number of dataset having broad range of salinity were able to capture more than 85 % of the variability except sulphate, calcium and magnesium. With the growing interest on high resolution hyperspectral satellite data applicability; our findings regarding rapid assessment of soil salinity and sodicity through hyperspectral models are encouraging as it might assist in real time monitoring of salinity over the spatio-temporal context and also helps to enrich spectral library; enabling the farmers to cope up with this degradation in a better way. We realize, however, that the model we obtained is based on controlled laboratory experiments and have not been validated for field applications, and therefore deserves further field investigation.

Acknowledgements

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