COMPARISON OF AL P AND OLSEN P TEST IN CALCAREOUS SOILS IN CROATIA

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SUMMARY

The purpose of this article was to compare soil P extraction by sodium bicarbonate solution (Olsen P) and by ammonium lactate (AL P) in calcareous soils in Croatia and to create a model for predicting AL P values using the correlation of these soil tests and common soil analysis data in Croatia. Soil samples were collected, near Opuzen city, in the valley of the River Neretva, in 2005. The results of these studies confirmed significant correlation between soil P extracted by Olsen ($NaHCO_3$) and by ammonium lactate (AL P) solution in calcareous soils from the Neretva river valley. The developed model is useful for providing fertilizer recommendations based on AL P soil-test results from Croatian soils using existing ammonium lactate-extractable P calibration expecially for the calcareous soils in Croatia in the valley of the Neretva River.

Key-words: AL P, Olsen P, phosphorus, calcareous soil, model

INTRODUCTION

The common use of soil-fertility control data in Croatia includes properties such as soil pH, organic matter content and plant-available phosphorus (P) and potassium (K) extracted by ammonium lactate (AL) solution. These data are commonly used for fertilizer recommendations for both field vegetable (Lončarić et al., 2003) and arable crops (Vukadinović et al., 1996).

Also, the same soil data have been used on acid and calcareous soils as well as the same extractant. A suitable extractant should extract a proportionate fraction of plant-available P from soils differing in other properties; the procedure should work with reasonable accuracy and speed; and the determined soil test P value should be in correlation with crop growth response to P or P uptake (Kamprath and Watson, 1980). Acidic extractants have been found to be very effective in estimating available P in acidic soils but the same methods may not be appropriate for using on calcareous soils because of neutralization of the extractant acidity by soil carbonates (Indiati et al., 2002).

In Croatia, use of the acidic Egner–Riehm–Domingo (ammonium lactate) soil P test (Egner et al., 1960) as an extractant for P fertilizer recommendation has been commonly practiced (Lončarić et al., 2003; Vukadinović et al., 1996) but the Olsen method (ISO, 1994a) recently became the standardized soil test for P in Croatia. It is

generally accepted that acid extractants are more appropriate for acid soils and bicarbonate-containing reagents are more suitable for calcareous soils and the Olsen ($NaHCO_3$) extraction could be better choice for calcareous soils in Croatia, therefore for soils in valley of the Neretva River, near Opuzen city too.

Another approach to improve P fertilizer recommendations is modeling plant availability of soil phosphorus using empirical constants or soil P test data to describe the reaction of applied soluble P with the soil (Fixen and Grove, 1990). It has been proposed that soil properties such as pH, calcium carbonate content and soluble Ca can be included in models describing plant availability of soil P (Fixen and Grove, 1990). This could be very useful for specific soil type as extra salted soils with high carbonate and/or high dissolved salts content.

The AL method is the most commonly used method for determination of soil phosphorus content and the AL method results are used for fertilizer recommendations for both field vegetable and arable crops in Croatia. However, in certain conditions these data may be insufficiently precise, especially for calcareous soils. In such cases, phosphorus recommendations based on AL P test could

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be incorrect and crop response to fertilization could fail. So, the aim of this study was to compare the amounts of phosphorus extracted from the same soil samples by different AL and Olsen methods. Also, the existing regression models based on comparison of AL and Olsen methods was validated with the new data set and new model with additional data was developed.

MATERIAL AND METHODS

Soil samples were collected, near Opuzen city, in the valley of the River Neretva, south Croatia, in 2005. Sampled soils were hidromeliorated soils with specific chemical properties like high pH, high content of calcium carbonate and high content of total and dissolved salts. These soils are seriously influenced by salt water that comes from the near Adriatic Sea and flows into the River Neretva.

Soils from agricultural areas (86 ha) were sampled to a depth of 30 cm and 175 samples in total were collected, grouped according to preliminary pH analyses and prepared for analyses. Soil samples were analyzed at the Institut for Soil in Osijek and included methods commonly used for soil-fertility assessment in Croatia: soil pH_{KCl} and pH_{H2O}, soil organic matter content, and plant-available P using ammonium lactate acid extractant. The same samples were also analyzed using the Olsen soil test method for plant available P. The Olsen soil test has recently become accepted as a standard soil P test in Croatia according to the State Office for Standardization and Metrology. Also, according to pH, the same samples were analyzed for carbonate and dissolved salts content. This data set of 175 soil samples was used to create regression models using AL P soil test values as the dependent variable (AL P prediction model) and for validation of existing models already described by Popović, 2009.

The soil samples were prepared for physicochemical analyses according to the ISO 11464 procedure (ISO 1994b) by drying in a thermostatically controlled drying oven at a temperature of $40°$ C $\pm$ $2°C$. The determination of soil pH was made in 1:5 (v/v) suspensions of soil in water or in a 1 M KCl solution according to ISO 10390 (ISO 1994c). Soil organic matter was determined by determination of organic carbon (C) by sulphocromic oxidation as prescribed by ISO 14235 (ISO 1998). A correction factor of 1.724 was used to calculate organic matter from organic C. The carbonate content was determined by ISO 10693 (ISO 1995) and dissolved salts by ISO 14869-2 (ISO 2002). Extractable P was determined

by two tests: Olsen (Olsen P) and Egner–Riehm–Domingo (AL P). Olsen P was determined by sodium bicarbonate extractant according to ISO 11263 (ISO 1994a), and AL P by ammonium lactate–acetic acid extractant described by Egner et al. (1960). Analytical details of two soil P methods are described in Table 1.

Table 1. Comparison of extraction solution, time and soil–solution ratio for soil P tests

Tablica 1. Usporedba ekstrakcijskih otopina, vremena ekstrakcije i odnosa tlo-ekstraktant

Method – *Metoda*	Olsen P	AL P
Solution *Ekstrakcijska otopina*	0.5 M NaHCO$_3$	0.1 M lactic acid + 0.4 M CH$_3$COOH + 0.1 M NH$_4$OH
Solution pH *pH otopine*	8.5	3.75
Soil to Solution Ratio (w/v) *Odnos tlo – ekstraktanat*	1:20	1:20
Extraction Time *Vrijeme ekstrakcije*	30 min	120 min

Data processing and statistical analyses were accomplished with the StatSoft Statistical data analysis software system.

RESULTS AND DISCUSSION

Analytical results of 175 soil samples used in the regression model for AL P prediction ranged as follows: pH_{KCl} from 6.21 to 7.97, organic matter from 0.88 to 4.20%, ammonium lactate–extractable P (AL P) from 9.0 to 392.0 mg kg^{-1}, NaHCO$_3$ extractable P (Olsen P) from 15.5 to 263.5 mg kg^{-1}, carbonate content from 0,40 to 91,30 % and dissolved salts content from 0.01 to 6.02 % (Table 2). This result indicated that ,according to pH, soils samples were slightly acid to slightly alkaline, highly calcareous and highly salinised soil. Organic matter content were in wide range from 0.88 to 4.20 % and reason of these appearance is existing of specific moss strip, because the one part of soil surfaces in Neretva River valley are permanently flooded (Čolak, 1977). AL phosphorus content showed that most samples belong to group of poorly supplied with phosphorus (86 %), and only 11 samples (6 %) were good and 15 (8 %) samples were highly supplied with phosphorus. These results indicate high phosphorus recommendation doses and Olsen results were useful in precise interpretation of soil phosphorus status.

Table 2. Soil properties results for 175 samples (average, maximum and minimum)

Tablica 2. Kemijska svojstva analiziranih uzoraka tla (n=175, prosjek, maksimum minimum)

Samples *Uzorci*	pH_{KCl}	pH_{H2O}	Organic matter (%) *Humus (%)*	AL P (mg kg^{-1})	Olsen P (mg kg^{-1})	CaCO$_3$ (%)	Dissolved salts (%) *Otopljene soli (%)*
Minimum *Minimum*	6.21	6.38	0.88	9.0	15.5	0.40	0.01
Maximum *Maksimum*	7.97	8.30	4.20	392.0	263.5	91.30	6.02
Average *Prosjek*	7.36	7.64	2.60	105.7	70.6	39.43	2.80

All results for phosphorus in soil are expressed as mg P$_2$O$_5$ kg^{-1}/ *Svi rezultati za fosfor u tlu iskazani su kao mg P$_2$O$_5$ kg^{-1}*

So, the results of analyzed soil properties (Table 2) showed that average Olsen P was considerably lower (33,21 % on the average) than the average of AL P (Olsen P 70.6 mg P_2O_5 kg^{-1} and AL P 105.7 mg P_2O_5 kg^{-1}). Also, Olsen P was lower than AL P in all pH groups (Figure 1). The results of the same range were reported by other authors (Popović, 2009; Lončarić et al., 2006).
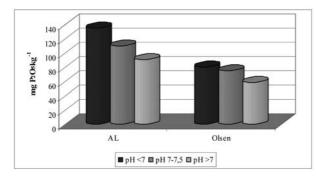

Figure 1. Average of AL P and Olsen P in three pH groups

Grafikon 1. Prosječno ekstrahirana količina fosfora Al i Olsen metodom u za tri pH grupe

The amounts of extracted P with the different soil P test correlated significantly (r = 0.87, n = 175), although the mechanism by which P was removed by each method may differ (Figure 2). It is known that the acid solution (AL) removes P preferentially by dissolution of sorbing components, and alkaline solution (Olsen) removes P principally by desorption (Indiati et al., 2002). These high correlation coefficients were confirmed by other investigations (Ivanov et al., 1992; Neyorud and Lischer, 2003; Lončarić et al, 2006; Popović, 2009).
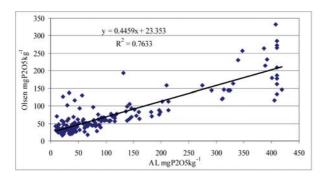

Figure 2. Correlation coefficients AL P and Olsen P tests (n=175)

Grafikon 2. Koeficijenti korelacije za AL P i Olsen P (n=175)

The objective of this study was to create a model for AL P prediction based on Olsen P test because in certain conditions, phosphorus recommendations based on AL P test and common soil data could be incorrect. Also, the existing models, developed for

the continental part of Croatia (Popović, 2009), were validated by the soil analysis results and the difference between predicted and analyzed AL P (model error) were on the average 51 mg P_2O_5 kg^{-1} (Figure 3). Only in cases when the model was fitted with values of calcium carbonate content, difference between predicted and analyzed AL P were higher (on the average 112 mg P_2O_5 kg^{-1}). At the same time carbonate content and model error showed statistically significant correlations suggesting that the alkalinity of the analyzed samples was not only consequence of the Ca ions. Also, the results showed that the carbonate content was in wide range from 0.4 to 91.30 % (Table 2) while the existing models equations include the carbonate content up to 30%. The similar problems were detected in some Hungarian soils and existing models based on AL P were corrected (Csato, 2002). Also, Nemet (2006) said that P supply limit values were determined for crops with high and low P requirements using the new AL P correction models.
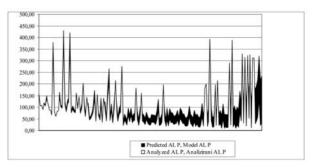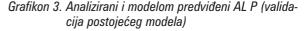

Figure 3. Analyzed and predicted AL P (validation of existing models)

Grafikon 3. Analizirani i modelom predviđeni AL P (validacija postojećeg modela)

For these reasons, new model based on Y = I + PX relation was developed for prediction of AL phosphorus where x presents analytical result of pH (S), Olsen P (P), carbonate content (B) and dissolved salt content (DS) in the soil samples of the River Neretva valley (Table 3). Based only on one soil properties (Olsen P) new model accurately predicted the amount of AL phosphorus with model error of 30.3 mg P_2O_5 kg^{-1} with statistical correlations 0,85. However, including soil pH_{KCl} in relations resulted in increment of the correlation coefficient from 0.85 to 0.92 and model error was lower (Table 3). At the same time, including more soil properties (P = Olsen P, S = pH_{KCl}, B = % $CaCO_3$, DS = dissolved salts) in relations resulted in further increment of the correlation coefficient up to r= 0.97 and the lowest model error (27.6 mg P_2O_5 kg^{-1}) was found when all soil properties were included in the regression (Table 3). This finding is quite reasonable because use of more parameters better describes the differences among analyzed soil samples. Evaluating carbonate content in relation to Olsen P and pH (PSB) specially dissolved salts content decreased model error (Table 3), as expected. Comparison of existing model with the new

Table 3. Regression parameters $(Y = ALP = Intercept + PX_1 + SX_2 + ... + KX_4)$ and model error (ME) in mg P_2O_5 kg^{-1} based on the $Y = I + PX$ relation

Tablica 3. Parametri regresijske jednadžbe (Y = ALP = Odsječak + PX$_1$ + SX$_2$ + ... + KX$_4$) i ostupanje modela u mg P$_2$O$_5$ kg^{-1}

Model Equation *Jednadžba modela*	r	Intercept *Odsječak*	Olsen P (P)	pH$_{KCl}$ (S)	CaCO$_3$ (B)	Disolved salts (DS) *Otopljene soli (DS)*	ME mgP$_2$O$_5$kg^{-1} *Odstupanje modela (mg P$_2$O$_5$kg-1*
	all samples						
P	0,85**	-1.347	1.607				30.3
PS	0,85**	-7.990	1.616	0.894			30.2
PSB	0,94**	-17.130	1.567	2.718	-0.099		28.3
PSBDS	0,94**	-17.822	1.639	2.873	-0.102	-0.826	27.6
	pH <7						
P	0,99**	-3.623	2.066				16.0
PS	0,99**	-22.245	2.117	2.718			15.4
PSB	0,99**	-30.198	2.098	4.053	-0.054		14.4
PSBDS	0,99**	-36.619	2.139	5.334	-0.109	-1.145	14.5
	pH 7-7.50						
P	0,89**	-0.571	1.393				33.4
PS	0,89**	-28.816	1.393	3.877			33.7
PSB	0,92**	-34.621	1.406	5.348	-0.120		29.8
PSBDS	0,92**	-33.121	1.374	5.133	-0.120	0.307	29.8
				pH > 7,50			
P	0,96**	-2.820	2.049				23.0
PS	0,96**	7.987	20.38	-1.409			23.1
PSB	0,97**	10.187	1.944	-1.00	-0.041		37.2
PSBDS	0,97**	15.384	1.991	-1.877	-0.055	-1.399	20.3

**Statistically very significant correlation coefficient, ** *Statistički vrlo značajno*

one showed that the model error on the average was decreased from 112 to 25.4 mg P$_2$O$_5$ kg^{-1} and the creation of the new model was justified. Also, the lowest model error means better phosphorus recommendations and cheaper crop productions.

The next step applied to improve the model was dividing samples into three groups according to soil pH using pH$_{KCl}$ value of 7 and 7.5 as a threshold category. The resulting correlation (r = 0.99) was greater for samples with pH$_{KCl}$ below 7 than for all samples (Table 3), although the number of samples was lower (n=11). All correlation coefficients for samples with pH between 7 and 7.50 and pH > 7.50 were higher than correlation coefficient for all samples (r= 0.89-0.92, r=0.96-0.97, respectivetly). Nevertheless, all the models in the "pH splitting" domain decreased model error with exception for model P and PS in 7-7.50 pH range (Table 3).

Sample domain splitting resulted in greater model accuracy with lower model error and improved correlation coefficients because of better equation suitability for a smaller range of soil properties. This was very useful for calcareous soils where difference between measured AL P and Olsen P could be high and phosphorus recommendations based on AL P test could be incorrect. Using the proper equations ensure the lower error in phosphorus recommendations dose and save the environment.

CONCLUSION

The results of these studies confirmed significant correlation between soil P extracted by Olsen (NaHCO$_3$) and by ammonium lactate (AL P) solution. Generally speaking, Olsen-P values were lower than AL-P values in the studied samples. The existing models, developed for the continental part of Croatia, were validated by the results obtained with soil analysis and the difference between predicted and analyzed AL P (model error) were on the average of 51 mg P$_2$O$_5$ kg^{-1}. This model was not precise enough in cases when the model was fitted with values of calcium carbonate content and different between predicted and analyzed AL P with the average of 112 mg P$_2$O$_5$ kg^{-1}, so the new model was developed. Comparison of existing model with the new one showed that the model error on the average was decreased from 112 to 25.4 mg P$_2$O$_5$ kg^{-1}. This model was very useful for calcareous soils in River Neretva valley where difference between measured AL P and Olsen P could be high and phosphorus recommendations based on AL P test could be incorrect. Using the proper equations ensures the smaller error in phosphorus recommendations dose and save the environment. In further investigations models should be upgraded with new data sets related to the physical properties of soils. Also, the correlation between Olsen and AL methods should be validated by conducting field trials, which will include the status of phosphorus in the soil, crop P removal and reaction of crops to phosphorus fertilizer based on different P tests.

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USPOREDBA AL I OLSEN PRISTUPAČNOGA FOSFORA U KARBONATNIM TLIMA HRVATSKE

SAŽETAK

Cilj ovoga rada bio je usporediti količine fosfora iz uzoraka tla različitim ekstraktivnim otopinama, otopinom natrij bikarbonata (Olsen P) i amonij laktata (AL P) u karbonatnim tlima Hrvatske te razviti model za predviđanje količine AL P na temelju dostupnih podataka o tlu. Uzorci su prikupljeni u dolini rijeke Neretve 2005. godine. Rezultati istraživanja potvrđuju prijašnjim istraživanjima utvrđenu statistički značajnu korelaciju između AL P I Oslen P metode. Razvijeni model predviđanja količine AL P na temelju analiziranih podataka o tlu može se uspješno primjenjivati za karbonatna tla u Republici Hrvatskoj, posebice u tlima u dolini rijeke Neretve.

Ključne riječi: AL P, Olsen P, fosfor, karbonatno tlo, model