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On-line Vis-Nir sensor determination of soil variations of sodium, potassium and magnesium

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Abstract. Among proximal measurement methods, visible and near infrared (Vis-Nir) spectroscopy probably has the greatest potential for determining the physico-chemical properties of different natural resources, including soils. This study was conducted to determine the sodium, potassium and magnesium variations in a 10. Ha field located in Karacabey district (Bursa Province, Turkey) using an on-line Vis-Nir sensor. A total of 92 soil samples were collected from the field. The performance and accuracy of the Na, K and Mg calibration models was evaluated in cross-validation and independent validation. Three categories of maps were developed: 1) reference laboratory analyses maps based on 92 points 2) Full-data point maps based on all 6486 on-line points Vis-Nir predicted in 2013 and 3) full-data point maps based on all 2496 on-line points Vis-Nir predicted in 2015. Results showed that the prediction performance in the validation set was successful, with average R2 values of 0.82 for Na, 0.70 for K, and 0.79 for Mg, average root mean square error of prediction (RMSEP) values of 0.02% (Na), 0.20% (K), and 1.32% (Mg) and average residual prediction deviation (RPD) values of 2.13 (Na), 0.97 (K), and 2.20 (Mg). On-line field measurement was also proven to be successful with validation results showing average R2 values of 0.78 (Na), 0.64 (K), and 0.60 (Mg), average RMSEP values of 0.04% (Na), 0.13% (K), and 2.19% (Mg) and average RPD values of 1.57 (Na) 1.68 (K) and 1.56 (Mg). Based on 3297 points, maps of Na, K and Mg were produced after N, P, K and organic fertilizer applications, and these maps were then compared to the corresponding maps from the previous year. The comparison showed a variation in soil properties that was attributed to the variable rate of fertilization implemented in the preceding year.

1. Introduction

In the last two decades, the number of studies evaluating other Vis-Nir spectroscopy applications in soil science and agronomy has increased rapidly, with a primary focus on measuring various basic properties of soils, such as the organic matter content, clay content and, more recently, chemical properties [1]. Current studies have shown that Vis-Nir spectroscopy is capable of providing accurate quantification of the main physical and chemical soil properties, and that it is a useful tool for digital soil mapping and for precision agriculture applications [2-5].

There is a natural accumulation of sodium (Na) in soil as a result of fertilizers, runoff from shallow, salt-laden waters, irrigation water and the breakdown of minerals which release salt. The excess

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sodium in the soil is taken up by plant roots and can cause serious vitality problems an addition to disrupting the soil structure. Potassium (K), as one of the macronutrients, has many vital physiological, metabolic and biochemical functions in crop plants which increase their crop yield and quality. Potassium increases root growth, improves drought and cold resistance, affects the time of harvest, improves the availability of nitrogen and helps to increase resistance to disease. On the other hand, a potassium deficiency affects shoot and root growth [6]. Magnesium (Mg) is a secondary nutrient which maize and other crops require to capture solar energy for growth and production through photosynthesis. Magnesium is an essential component of chlorophyll molecules, each of which contains 6.7% Mg. It has been suggested that the interaction of Mg with common bean varieties has a significant effect on the crop yield, foliar content, and yield components [7]. The conventional analytical methods used for the determination of Na, K and Mg are expensive, complex and time-consuming. Consequently, researchers have been attempting to find alternative solutions that are fast, simple and cost-effective. Vis-Nir spectroscopy is one of the main methods that have been explored. This can be attributed to the fact that, by using suitable chemometric methods, large sets of spectral information can be extracted from the Vis-Nir spectra of soils. The complex relationship between spectral signatures and soil properties can be better modeled via multivariate regression methods, which have an advantage over the simple bivariate relationships, e.g., those based on peak intensity measurements [8]. Partial least squares (PLS) regression is the most common technique adopted today to model the relationships between the infrared spectral intensity characteristics of the soil components and the soil properties through derived PLS loadings, scores, and regression coefficients [9]. The PLS regression establishes a series of components or latent vectors that provide a simultaneous reduction or decomposition of X and Y such that these components explain, as much as possible, the covariance between X and Y [10]. One of the advantages of PLS regression compared to other chemometric methods, such as principal component regression analysis, is the possibility of interpreting the first few latent variables, because these show the correlations between the property values and the spectral features [11]. The calibration samples should cover the variability expected in the full sample set, and the future unknown data and the validation (test) set must be independent of the calibration set in order to avoid an optimistic assessment of predictive performance [8, 12, 13].

The aim of this study was to explore the potential of a Vis-Nir on-line sensor to measure Na, K and Mg. Laboratory-measured, laboratory Vis-Nir-predicted and on-line Vis-Nir-predicted maps were produced and used with independent validation sample sets. Based on 3297 points, maps of Na, K and Mg were produced after N, P, K and organic fertilizer applications, and these maps were then compared to corresponding maps from the previous year. This comparison showed variations in soil properties that were attributed to the variable rate of fertilization implemented in the preceding year.

2. Material and methods

2.1. On-line sensor

A simple metal frame for the on-line sensor was manufactured at Uludag University using the patented design [14] of A.M. Mouazen (Figure 1). The optical unit was attached to the backside of the subsoiler chisel in order to acquire soil spectra from the smooth bottom of the trench in the diffuse reflectance mode. The subsoiler (acting as a soil-cutting tool) and the optical probe were set on the metal frame. The on-line soil sensor was then mounted on the three-point linkage of a tractor for collecting soil spectra under mobile conditions. The sensor was equipped with an AgroSpec mobile, fiber-type vis–NIR spectrophotometer (Tec5 Technology for Spectroscopy, Germany) to measure the soil spectra. A differential global positioning system (DGPS) (EZ-Guide 250, Trimble, USA) was used to record the position of the on-line-measured spectra with sub-meter accuracy. The frame and the on-line sensor were tested at the Uludag University farm before performing the actual field measurements in order to avoid unexpected malfunctions of either software or cable connections during the field measurements.

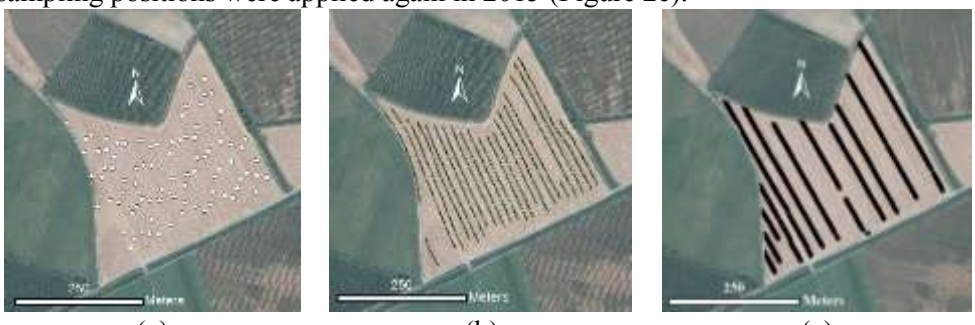


Figure 1. The on-line Vis-Nir soil sensor, as designed by Mouazen [14].

2.2. Experimental site

Karacabey and its environs lie in one of the most active tectonic areas of Turkey due to their location on the Northern Anatolia Fault Zone. This fault was a primary cause of important geomorphic environmental changes in this area during the Quaternary period. The Karacabey district has many creeks and a depression basin. The parallel and/or subparallel drainage patterns of the creeks that reach the Karacabey basin from the north have evolved as a result of the lithological character of the area.

This study was carried out in an irrigated field of 10 ha, cultivated for sweet corn (maize), having soil classified as clay-type (sand 26%, silt 30.4%, clay 43%) and located in a semiarid environment (Figure 2). This field was chosen because of the soil variability of different zones according to yield. This field was commissioned after the crop was harvested. In past years, generally, fertilizers composed of N, P and K were employed on the field. For laboratory analysis, a total of 92 soil samples were collected from the field, respectively, from the bottom of the trench opened by the subsoiler (Figure 2a). In the year 2013, raw spectra were collected along parallel transects at a speed of approximately 3 km h^{-1} (Figure 2b). Raw spectra on soil were collected along with parallel transects at a speed of approximately 3 km h^{-1}. The sampling positions were recorded with the DGPS. Sampling lines and sampling positions were applied again in 2015 (Figure 2c).



(a) (b) (c)

Figure 2. Field location in Karacabey, Turkey: (a) soil sampling positions, (b) on-line soil measurement points (2013), and (c) on-line soil measurement points (2015).

2.3. Laboratory analyses

The 92 soil samples (Figure 2a) were equally divided into two parts. The first half was used for laboratory reference measurements of Na, K, Mg and particle size distribution (PSD), and the second half was used for optical scanning in the laboratory. Exchangeable Na, K and Mg ions were

determined after extraction with 1 N ammonium acetate (pH 7.0). The PSD of the soil was measured using a hydrometer [15]. Soil texture classification was determined according to the United State Department of Agriculture system. Soil samples were scanned in the laboratory using the same Vis-Nir spectrophotometer employed during the on-line field measurements. Each sample was put into three plastic cups (1.2 cm deep and 1.2 cm in diameter) and carefully levelled to form a smooth scanning surface [2]. A white reference was scanned before the soil scanning, which was repeated every 30 min. Each cup was scanned 10 times, and the readings were averaged. The final spectrum for each sample, to be used for further analysis, was the average of the three spectra obtained for the three cups.

2.4. Pre-processing of spectra

First, soil spectra of 305-370 and 2151-2200 nm were deleted to eliminate noise at the edges of each spectrum. Then, the spectra between 371 and 1000 nm were reduced by 3, and between 1001 and 2150 nm reduced by 6. Maximum normalization was followed, which is typically used to get all data to approximately the same scale, or to get a more even distribution of the variances and the average values. The spectra were then subjected to the Savitzky-Golay [16] first derivation to enable the computation of the first or higher order derivatives, including a smoothing factor, which determined how many adjacent variables would be used to estimate the polynomial approximation for derivatives. The second order polynomial approximation was selected. A 2:2 smoothing was carried out after the first derivative [17]. The pre-processing of the spectra and PLS regression with one-leave-out cross validation were carried out using the calibration set in order to develop a calibration model via Unscrambler 7.8 software (Camo Inc., Oslo, Norway).

2.5. Modeling

Detailed statistical information about the laboratory-measured chemical analyses is provided in Table 1.

Table 1. Sample statistics of laboratory and on-line-measured chemical properties of the field calibration and prediction sets.

Nutrients	Sample sets	Sample number	Min.	Max.	Mean	SD
Na, ppm	All samples	92	0.26	0.57	0.45	0.07
	Cross-validation set	74	0.28	0.56	0.45	0.06
	Laboratory prediction set	18	0.3	0.58	0.44	0.07
	On-line prediction set	18	0.27	0.50	0.41	0.06
K, cmol kg^{-1}	All samples	92	0.39	1.79	1	0.25
	Cross-validation set	207	0.07	1.60	0.77	0.32
	Laboratory prediction set	18	0.39	1.52	0.88	0.28
	On-line prediction set	18	0.6	1.46	0.97	0.22
Mg, cmol kg^{-1}	All samples	92	5.53	18.45	11.37	2.80
	Cross-validation set	73	5.53	18.45	11.29	2.95
	Laboratory prediction set	18	5.54	16.94	11.10	3.33
	On-line prediction set	18	5.54	17.11	10.70	3.43

SD: Standard deviation

The performance and accuracy of the chemical property calibration model was evaluated in cross-validation and prediction. The model performance was evaluated by means of the coefficient of determination (R^2), root mean square error of prediction (RMSEP) and ratio of prediction deviation (RPD), which is the standard deviation divided by the RMSEP.

2.6. Fertilizer applications

Amount of N, P_2O_5, K_2O (kg) applied for the entire field are shown in Table 3.

Table 2. Total amount of N, P_2O_5, K_2O application for the entire field.

Years	N(kg)	P_2O_5 (kg)	K_2O (kg)
2013	3264	712	950
2014	9740	2710	0
2015	8700	6600	2100

2.7. Map development

All maps were developed using ArcGis 10 (ESRI, USA) software. Three maps were used for the comparison of chemical properties. The first one was for the laboratory measurement points based on 92 soil samples measured in 2013. The second one was for the on-line measurement in 2013 based on 6486 points. The inverse distance weighing (IDW) interpolation method was used to develop the laboratory-measured maps. IDW method is based on the extent of similarity of cells, while methods, such as trend fitting of a smooth surface, are defined by mathematical function. Robinson and Metternicht [18] concluded that interpolation methods give similar RMSEP values, using the cross validation technique for evaluation. The full-point maps were developed via the Kriging interpolation. Kriging is a statistical method used in diverse application modeling. Kriging is most appropriate when you know there is a spatially correlated distance or directional bias in the data.

3. Results and discussion

3.1. Model performance

The model performances in cross-validation, laboratory and on-line predictions of chemical properties for the field are shown in Table 4. Viscarra Rossel et al., [19] classified RPD values as follows: RPD < 1.0 indicates very poor model predictions and their use is not recommended; RPD between 1.0 and 1.4 indicates poor model predictions, where only high and low values are distinguishable; RPD between 1.4 and 1.8 indicates fair model predictions, which may be used for assessment and correlation; RPD values between 1.8 and 2.0 indicates good model predictions, where quantitative predictions are possible; RPD between 2.0 and 2.5 indicates very good, quantitative model predictions; and RPD > 2.5 indicates excellent model predictions. This classification system was adopted in this study.

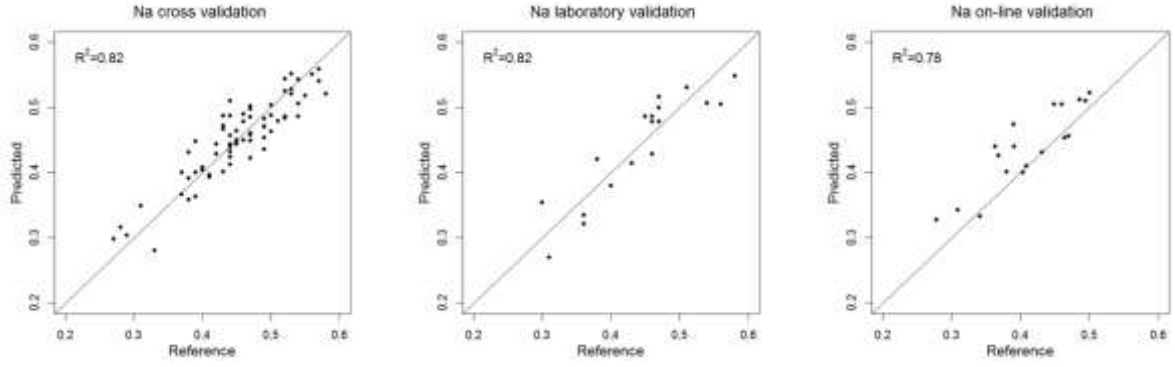
Table 3. Summary of model performances in cross-validation, laboratory and on-line predictions of chemical properties.

Nutrients	Sample sets	R^2	RMSEP	RPD	Slope
Na	Cross-validation	0.82	0.02	2.13	0.99
	Laboratory prediction	0.82	0.03	2.33	0.92
	On-line prediction	0.78	0.04	1.57	0.85
K	Cross-validation	0.70	0.20	0.97	0.96
	Laboratory prediction	0.80	0.12	2.27	0.74
	On-line prediction	0.64	0.13	1.68	0.70
Mg	Cross-validation	0.79	1.32	2.20	0.69
	Laboratory prediction	0.88	1.14	2.90	0.98
	On-line prediction	0.60	2.19	1.56	0.60

RMSEP: Root mean square error of prediction
RPD: Residual prediction deviation

Literature [20-21] proves that the worst properties to be measured with NIR are K and Na. Measurement of pH, Ca, and Mg were reported to be more successful as compared to K and Na, but underperformed those properties with direct spectral response in NIR [22]. Chang et al., [23] concluded that exchangeable Na could not be predicted using the NIR spectroscopy technique since R^2<0.50. On the contrary, in this research R^2 was found 0.82 while RPD is 2.13 for Na in cross validation.

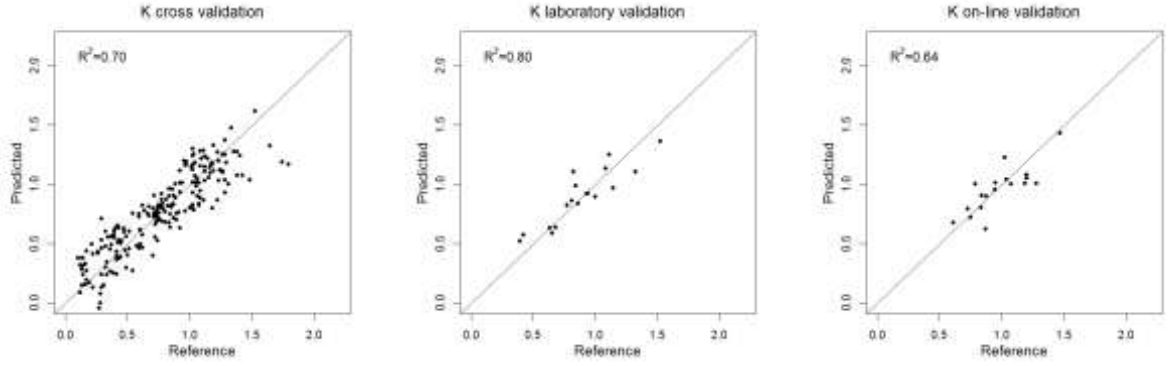
The calibration set of the field consisted of 74 randomly selected soil samples, whereas the remaining 18 samples were used as the Na prediction set. Figure 3 shows the scatter plots of measured versus predicted Na in cross- validation, laboratory validation and on-line validation.



(a) (b) (c)

Figure 3. The scatter plots of measured versus predicted Na for laboratory and on-line predictions.

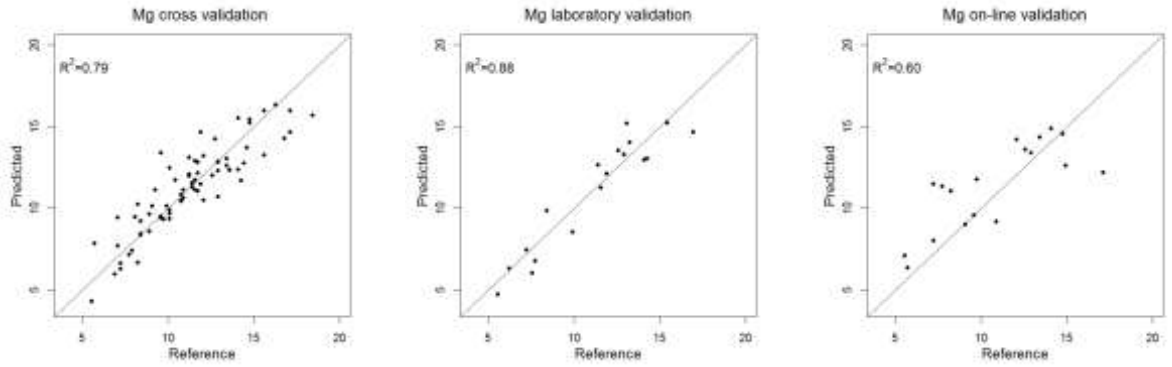
The Vis–NIR predicted K was chosen as the exhaustive variable, because it was the most correlated with the soil variables [24]. 72 samples from the field were pooled together in one matrix with other 135 samples, collected previously from UK (62 samples), Denmark (28 samples), from Czech Republic (22 samples), Netherland (23 samples). The remaining 18 samples were used for validation of the on-line measurement. Figure 4 shows the scatter plots of measured versus predicted K in cross-validation, laboratory validation and on-line validation.



(a) (b) (c)

Figure 4. The scatter plots of measured versus predicted Na for laboratory and on-line predictions.

Udelhoven et al. [25] evaluated the ability of NIR spectroscopy to estimate soil Fe, Mn, Ca, Mg, and K, and they found that only Ca and Mg (R^2 =0.67 and 0.69, respectively) were predictable under in situ conditions. A total of 92 samples were collected from F1. 74 samples of 92 were designated for Cross-validation. Figure 5 shows the scatter plots of measured versus predicted Mg in cross-validation, laboratory validation and on-line validation.

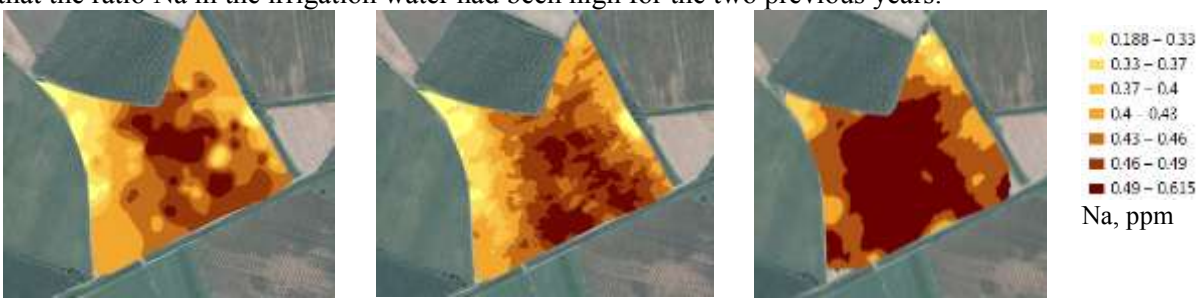


(a) (b) (c)

Figure 5. The scatter plots of measured versus predicted Na for laboratory and on-line predictions.

3.2. Mapping

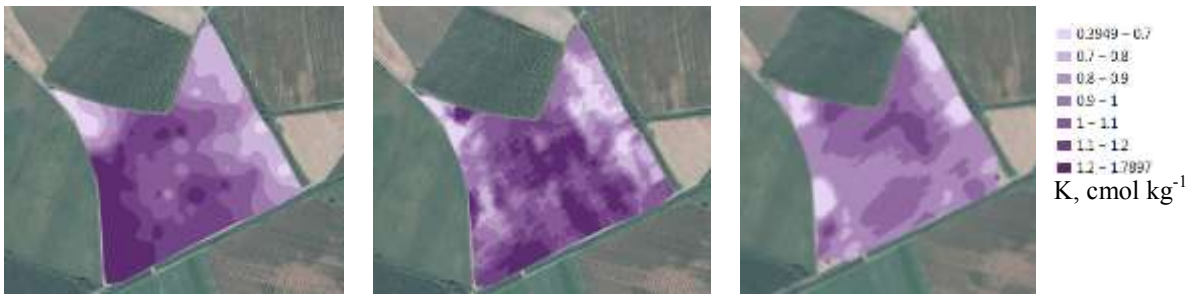
As can be seen in Figure 6, the Na content of the soil was increased in 2015. The reason for this was that the ratio Na in the irrigation water had been high for the two previous years.



(a) (b) (c)

Figure 6. Na Comparison maps: (a) laboratory-measured, based on 92 samples, (b) on-line Vis-Nir predicted (6486 points) measured in 2013, and (c) on-line Vis-Nir predicted (2496 points) measured in 2015.

Figure 7 shows K variation maps. K content of the soil has been decreased in 2015. The reason can be attributed that two years corn grain were grown. Corn takes up high amount of K from the soil.

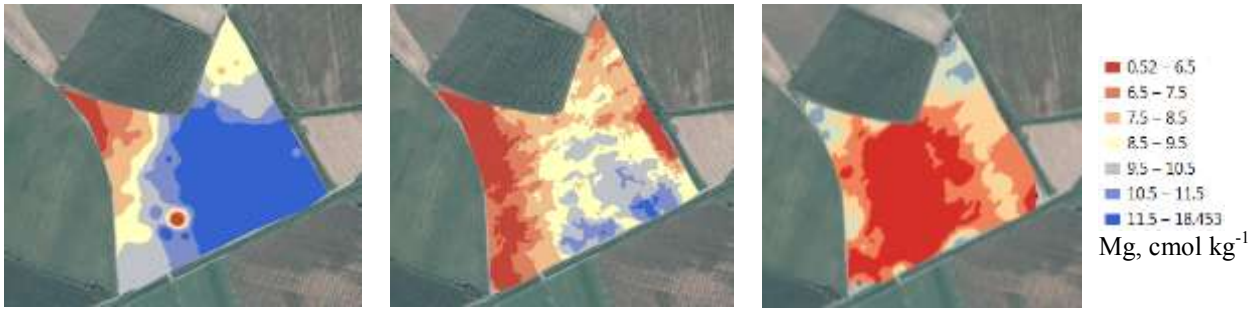


(a) (b) (c)

Figure 7. K Comparison maps: (a) laboratory-measured based on 92 samples, (b) on-line Vis-Nir predicted (6486 points) measured in 2013, and (c) on-line Vis-Nir predicted (2496 points) measured in 2015.

Magnesium is one of thirteen mineral nutrients coming from soil that, when dissolved in water, is absorbed through plant roots. Magnesium is the main component of the chlorophyll that gives green

color to the leaves; therefore, it is a very important element for chlorophyll formation. Heavy rains can cause a Mg deficiency by leaching the Mg out of sandy or acidic soil. In addition, if soil contains high amounts of K, plants may take this up instead of Mg, again, leading to a deficiency. Figure 5 shows the Mg variation maps. In the spring of 2015, before the measurements were taken, there were heavy rains in Karacabey region. According to the Turkish Meteorological Station, the Marmara Region received 25% more rainfall than average at that time.



(a) (b) (c)

Figure 8. Mg Comparison maps: (a) laboratory-measured based on 92 samples, (b) on-line Vis-Nir predicted (6486 points) measured in 2013, and (c) on-line Vis-Nir predicted (2496 points) measured in 2015.

4. Conclusion

This study described the potential of visible and near infrared (Vis-Nir) spectroscopy for the measurement of soil Na, K and Mg in fields with clay soils in a semiarid environment in Turkey. The results were evaluated under laboratory and on-line field measurement conditions. It was concluded that:

1- Vis-Nir spectroscopy can be successfully used for the measurement of Na, K and Mg in clay soils under semiarid conditions.

2- The Vis-Nir prediction maps of soil Na, K and Mg were similar to the corresponding measured maps. However, with the full-point maps, more details showing different spatial distribution were observed compared to the maps developed with a limited number of points.

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On-line Vis-Nir sensor determination of soil variations of sodium, potassium and magnesium

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