PREDICTION OF SOIL AVAILABLE PHOSPHOROUS CONTENT USING SPECTRA-RADIOMETER AND GIS IN SOUTHERN OF IRAQ

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ABSTRACT

In this study, soil samples were collected from two locations: Samawa and Rumetha in southern Iraq. The samples from each location were split into two datasets: calibration set and validation set. A representative soil sample for each location was chosen for application of 5 levels of potassium phosphate fertilizer in 3 replications. Vis-NIR reflectance (350-2500 nm) and GIS-Kriging were used in combination with Partial Least Square (PLS) to predict soil available P. According to the results of this study, three wavelength regions were reported as a main sensitive bands for soil available P. The best prediction ability was achieved for Rumetha location at 1400-1600 nm with an R^2 of 0.85, lowest RMSE of 1.405, and lowest standard deviation of 1.577 and for Samawa location at 900-1000 nm with an R^2 of 0.81, RMSE of 2.666 and lowest standard deviation of 2.879. The capability of the Vis-NIRS-based and GIS-Kriging prediction models were evaluated by using cross-validation values Q^2 and R^2 between measured and predicted soil available P of each model. The selection principle parameters showed best prediction by NIRS-models with an R^2 of 0.79 for Rumetha and 0.75 for Samawa location. While the prediction ability of GIS-Kriging models were in worst with an Q^2 of 0.17 for Samawa location and reasonable with an Q^2 of 0.58 for Rumetha location. These empirically result is an evident of the superiority of NIRS-based models for prediction soil available P over the GIS-Kriging models.

Key Words : NIR reflectance , GIS-Kriging, Available P

Part of PhD Dissertation of the first Author.

التنبؤ بمحتوى الترب من الفسفور الجاهز بإستعمال السبكترراديوميتر ونظم المعلومات الجغرافية في جنوب العراق

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المستخلص

لاجل التنبؤ بمحتوى التربة من الفسفور الجاهز أخذت عينات تربة من موقعين ضمن محافظة المثنى جنوب العراق الموقع الاول بالقرب من مدينة السماوه والموقع الثاني في قضاء الرميثة. تم تقدير محتوى الفسفور الجاهز لهذه العينات بالاضافة الى قراءة الانعكاسية باستعمال جهاز قياس الطيف الكهرومغناطيسي ,وقسمت العينات الى مجموعتين الاولى لاجراء المعايرة (Calibration) والثانية خصصت للتحقيق (Validation) لنتائج المعايرة. كما وتم اخذ عينة تربة ممثلة لكل موقع للإضافات السمادية (خمس مستويات اضافة بثلاثة مكررات من سماد فوسفات البوتاسيوم ولكل موقع). وتم إعتماد الانعكاسية الطيفية ضمن المدى (Vis-NIRS (350-2500 nm وبرمجيات GIS لاجل التنبؤ بمحتوى التربة من الفسفور الجاهز باستعمال برنامج تحليل الانحدار(PLS). أوضحت النتائج بان التنبؤ بقيم الفسفور الجاهز بالتربة قد اعطى ارتباط مع قيم الانعكاسية ضمن اكثر من حزمة طيفية فقد كانت قيم (R^2= 0.85) مع قيم الجذر التربيعي لمتوسط الخطأ RMSE والانحراف المعياري 1.405 و 1.577 بالترتيب، ضمن الحزمة الطيفية 1400−1600.في حين كانت قيم كل من RMSE والانحراف المعياري 2.666 و2.879 على التوالي للحزمة 900−1000 مع قيمة (R^2=0.81). وبالاستعانة بقيم (Q^2) مع قيمة R^2 لاجل المفاضلة بين فعالية كل من طريقة التنبؤ بالانعكاسية مع طريقة التنبؤ باعتماد برنامج GIS ومن خلال تطبيق (Kriging) لوحظ بان قيم الفسفور الجاهز قد ارتبطت مع القيم المتوقعة من خلال قيم (R^2) التي بلغت 0.79 و 0.75 للموقعين الرميثة والسماوه بالترتيب. في حين كانت قيم (Q^2) واطئة نسبيا مع استخدام تطبيق (Kriging) حيث بلغت قيمته 0.17 و 0.51 للسماوه والرميثة بالترتيب.وهذا يشير الى ان طريقة اعتماد الانعاكاسية وسيلة للتنبؤ بقيم محتوى التربة من P اكثر واقعية من طريقة استخدام (Kriging) .

الكلمات المفتاحية :الانعكاسية القريبة من تحت الحمراء وتطبيق GIS-Kriging والفسفور الجاهز.

مستل من اطروحة دكتوراه للباحث الاول.

INTRODUCTION

There are several factors contribute in the bandwidth of infrared absorptions (narrow or broadening). Collision between molecules and the limited of time life of an excited state are the main sources of line broadening; where the less well describe energy associated with the shorter lifetime of transition to the excited state (25). In spite of that the absorption intensity is highly related to the change in molecular dipoles, hence, the large change lead to a very strong absorption and inversely, a very weak absorption associated with a very small change in dipole (12,13,24). Generally, this review intended to provide important information on the use of VNIR-Spectroscopy in soil analysis. To this end, a review on issues related to the essential soil attributes such as soil texture, soil organic matter, minerals, water, and fertility with focusing on nutrients (N,P, and K) will be provided into the following sections. Many studies have been devoted to determine soil nutrients and micronutrients concentration, as a crucial factor in soil fertility assessment. In particular, very acceptable estimations have been reported by using Vis-NIR spectroscopy under laboratory condition and in-situ field measurements. The assessment of soil fertility is usually routine work associated with soil nutrients level and organic matter content as main soil properties for either to precision agriculture or to maintain soil from degradation (11). Such estimation needs to acquire data, since the soil sampling and laboratory analysis are costly and time consuming. At this point, spectroscopic techniques become a promising method to make rapid laboratory soil analysis as well as on-line field soil analysis with aid of a field portable instrument (6, 8, 18, and 22). As described by Desbiez *et al.* (10), soil fertility is function of soil properties therefore; it is comprehensive concept more than to measure directly. When connected to soil P forms, P in soil has been well studied by soil scientist as the second nutrient after N in terms of its importance for plant. Soil P is not easy to determine from spectral data like SOM and total N. Some authors reported Vis-NIR as a good way to predict soil P with very successful correlations (R^2> 0.90) and others reported absolutely failure prediction with very low correlations (R^2<0.50). Udelhoven et al. (27) attributed poor prediction of extractable P to the size of the yield as P and other nutrients are removed with the yield. Other authors attributed low correlations to the measurement methods (16, 31). Moron and Cozzolino (17) has identified poor accessibility prediction with R^2 of 0.61, they suggested that the extractable and available P measurement methods are not at all times very well correlated with absorbance. Bogrekci and Lee (2,3) investigated the effects of mostly common four different P compounds on reflectance spectra using UV-VIS-NIR. Their results recognized highest absorbance for calcium phosphate at 2516 nm, while the Aluminum phosphate showed lower absorbance between 1374 and 2550 nm and highest absorbance at 228 nm in the UV range. The same study observed four small distinguishable peaks at 871, 1413, 1934, and 2213 nm for Fe-associated P and very significant peak at 281 nm in the UV region. According to Daniel *et al.* (9) has recognized high absorbance peaks at 400-1100 nm for available P with well correlation (R^2=0.81) between actual concentration and absorbance. Factors that affecting on P prediction by Vis-NIR spectroscopy are also used in literature to improve the prediction of soil P. Bogrekci *et al*. (4) obtained very strong correlation R^2 of 0.92 between total P and absorbance of dried and sieved soil samples. For the same aim, Bogrekci *et al.* (4) obtained more accurately prediction of soil P from spectra of moisture free soil than those of moist soil. The main objectives of this study are to evaluate the efficiency of using Vis-NIR Spectroscopy technique to develop prediction models for soil available P determination and evaluation the predictive power of NIR-based models in comparison to Kriging-based models.

MATERIALS AND METHODS

Two study locations were selected in Al-Muthana province, located in Southern Iraq. The second location is located in Al-Rumetha (45.252034-45.255029º E, 31. 497139-31. 498901º N) the northern border of the first study location Al-Samawa (45.255029-45.2525034ºE, 31497139-31.498901ºN), about 25 Km from the center of Al-Samawa. In the laboratory, the soil samples were air dried, hand cleaned to remove foreign particles and ground to pass through a 2 mm sieve and analyzed according to (1, 6, and 21) and listed at Table 1. Following the common soil preparation steps, soils were mixed with Mono-potassium Phosphate fertilizer to simulate soils having varying concentrations of phosphorus. Mono-potassium phosphate fertilizer was applied at 36,57,91,114,and 160 Kg P ha^{-1}. The application of fertilizer is usually performed together with the addition of water into soil to dissolve the fertilizer in soil solution. Finally, the mixture was mixed thoroughly to obtain homogenous dispersion. The mixture was stored for one month to led the added fertilizers equilibrate in the soil. The concentration of available phosphorus was conducted after spectral measurements. Available P was analyzed by Olsen extraction; P concentrations were measured with a spectrophotometer which can detect the complex absorption at 882 nm. (20).

Table 1. Some Soil properties of the study locations

Properties	Location		Unit
	Rumetha	Samawah	
Soil Classification	Typic-Torrifluvent	Typic-Torrifluvent	
Parent Material	Alluvium	Alluvium	
Climate	S Arid	Arid	
ECe	8.7	23	dS m^{-1}
pH	7.5	7.7	
Total Carbonate	215	190	gm Kg^{-1} soil
Soil Organic Matter	12	9	
CEC	24.4	21.3	$Cmol_{+}$ Kg^{-1} Soil
Clay	395	325	gm Kg^{-1} soil
Silt	235	175	
Sand	370	500	
Texture	Clay loam	Sand Clay Loam	

The reflectance spectra of air-dry soil samples were obtained in the laboratory by ASD spectrometer- Field Spec® 3, with a spectral range of 350-2500 nm. The near infrared reflectance spectra were transformed into absorbance spectra using the Log (1/Reflectance) function. According to Beer Lambert Law, absorbance is directly proportional to the concentration of studied properties. Prior to any model development the soil samples were randomly divided into a calibration set with soil samples and a validation set with 11 soil samples for Rumetha and Samawah. Spectral absorbance were correlated to soil available P concentration using statistical analysis software XLSTAT 2014 program to create predictor models. Models with the highest coefficient of determination (R^2) and lowest root mean square error (RMSE) were plotted to identify the significant portion of wavelength for soil available P prediction.

RESULT AND DISCUSSION

Partial least squares (PLS) regression analysis was used to predict the concentration of soil available P in soil samples collected from Rumetha and Samawa locations. As showed in Table 2, only wavelength regions with high determination coefficients R^2 are tabulated. The best predictive ability was achieved for Rumetha location at 1400-1600 nm with R^2 of 0.85, lowest RMSE of 1.405, and lowest standard deviation of 1.577 and for Samawa location at 900-1000 nm with highest $R^2$of 0.81, lowest RMSE of 2.666, and lowest standard deviation of 2.879. At wavelength region 2100-2200 nm, both studied locations showed lowest R^2, highest RMSE, and highest standard deviation (Std). The determination coefficient values for soil available P at the three reported wavelength regions were less than those have been obtained for T N. In literature, generally the mentioned above wavelength regions were well-known as P bands. According to these literatures, the absorption wavelength regions as much related to the level of P in solution, the chemistry of soil, and the type of the target P compounds (3,4,5,6,8,14,26,28). All primary soil properties like N, C, SOM, moisture content, and particle size distribution have possible absorption in NIR regions arise from bonds like O—H, C—H, and N—H (7,15,19). Generally, soil spectrum is obtained by passing radiation through a soil sample, which excite molecule with dipole moment to vibration stretching of atoms form molecule. This means that, the energy at which peak appears corresponding to the chemistry of the soil matrix. Unlike N, P is one of the secondary soil properties in responding to NIRS radiation due to the weak P—O dipole moment (15).

Table 2. Statistical characteristics (calibration) for available Phosphorous in samples of Rumetha and Samawa locations.

Location	Wavelength (nm)	Observ-ations	R^2	RMSE	Std.deviati-on
Rumetha	900-1000	28	0.81	1.958	2.109
	1400-1600	28	0.85	1.405	1.577
	2100-2200	28	0.65	2.455	2.698
Samawa	900-1000	28	0.81	2.666	2.879
	1400-1600	28	0.75	2.910	3.143
	2100-2200	28	0.75	3.192	3.522

Despite of specific absorption peak is not observed for available P, the prediction worked well for both studied locations. Each calibration equation developed from 28 soil samples as calibration set and validated with 11 soil samples as validation set. For each, the NIR-predicted values were correlated with their measured values. The parameter coefficient of determination (R^2v) of the cross-validation was used as selection principle to build a strong model. Based on R^2v values, both studied locations showed best predicted by model built from measurements at 900-1000 nm with R^2v of 0.79 for Rumetha location and 0.75 for Samawa location. The determination coefficient of validation represents empirical evidence of the capacity of the prediction model to make accurate predictions for new unknown data. Depending on the cross-validation results, the best wavelength was selected to make accurate estimate of the prediction performance of calibration. The main goal of using PLS analysis is to predict the value of dependent variable for new samples from the same location. In this case, the results presented in Tables 3 and 4 show the potential of NIRS to predict soil available P concentration. The values of the lowest predicted soil available P were 1.736 and 0.359 mg kg^{-1} soil and the highest predicted soil available P were 15.385 and 22.004 mg kg^{-1} soil for Rumetha and Samawa locations, respectively. While the values of the lowest measured soil available P were 2.600 and 1.500 mg. Kg^{-1} and the highest measured soil available P were 16.300 and 24.200 mg kg^{-1} soil. These results verify the potential of the prediction model to capture the variation of soil available P concentrations in the locations under study. Several studies reported that smaller or more similar areas have resulted in better prediction and more applicable in practice for most of soil properties (23,29,30).

Table 3. Prediction results for soil available P by PLS model for Rumetha location

Sample No.	PLS Model for (900-1000 nm) Measured available P (mg kg^{-1} soil)	Predicted available P (mg kg^{-1} soil)	Residual
1	5.9	5.85	0.05
2	6	4.22	1.78
3	4.3	6.61	-2.31
4	10.2	11.91	-1.71
5	5.5	7.32	-1.82
7	5.8	5.28	0.52
8	9.9	7.39	2.51
10	10.9	10.26	0.65
11	16.3	11.66	4.64
12	11.3	11.57	-0.27
13	2.6	4.81	-2.21
16	4.2	8.30	-4.10
17	3	1.74	1.26
18	2.9	5.01	-2.11
19	2.9	2.86	0.04
20	9.2	9.84	-0.64
21	9.8	5.33	4.47
25	4.2	2.03	2.17
26	5.2	4.74	0.47
27	3.8	3.38	0.42
30	3.8	6.28	-2.48
31	5.5	5.11	0.39
33	16.2	15.39	0.82
34	9.5	7.88	1.62
35	8.8	8.96	-0.16
36	5.8	7.20	-1.40
37	2.7	5.09	-2.39
38	2.6	3.56	-0.96

Laboratory-measured soil data set of 32 and 28 point samples from rumetha and samawa were used for statistical modeling and prediction process. The spatial concentration of available P was generated with the use of GIS-Kriging Ordinary Spherical technique for the (x, y) locations point samples from Samawa and Rumetha. The quality of the predicted available P values by GIS-Kriging models was generally assessed by using validation dataset with 11 soil points. The same validation dataset as was used in the validation of NIRS model prediction was used to evaluate the Kriging model's prediction accuracy. PLS analysis was done between available P Kriging-predicted values and lab-measured values. The evaluation criteria for assessing the final prediction GIS-Kriging model are summarized in Table 5. The results as shown in Table 5 indicated that the coefficient of determination R2 were in worst for available P with value of 0.22 for Samawa and reasonable value of 0.65 for Rumetha. Compared with R2 results, other statistical measurements values were unsatisfactory predicted with low values of Q2 and high values of standard deviation and Root Mean Square Error as presented in Table 5 Based upon these evaluation criteria, the smaller the RMSE and Standard deviation values, the better the prediction ability of the model .

Table 4. Prediction results for soil available P by PLS model for Samawa location

PLS Model for (900-1000 nm)			
Sample No	Measured available P (mg kg^{-1} soil)	Predicted available P (mg kg^{-1} soil)	Residual
2	8.100	3.762	4.338
3	8.700	9.215	-0.515
4	9.300	8.719	0.581
6	8.400	14.555	-6.155
7	7.500	8.101	-0.601
8	6.400	4.276	2.124
11	7.100	5.860	1.240
12	2.100	7.658	-5.558
13	3.000	5.028	-2.028
14	3.000	4.620	-1.620
15	6.300	5.733	0.567
16	1.800	1.754	0.046
17	1.800	4.292	-2.492
18	10.400	5.296	5.104
19	1.500	0.359	1.141
21	14.800	12.717	2.083
23	14.000	11.246	2.754
25	13.000	14.499	-1.499
26	11.800	11.881	-0.081
27	14.200	12.497	1.703
28	13.600	11.367	2.233
30	8.700	10.667	-1.967
31	7.300	10.702	-3.402
32	7.800	11.654	-3.854
34	24.000	21.773	2.227
35	18.900	17.656	1.244
37	24.200	22.004	2.196
39	19.800	19.611	0.189

Table 5. Summary of validation of available P predicted by GIS-Ordinary Kriging

Location	Obs	R2	Q2	RMSE	Std
Rumetha	11	0.65	0.58	0.866	0.957
Samawa	11	0.22	0.17	3.023	3.342

To define the potential of prediction models, it is always important not to look at a single measurement. In this study, prediction capability of the Ordinary Kriging models for available P were generally poor in terms of all statistical evaluation parameters (Table 5). The available P predicted with both the NIRS-based models and GIS-Kriging models was compared to the laboratory- measured in the validation dataset. In term of cross-validation, coefficient of determination for validation was as much higher for NIRS-based models with R2v values of 0.75 and 0.79 for available P in Samawa and Rumetha, respectively. This statistically comparison is evident of the superiority of NIRS-based models over the GIS-Kriging models. At this point, the Vis-NIR method can be recommended for practical prediction of available P with sufficient goodness of model fit. A number of limitations of using GIS-Kriging for practical prediction of soil parameters have been identified by several previous studies.

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