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SIMPLE REGRESSION MODELS FOR PREDICTING SOIL HYDROLYTIC ACIDITY

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Abstract

Soil acidity is global factor limiting soil fertility of about 40% of the cultivable land which are acid. The common liming recommendations are based on different soil properties and therefore the calculation could differ according to available and used soil data. The aim of this paper was to determine the suitability of simple regression models for prediction soil hydrolytic acidity for precise liming recommendation using just actual (pH_{H2O}) and exchangeable soil pH (pH_{KCl}) and humus content as basic soil data. These agrochemical analyses were done on basic set of 2600 soil samples and on validation set of 375 soil samples. The simple regression model could be accurate enough using just actual soil pH only for soils with lower humus content. Model accuracy increases including more soil data in prediction model, starting from adding soil exchangeable pH and then including humus data. Because of possible high soil sample variance, the best simple models are model including both actual and exchangeable soil pH, and humus, but with different regression equation for each range of soil pH or/and for each range of humus content. These kinds of models are sensitive to soil cation exchange capacity, humus content, texture and soil acidity, indicating that model adjustment to soil types could result in increasing model accuracy. The model error correlate to humus content and soil acidity, and the lowest model error were about 14% in average for soil pH_{KCl} 4-5, and 16% for soil pH_{KCl} <4.

Keywords: Soil acidity, cation exchange capacity, liming, soil texture

Introduction:

Soil acidity is global factor limiting soil fertility, and acidification is a slow, continuous natural process resulting in acid soils being common in areas where soil development continued for long, geological periods of time and under climatic conditions which rainfall exceeds evapotranspiration (Rengel, 2002). Human activities may intensify and speed up the acidification process (Rastija, 2006), therefore about 40% of the cultivable land were acid. In Croatia, acid soils participate in 1.6 million ha (Bogunović et al., 1997), and Mesić et al. (2009) noted that 831.704 ha of agricultural land were acid. The widely accepted ameliorative measure for acid soils is liming with goal to increase soil pH. Radić (1989) published that the first written evidence of liming in Croatia is the report of unknown author (Anonymous, 1789), and Kovačević (1947) published handbook to promote liming. There are numerous data about liming effect on crop yields in the eastern Croatia (Kovacevic et al. 2003, 2008, 2009, Kovacevic and Rastija, 2010; Kovacevic et al.,2011). The influence of fertilization and liming on soil properties were investigated by numerous authors (Bowszys et al., 2005; Hughes et al., 2004; Rahman et al., 2002; Zhang et al., 2004; Lončarić et al., 2005; Lončarić et al., 2007; Rastija et al., 2008; Popović et al., 2010). The soil adsorption complex plays an important part in soil formation and in the evolution and genesis of soils. Optimal composition of soil adsorption complex for arable crop production is 65 – 85 % Ca, 5 – 15 % Mg, 2 – 3,5 % K and with total content of basic cations above 85 % with at least 70 % Ca (Karalić et al., 2011). The total content of basic cations is much lower than optimum in all soils with excessive acidity. Common agrotechnical measure to neutralize excessive acidity is liming with material containing Ca^{2+} and/or Mg^{2+} cations. The determination of precise amount of liming material needed to neutralize acidity is very important since too high amounts result in unnecessary excessive production costs, and may result in lower availability of plant nutrients (phosphorus, iron, zinc). On the other hand, too low amounts are not effective enough and require additional application, that is additional costs.

The common liming recommendations are based on different soil properties and therefore the calculation could differ according to available and used soil data (Lončarić et al. (2005). Liming recommendations are made according to soil pH values, hydrolytic acidity and base saturation, what requires laboratory results of hydrolytic acidity and cation exchange capacity. However, common agrochemical analyses in soil laboratories in Croatia includes analyses of soil pH, humus content and plant available phosphorus and potassium. Hence, usually there aren't available data of hydrolytic acidity and cation exchange capacity for liming recommendations, but soil pH and humus content are providing much more information about cation exchange capacity and base saturation if there are used by model for prediction hydrolytic acidity. The aim of this paper was to determine the suitability of simple regression models for prediction of soil hydrolytic acidity and, therefore for precise liming recommendation using just soil pH, humus content and simple regression model.

Material and methods:

Soil samples were collected in continental part (Pannonian basin) of Croatia. The topsoil layers of arable land were sampled using agrochemical probe on depth 0-30 cm after crop harvests (mainly after harvest of winter wheat, barley or rapeseed). During period 2010-2012 years 2600 soil samples were collected and analyzed as basic data set, and during year 2013 additional 375 soil samples were collected in a wider range of soil types as validation set.

The soil samples were prepared, dried (in a thermostatically controlled drying oven at a temperature of 40° C ± 2°C), ground and stored for physicochemical analyses according to the ISO 11464 procedure (ISO, 1994a). The determination of soil pH was made in 1:5 (v/v) suspensions of soil in water (pH_{H2O}) and in a 1 M KCl solution (pH_{KCl}) according to ISO 10390 (ISO, 1994b). Soil organic matter was determined by determination of organic carbon (C) by sulfochromic oxidation as prescribed by ISO 14235 (ISO, 1998). A correction factor of 1.724 was used to calculate organic matter from organic C. In addition, hydrolytic acidity was analyzed using soil extraction by Na-acetate. A statistical analysis of basic samples set (2600 samples) and validation set (375 samples) was performed by SAS Program for Windows (SAS Institute INC., Cary, NC, USA), and using Microsoft Excel 2010.

Results:

The actual soil acidity of 2600 analyzed samples (Table 1) used for model were in the range of 2.57 pH units (4.06 to 6.63), very similar to the range of exchangeable acidity 2.63 pH units (from 3.41 to 6, 04). Soil samples represented all classes of soil humus content, ranging from very poor (0.33% humus), to soil rich in humus content (5.41% humus), with a wide range of hydrolytic acidity of soils, from soils where liming is not recommended (0.42 cmol/kg) to soils were liming is necessary agrotechnical measure for soil conditioning (9.14 cmol/kg).

Table 1. The agrochemical properties of 2600 soil samples used for regression model

Soil properties (Mark)	pH_{H2O} (A)	pH_{KCl} (S)	pH_{Diff}. (A-S)	Humus (%) (H)	Hy (cmol/kg) (HA)
Minimum	4,06	3,41	0,52	0,33	0,42
Maksimum	6,63	6,04	1,79	5,41	9,14
Average	5,42	4,51	0,91	1,83	4,64

All developed regression models resulted in very significant correlations (Table 2) of predicted hydrolytic acidity and actual measured values. However, the lowest correlation was in cases when only one soil properties was incorporated into model, like pH_{H2O} as actual soil acidity (model A_{2600}) or pH_{KCl} as exchangeable soil acidity (model S_{2600}). The model errors (ME) in predicting hydrolytic soil acidity were in range 0 - 2,5 cmol/kg or in average 0,71 (15,3 %) for both, A_{2600} and S_{2600} models.

Using both soil data, actual and exchangeable soil acidity in the same model (model AS_{2600}) resulted in ME decreasing for 0,08 units and average ME was 0,63 (13,6 %). Such decreasing of ME was expected since using actual and exchangeable soil acidity present additional information about cation exchange capacity (CEC) of soil. Namely, since hydrolytic acidity correlate to sum of all acid cations on soil adsorption complex represented mainly by clay particle and organic humus colloids, the difference between actual and exchangeable soil acidity could be connected to percentage of clay and organic particels in soils. Moreover, additional information about CEC was certainly humus content, therefore using information about humus content in model ASH_{2600} (Table 2) resulted in further ME decreasing to 0,57 cmol/kg in average (12,3 %).

Table 2. Regression parameters (Y = Hydrolitic acidity = Intercept + AX1 + SX2 + HX3) and decrease of model error (ME) in cmol/kg based on the Y = I + AX relation

Model equation	r^2	Intercept	pH_{H2O} (A)	pH_{KCl} (S)	Humus (%) (H)	ME decrease
A_{2600}	0,646**	16,101	-2,11	-	-	0
S_{2600}	0,634**	14,208	-	-2,12	-	0,01
AS_{2600}	0,678**	15,593	-1,26	-0,91	-	0,08
ASH_{2600}	0,707**	15,546	-1,37	-0,89	+0,285	0,09

Still, the model sensitivity on humus content was rather low, since humus content difference of 4 % (1,01% vs. 5,01%) resulted in increasing predicted hydrolytic acidity only 1,14 cmol/kg (7,52 – 6,38), presuming no changes in soil pH:

15,546 – 1,37 × **4,57** (A) – 0,89 × **3,59** (S) + 0,285 × **1,01** (H) = **6,38** cmol/kg

15,546 – 1,37 × **4,57** (A) – 0,89 × **3,59** (S) + 0,285 × **5,01** (H) = **7,52** cmol/kg.

Therefore a new data set was used for model validation. These set includes 375 soil samples with similar ranges of soil pH (Table 1 and Table 3), but with higher differences between soil pH_{H2O} and pH_{KCl} ($pH_{H2O} – pH_{KCl} = pH_{Diff}$.), and with higher soil humus content (0,33-5,41 vs. 1,01-6,41, or in average 1,83 vs. 2,26) and higher hydrolytic acidity (up to 9,14 vs. up to 21,04).

Table 3. The chemical properties of 375 soil samples used for model validation

Soil properties (Mark)	pH_{H2O} (A)	pH_{KCl} (S)	pH_{Diff}. (A-S)	Humus (%) (H)	Hy (cmol/kg) (HA)
Minimum	4,39	3,70	0,55	1,01	0,11
Maksimum	7,00	6,02	1,79	6,41	21,04
Average	5,89	4,65	1,24	2,26	4,80

The values of hydrolytic acidity (Hy) predicted by ASH_{2600} model were in range 1,22 – 6,95 cmol/kg and measured values were in quite wider range 0,11 – 21,04. The model error was in average 1,11 cmol/kg, or 25,8%, what is significantly higher error than for basic data set with 2600 soil samples. The reason for so high ME was higher humus content in new data set than in basic data set, and as higher humus content was, the higher was ME (humus <2, 2-3, 3-4, >4 for ME 23, 22, 35 and 51%, respectively).

Also, the validation data set has higher standard error (5-fold), standard deviation (2-fold) and sample variance (3,5-fold) that basic data set for humus, and similar were data set comparisson for pH difference (pH_{H2O}-pH_{KCl}) and measured hydrolytic acidity (Hy), but not for pH_{H2O} and pH_{KCl} (Table 4).

Table 4. Standard error, standard deviation and sample variance for basic and validation data sets

Descriptive statistic	basic data set (2600 samples)			validation data set (375 samples)		
	humus	pH_{H2O}-pH_{KCl}	Hy	humus	pH_{H2O}-pH_{KCl}	Hy
standard error	0,0090	0,0033	0,026	0,0429	0,0121	0,128
standard deviation	0,4577	0,1662	1,320	0,8315	0,2352	2,483
sample variance	0,2095	0,0276	1,742	0,6913	0,0553	6,168

Considering all differences of data sets, model ASH_{2600} wasn't precise enough for prediction hydrolytic acidity in soils with higher hydrolytic acidity (Graph 1, Figures A and B) or higher humus content, or basically in all data sets with higher deviation or variance. Therefore new regression models were calculated using validation data set (Table 5).

The highest ME (30,9 and 27,6 %) was in models which include only pH_{H2O} (A_{375} model) or pH_{KCl} (S_{375} model), but S_{375} model reduced ME 8,9% comparing A_{375} model. Next model improvement was including both pH data (AS_{375} model) with ME decreasing 11,2% comparing to A_{375} model. Finally, the best model for validation set was ASH_{375} model with all data (pH_{H2O}, pH_{KCl} and humus) with decreasing model error 33,3%. Model error was 20,9 % in average, with higher error for samples with higher humus content (>4 and 3-4%, ME was 22,9 and 25,5%, respectively), but correlation of predicted and measured hydrolytic acidity was very significant (Graph 1, Figure C).

Table 5. Regression parameters (Y = Hydrolitic acidity = Intercept + AX1 + SX2 + HX3) after validation and decrease of model error (ME) based on the Y = I + AX relation

Model equation	Intercept	pH_{H2O} (A)	pH_{KCl} (S)	Humus (%) (H)	ME decrease	ME decrease (%)
A_{375}	20,356	-2,64	-	-	0	0
S_{375}	18,156	-	-2,87	-	0,12	8,9
AS_{375}	19,193	-0,61	-2,32	-	0,15	11,2
ASH_{375}	16,690	-0,47	-2,83	+1,786	0,45	33,3

However, further ME decreasing and model improvement, were made by splitting validation set into 4 groups according to soil pH_{KCl} (Table 6). Model errors in all 4 groups were decreased using ASH_{375pH} model comparing to ASH_{375} model. ME decreasing was 11,1% up to 44,2% (Table 6). This approach reduced ME for 375 samples in validation set on 16,7 % with lowest error with pH_{KCl} 4-5 (ME 14,2%) and pH_{KCl} < 4 (16,7%), and correlation of predicted and measured Hy was higher than for model ASH_{375} (Graph 1, Figure D).

Table 6. Regression parameters of ASH_{375pH} model after splitting samples into 5 groups according to soil pH

Model equation pH_{KCl} range	Intercept	pH_{H2O} (A)	pH_{KCl} (S)	Humus (%) (H)	ME decrease	ME decrease (%)
< 4,0	57,583	0,493	-15,232	+3,158	0,40	21,1
4,0-5,0	15,975	0,082	-3,366	+1,621	0,08	11,1
5,0-5,5	9,281	1,485	-2,969	+0,120	0,46	44,2
> 5,5	15,067	-0,885	-1,424	+0,095	0,23	30,7

The ASH_{375pH} model sensitivity on humus content is quite high and pH sensitive, since humus content difference of 4 % (1,01% vs. 5,01%) resulted in increasing predicted hydrolytic acidity for example 12,63 cmol/kg (20,97 – 8,34), presuming no changes in soil pH and if soil was very acid (pH_{KCl} < 4):

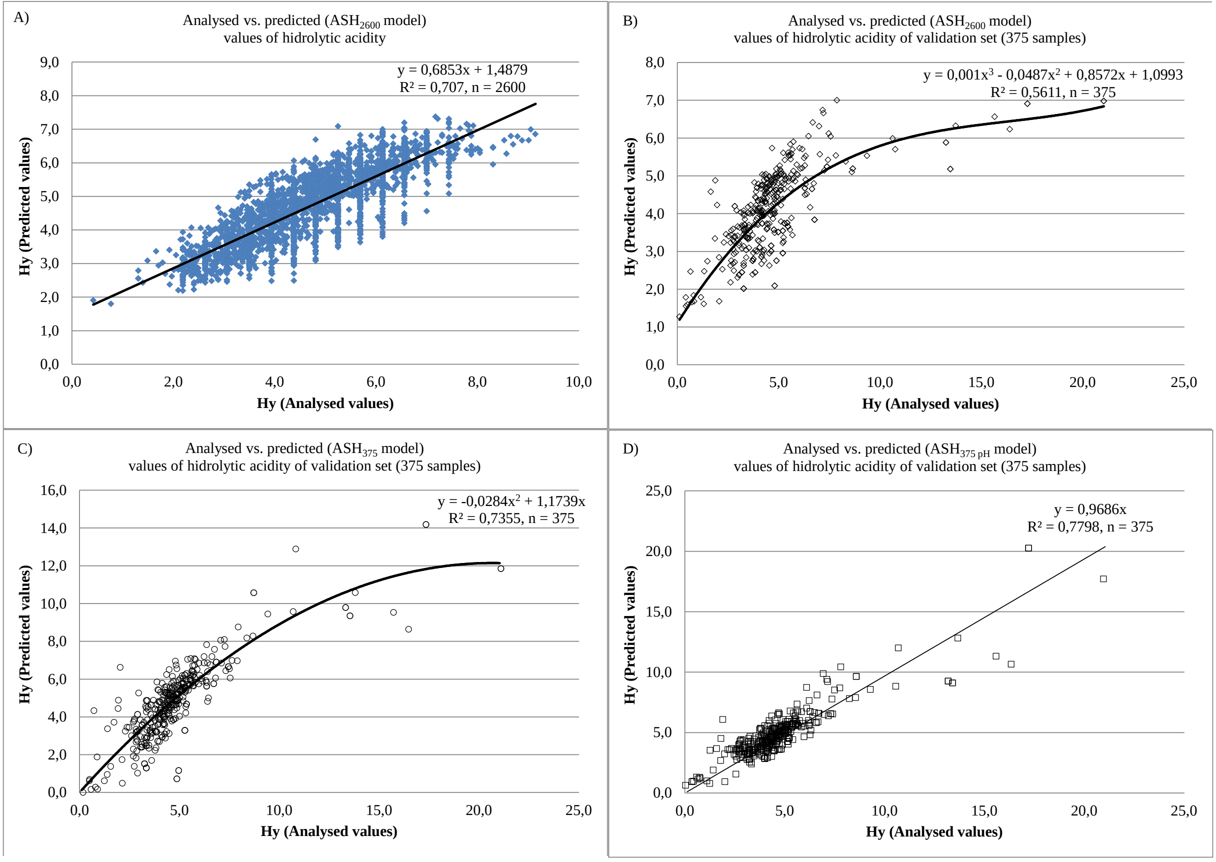
57,583 + 0,493 × **4,57** (A) – 15,232 × **3,59** (S) + 3,158 × **1,01** (H) = **8,34** cmol/kg

57,583 + 0,493 × **4,57** (A) – 15,232 × **3,59** (S) + 3,158 × **5,01** (H) = **20,97** cmol/kg.

Simultaneously, if soil was slightly acid (pH_{KCl} > 5), humus content difference of 4 % will resulted in increasing predicted hydrolytic acidity for example only 0,48 cmol/kg (3,23 – 2,75).

$$9{,}281 + 1{,}485 \times \mathbf{5{,}70}\ (A) - 2{,}969 \times \mathbf{5{,}09}\ (S) + 0{,}120 \times \mathbf{1{,}01}\ (H) = \mathbf{2{,}75}\ \text{cmol/kg}$$

$$9{,}281 + 1{,}485 \times \mathbf{5{,}70}\ (A) - 2{,}969 \times \mathbf{5{,}09}\ (S) + 0{,}120 \times \mathbf{5{,}01}\ (H) = \mathbf{3{,}23}\ \text{cmol/kg.}$$



Graph 1. Regression of measured (analytical) and predicted (model) hydrolytic acidity for: A) prediction model ASH_{2600} for 2600 samples, B) the same ASH_{2600} model for new validation set of 375 samples, C) corrected prediction model ASH_{375} after model validation, D) prediction model ASH_{375} corrected for four different class of soil pH

Conclusion:

Basic agrochemical soil data (actual and exchangeable soil pH, and humus) could be enough for prediction of soil hydrolytic acidity using simple regression model. The simple regression model could be accurate enough using just actual soil pH only for soils with lower humus content. Model accuracy increases including more soil data in prediction model, starting from adding soil exchangeable pH and then including humus data. Because of possible high soil sample variance, the best simple models are model including actual and exchangeable soil pH, and humus, but with different regression equation for each range of soil pH or/and for each range of humus content. These kinds of models are sensitive to soil cation exchange capacity, humus content, texture and soil acidity, indicating that model adjustment to soil types could result in increasing model accuracy. The model error correlate to humus content and soil acidity, and the lowest model error were about 14% in average for soil pH_{KCl} 4-5, and 16% for soil pH_{KCl} <4.

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