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REMAINING PHOSPHORUS ESTIMATED BY PEDOTRANSFER FUNCTION⁽¹⁾

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SUMMARY

Although the determination of remaining phosphorus (Prem) is simple, accurate values could also be estimated with a pedotransfer function (PTF) aiming at the additional use of soil analysis data and/or Prem replacement by an even simpler determination. The purpose of this paper was to develop a pedotransfer function to estimate Prem values of soils of the State of São Paulo based on properties with easier or routine laboratory determination. A pedotransfer function was developed by artificial neural networks (ANN) from a database of Prem values, pH values measured in 1 mol L⁻¹ NaF solution (pH NaF) and soil chemical and physical properties of samples collected during soil classification activities carried out in the State of São Paulo by the Agronomic Institute of Campinas (IAC). Furthermore, a pedotransfer function was developed by regressing Prem values against the same predictor variables of the ANN-based PTF. Results showed that Prem values can be calculated more accurately with the ANN-based pedotransfer function with the input variables pH NaF values along with the sum of exchangeable bases (SB) and the exchangeable aluminum (Al³⁺) soil content. In addition, the accuracy of the Prem estimates by ANN-based PTF were more sensitive to increases in the experimental database size. Although the database used in this study was not comprehensive enough for the establishment of a definitive pedotransfer function for Prem estimation, results indicated the inclusion of Prem and pH NaF measurements among the soil testing evaluations as promising in order to provide a greater database for the development of an ANN-based pedotransfer function for accurate Prem estimates from pH NaF, SB, and Al³⁺ values.

Index terms: Artificial neural networks, Modeling, Multiple regression analysis.

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RESUMO: ESTIMATIVA DO FÓSFORO REMANESCENTE POR FUNÇÃO DE PEDOTRANSFERÊNCIA

Embora de simples determinação, valores exatos de fósforo remanescente (Prem) poderiam ser estimados com uma função de pedotransferência visando ao aproveitamento adicional de resultados de análises de avaliação da fertilidade do solo ou sua substituição por uma determinação ainda mais simples. O objetivo do presente trabalho foi desenvolver uma função de pedotransferência para estimar o Prem em amostras de solos do Estado de São Paulo a partir de atributos de mais fácil ou rotineira determinação laboratorial. Uma função de pedotransferência foi desenvolvida por meio de redes neurais artificiais a partir de um conjunto de dados formado por valores de Prem, de pH determinado em solução de NaF 1 mol L⁻¹ (pH NaF) e de outros atributos de amostras coletadas durante as atividades de classificação de solo realizadas no Estado de São Paulo pelo Instituto Agrônomo de Campinas. Adicionalmente, uma função de pedotransferência foi ajustada por meio de regressão linear múltipla, considerando-se o Prem como variável dependente das mesmas variáveis de entrada da função de pedotransferência desenvolvida via redes neurais artificiais. Os resultados indicaram que valores mais exatos de Prem podem ser estimados pela função de pedotransferência baseada em redes neurais artificiais tendo como variáveis de entrada valores de pH NaF, da soma de bases trocáveis (SB) e do teor de alumínio trocável (Al³⁺). Adicionalmente, observou-se que a exatidão das estimativas de Prem fornecidas pela rede neural artificial foi mais sensível ao aumento do número de dados experimentais utilizados para o desenvolvimento da função de pedotransferência. Apesar de o conjunto de dados utilizado não ser suficientemente abrangente para o estabelecimento de uma função de pedotransferência definitiva para estimativas de Prem, os resultados sugerem como promissora a inclusão de medidas de Prem e de pH NaF entre as análises de avaliação da fertilidade do solo com vistas à formação de um maior banco de dados, que permita o desenvolvimento de uma função de pedotransferência baseada em redes neurais artificiais para o cálculo de valores suficientemente exatos de Prem a partir de valores de pH NaF, SB e Al³⁺.

Termos de indexação: regressão linear múltipla, modelagem, redes neurais artificiais.

INTRODUCTION

The remaining phosphorus (Prem) refers to the P concentration that remains in solution after shaking a soil sample for a certain period with a solution with known initial P concentration. Since the soil adsorbs part or almost all added P, the Prem values are lower than the initial P concentration. This index was proposed by Bache & Williams (1971) to estimate the P adsorption capacity based on only one measurement and similarly to the adsorption isotherm method. The reference method for Prem measurement consists of shaking 2.5 g of air-dried fine earth (ADFE) for one hour with 25 mL of 0.01 mol L⁻¹ CaCl₂ containing 60 mg L⁻¹ P, filtering and/or centrifuging the soil suspension and determining the P concentration in the clear solution (Alvarez V. et al., 2000).

Although unlike anions such as nitrate that are adsorbed through electrostatic attraction, phosphate is mainly adsorbed by exchange with surface –OH groups of minerals such as kaolinite, gibbsite, and goethite (Mott, 1981), it can be stated that soils with low Prem values tend to have higher levels of positive surface charges. In general, minerals such as gibbsite and goethite are more abundant in highly weathered

soils; since these minerals have surface –OH groups that can be changed with the phosphate anion and high values of point of zero charge, not only P adsorption is high in gibbsite and goethite-rich soils but also the number of positive surface charges, even under moderate acidity. Therefore, one can infer that soils with low Prem values can adsorb greater amounts of anions through both inner- and outer-sphere complexations.

The advantage of using Prem as anion-adsorption index is associated to its simpler and faster determination and the greater Prem dependency on the soil mineralogy than the clay content. The values of Prem and anion exchange capacity (AEC) in two soils with identical contents of clay-sized particles and same pH value measured in 0.01 mol L⁻¹ CaCl₂ can therefore differ considerably. Although the organic matter can delay P adsorption (Afif et al., 1995), in general, most tropical soils have low organic C contents and it can therefore be considered that the Prem values are essentially defined by the mineralogical compositions of the silt and clay fractions.

Phosphorus adsorption is related to the agronomic efficiency of P-bearing fertilizers (Novais & Smyth, 1999); for this reason, the amount of P fertilizer applied

to a soil to ensure an adequate P nutrition of a crop must be greater in soils with higher gibbsite and goethite amounts; therefore, it is possible that the values of phosphate buffering capacity differ in two soils with the same clay contents. Likewise, tropical soils with low organic matter contents and identical clay contents can also differ in the acid buffering capacity due to mineralogical differences. The existence of soils with equal clay contents but different mineralogies makes Prem more adequate than the clay content as an auxiliary attribute for the interpretation of chemical soil analysis results in relation to the availability of some plant nutrients such as phosphorus, sulfur, and zinc, as well as for the calculation of the soil lime requirement as suggested by Alvarez V. et al. (2000).

In general, the soil P adsorption capacity is evaluated by the adsorption isotherm method; this approach is however rather time-consuming for routine chemical analyses in soil testing laboratories. Besides Prem, another possibility of evaluating the soil P adsorption consists of the soil pH values measured in 1 mol L⁻¹ NaF (pH NaF). This measurement was promising for the indirect evaluation of P adsorption in Australian soils (Singh & Gilkes, 1991; Gilkes & Hughes, 1994; Bolland et al., 1996). Afterwards, Alves & Lavoretti (2004) verified that higher pH NaF values are observed in soils with greater gibbsite contents, which partially explains the inverse correlation between Prem and pH NaF values. This consistent correlation and the simpler measurement could suggest the use of pH NaF instead of Prem as ancillary variable for the recommendation of P, S and lime requirements. However, the logarithmic scale makes the capacity of differentiating soils of pH NaF far lower than that of Prem, i.e., two soils having different Prem values can present similar pH NaF ones. Nevertheless, Alves & Lavoretti (2006) observed that the soil clay content could be replaced by pH NaF as predictive variable of Prem in multiple regression models.

Although the laboratory determination of Prem is quite simple, the possibility of estimating it with sufficient accuracy by other variables of routine or even simpler determination can make this determination quicker and cheaper. Such estimates can be obtained by so-called pedotransfer functions, which consist of equations or sets of equations that allow for estimating the value of a soil property from others with simpler and faster determination (Budiman et al., 2003). Usually, pedotransfer functions are developed from multiple linear regression models; however, more recently, these functions can be developed by using the artificial neural networks (ANN) approach, which are capable of identifying non-explicit relationships among the variables of a dataset (Tafner et al., 1996; Haykin, 2001; Braga, et al., 2007).

The purpose of this study was to develop pedotransfer functions by artificial neural networks

and multiple linear regression for the calculation of remaining P values for soils in the State of São Paulo.

MATERIAL AND METHODS

The 89 soil samples used in this research were gotten from the collection formed along the soil classification activities carried out by the Agronomic Institute of Campinas (IAC) on the São Paulo State. These samples were collected from profiles and used as air-dried fine earth for Prem determinations according to the reference method proposed by Alvarez V. et al. (2000). Furthermore, pH measurements were conducted after shaking 1 g of soil for 1 h with 40 mL of 1 mol L⁻¹ NaF (Bolland et al., 1996). The other data characterized were the soil contents of clay-sized particles, of oxidizable C, and of exchangeable Al, Ca, Mg, and K. Additionally, the total acidity (H + Al), the pH values measured in water and in 1 mol L⁻¹ KCl and the soil contents of Fe, Al, and Si extractable with 9 mol L⁻¹ H₂SO₄ under boiling were also considered in the dataset used for the pedotransfer function development. Except for Prem and pH NaF, the values of the above-mentioned properties were provided by IAC; some of them had been cited in publications of Valladares et al. (1971), Oliveira et al. (1976), Oliveira et al. (1979), Oliveira & Prado (1984; 1987), Prado et al. (1999), Bertolani et al. (2000), Menk & Coelho (2000), Bognola et al. (2003), and Prado et al. (2003).

The artificial neural network-based pedotransfer function was developed with the option neural network toolbox of the MATLAB software. The applied network consisted of the perceptron multilayer whose topology was defined through successive tests. The dataset was normalized in the interval [0;1] and split in test subsets consisting of 50, 70, and 90 % of the total data. Several trainings and validations were carried out in order to find the best combination of input variables and the best network topology. Basically, the ANN was developed based on the so-called supervised training (Braga et al., 2007), a procedure in which the inputs and outputs are provided so as to fit the network parameters. The linear, the hyperbolic tangent sigmoid and the logistic sigmoid activation functions were tested, whereas the learning algorithms consisted of variations of backpropagation one (Levenberg-Marquardt, resilient backpropagation, and scaled conjugate gradient). The conclusion criterion used in the network test was the early stopping whereas the network performance was evaluated by the mean square error in the test stage and by the sum of the squared differences between measured and estimated Prem values by the pedotransfer function.

A second pedotransfer function was developed by multiple linear regression analysis with the software Statistical Analysis System – SAS 9.1 with the

objective of establishing a functional relationship between Prem and the input variables that gave rise to the best artificial neural network. Similarly to the ANN, the regression equations were fitted with 50, 70 and 90 % of the total data and tested with the respective complimentary validation datasets.

The predictive capacities of the two pedotransfer functions were compared based on the fitting of the equation $Prem_e = a + b Prem_m$ and by the calculation of the sum of the squared differences between the estimated ($Prem_e$) and the respective measured remaining phosphorus ($Prem_m$) values.

RESULTS AND DISCUSSION

The studied samples derived from different soil orders, mainly Latosols and Argisols (Embrapa, 2006) (Table 1). Most soils were clayey or very clayey (clay > 350 g kg⁻¹), strongly (4.3 < pH H₂O < 5.3) to moderately acidic (5.4 < pH H₂O < 6.5) (Embrapa, 2006) with differing weathering degrees (0.21 < Ki < 4.98). Although 73 % of the samples can be considered highly weathered (Ki < 2.0), only 17 % can be considered oxidic (Kr < 0.75) (Embrapa, 2006). The pH NaF values ranged from 8.3 to 10.5 and were inversely correlated with the Kr index ($r = 0.51^{**}$), indicating an increasing trend of pH NaF when the samples become less kaolinitic (Alves & Lavorenti, 2004). Base saturation was low ($V < 50$ %) in about 75 % of the samples and the clay fraction activity low ($T < 27$ cmol_c kg⁻¹) (Embrapa, 2006) in almost all samples and the net surface charge negative ($\Delta pH < 0$) (Mekaru & Uehara, 1972). The exchangeable Al³⁺ contents ranged from 0 to 5 cmol_c kg⁻¹ whereas the respective values of Al saturation and total acidity (H + Al) ranged from 0 to 98.5 % and from 0 to 15.4 cmol_c kg⁻¹. The sum of bases was directly correlated with the Ki index ($r = 0.53^{**}$), in agreement with the loss of exchangeable bases that occurs as weathering advances.

The Prem values ranged from 0 to 47.3 mg L⁻¹ and although being inversely correlated with the soil clay content ($r = -0.67^{**}$), were better correlated with pH NaF ($r = -0.92^{**}$). This higher correlation can be ascribed to the inclusion in the pH NaF values of OH⁻ ions displaced from the mineral surfaces by the F⁻ ion (Perrott et al., 1976). Considering that the released OH⁻ surface groups are those that would be exchanged with phosphate ions in the adsorption process, higher pH NaF imply in lower Prem values.

The ANN-based pedotransfer function indicated that Prem values could be estimated from pH NaF values along with the correspondent soil contents of exchangeable Al³⁺ and of the sum of exchangeable bases (SB) ($SB = Ca^{2+} + Mg^{2+} + K^{+}$). The best developed network used the logistic sigmoid model as activation

function and the resilient backpropagation test algorithm with 21 cycles. The network topology was [3 14 1], corresponding to 3 neurons in the activation layer, 14 neurons in the intermediary and one neuron in the output layer.

Despite the high correlation of pH NaF with Prem, the latter was not correlated with Al³⁺ nor with SB values. On the other hand, Falcão & Silva (2004) observed that the soil maximum P adsorption capacity was directly correlated with the soil content of exchangeable Al and inversely correlated with base saturation in Amazonian alic soils. These correlations are possibly associated to the soil pH effect on P adsorption since soils rich in exchangeable Al are necessarily acidic, which favors P adsorption; likewise, pH values in soils with higher base sum and/or base saturation are normally higher, which, in turn, hampers P adsorption (Novais & Smyth, 1999). The fact that the variables SB and Al³⁺ are not correlated with Prem but nevertheless constitute, along with pH NaF, the best set of Prem predictive variables in the ANN-based pedotransfer function can be ascribed to the ANN capability of extracting non-explicit information from the dataset as well as solving non-linear problems.

The pedotransfer function developed by multiple regression analysis was fitted from the variables pH NaF, SB, and Al³⁺ considering the three subsets of adjustment (50, 70, and 90 % of total data) and validation (50, 30, and 10 % of total data). In all cases, the estimate of Al³⁺ coefficient was statistically zero ($p > t > 5$ %); for the adjustment subset with 90 % of data, only the pH NaF coefficient was statistically not zero (Table 2).

Although for both pedotransfer functions the accuracy of the Prem estimates increased with the augment of the dataset used for training or fitting (Figure 1), it was observed that this effect was greater for the ANN-based pedotransfer function. The summarized results (Table 3) show a reduction of almost 10 times in the sum of squared differences between the estimated and the respective Prem values of the validation subset when the network training subset consisted of 90 % instead of 50 % of the total data. For this same variation in the data subsets used to fit the multiple linear regression model, the sum of squared differences between estimated and measured Prem values was reduced by about six times.

The superior performance of artificial neural networks can be ascribed to their capacity of detecting relationships between input and output variables, which in most cases are either unknown or unnoticed. Another probable reason can be associated to the presence of distorted or incorrect information in the dataset. The artificial neural networks are less vulnerable to approximated data and/or to the presence of distorted data since they are able to manipulate approximated or even inaccurate information, a rather unusual feature in other mathematical models.

Table 1. Classification, localization and summarized properties of the studied soils

Sample	Profile ⁽¹⁾	Depth	Classification ⁽²⁾	Localization	Prem ⁽³⁾	Clay ⁽⁴⁾	$\frac{\text{pH}^{(5)}}{\text{H}_2\text{O KCl NaF}}$	$\Delta\text{pH}^{(6)}$	$\text{Ca}^{3+ (7)}$	$\text{Mg}^{2+ (8)}$	$\text{K}^{+ (9)}$	$\text{Al}^{3+ (10)}$	$\text{H}+\text{Al}^{(11)}$	$\text{SB}^{(12)}$	$\text{T}^{(13)}$	$\text{V}^{(14)}$	$\text{SiO}_2^{(15)}$	$\text{Al}_2\text{O}_3^{(16)}$	$\text{Fe}_2\text{O}_3^{(17)}$	$\text{K}^{(18)}$	
		cm			mg L ⁻¹	g kg ⁻¹						cmol kg ⁻¹				%		g kg ⁻¹		—mol mol ⁻¹ —	
1	980	62-80	nd.	Jundiáí	18.5	428	5.4	4.7	9.6	-0.7	0.2	0.0	0.1	2.2	4.5	0.2	4.7	202.0	204.0	61.0	1.68
2	981	74-200	LVA	Jundiáí	4.9	417	4.9	5.1	10.0	0.2	0.2	0.0	0.1	0.0	2.0	0.2	2.2	126.0	119.0	65.0	1.80
3	983	53-90	R	Jundiáí	25.7	285	5.5	4.6	9.0	-0.9	0.1	1.5	0.3	3.1	5.5	1.8	7.2	227.0	168.0	58.0	2.30
4	984	85-200	PVA	Jundiáí	20.0	407	5.0	4.8	9.5	-0.2	0.7	0.1	0.8	3.4	3.4	1.4	4.8	166.0	156.0	41.0	1.81
5	985	68-77	PVA	Jundiáí	21.2	405	5.3	4.9	9.5	-0.4	0.5	0.3	0.2	0.6	2.8	1.0	3.8	202.0	192.0	65.0	1.79
6	987	37-60	R	Jundiáí	21.6	245	4.9	4.3	9.3	-0.6	0.3	0.2	0.2	2.8	5.4	0.7	6.0	151.0	139.0	48.0	1.85
7	990	120-170	LVA	Jundiáí	7.3	478	5.0	4.4	10.2	-0.6	0.0	0.2	0.0	1.3	6.0	0.2	6.2	105.0	68.0	68.0	2.63
8	1011	15-35	R	Nazaré Paulista	17.2	351	4.9	4.1	9.9	-0.8	0.5	0.1	0.2	2.0	8.0	0.7	8.7	104.7	215.5	96.7	0.83
9	1021	30-60	R	Socorro	14.0	440	6.5	5.1	9.9	-1.4	7.3	0.3	0.3	0.0	7.1	7.8	14.9	193.6	217.5	93.8	1.51
10	1026	36-59	G	Socorro	36.6	180	5.7	4.7	9.0	-1.0	3.3	0.4	0.1	0.0	6.5	3.8	10.3	96.8	107.1	37.1	1.54
11	1029	20-35	PVA	Socorro	37.1	320	5.5	4.6	9.1	-0.9	1.9	0.2	0.3	0.0	3.1	2.4	5.5	167.0	160.6	51.5	1.77
12	1030	40-61	PVA	Socorro	20.3	420	5.1	4.2	9.7	-0.9	0.6	0.1	0.1	1.9	5.9	0.7	6.6	111.1	193.6	198.6	1.66
13	1031	100-200	LVA	Nazaré Paulista	0.7	595	5.0	4.1	10.3	-0.9	0.0	0.1	0.1	0.0	4.4	0.2	4.6	188.0	279.0	88.0	1.15
14	1032	60-76	-	Nazaré Paulista	21.3	320	4.7	4.1	9.7	-0.6	0.0	0.0	0.0	2.0	9.5	0.1	9.6	165.0	174.0	43.0	1.61
15	1039	45-78	P	Nazaré Paulista	7.9	620	6.0	5.2	10.0	-0.8	1.1	0.3	0.0	0.0	2.4	1.4	3.8	228.0	294.0	72.0	1.32
16	1044	38-67	PVA	Socorro	9.5	535	5.6	5.4	9.9	-0.2	2.2	0.2	0.0	0.0	3.4	2.4	5.8	217.8	251.9	59.5	1.47
17	1055	26-44	PVA	Nazaré Paulista	15.3	440	4.9	3.9	9.7	-1.0	0.2	0.1	0.1	2.3	5.5	0.4	5.9	174.2	197.9	41.7	1.50
18	1056	16-46	P	Nazaré Paulista	17.8	410	4.6	3.7	9.4	-0.9	0.2	0.1	0.1	3.0	6.0	0.3	6.2	215.0	215.0	52.0	1.75
19	1062	25-70	PVA	Nazaré Paulista	4.6	805	5.3	4.1	10.3	-1.2	2.0	0.6	0.2	5.0	15.4	2.8	18.2	358.4	328.4	35.5	1.86
20	1064	62-100	PA	Nazaré Paulista	21.9	455	5.1	4.7	9.5	-0.4	0.5	0.2	0.0	1.4	4.4	0.7	5.1	163.8	220.5	96.0	1.26
21	1070	60-92	LV	un.	1.1	745	4.5	4.3	10.5	-0.2	0.1	0.0	0.1	0.0	1.1	8.7	0.1	236.5	319.8	109.7	1.26
22	1071	80-130	LV	un.	5.6	660	4.6	4.0	10.2	-0.6	0.1	0.0	0.0	1.8	10.2	0.1	10.3	172.8	238.9	163.4	1.23
23	1072	38-60	NV	un.	15.8	660	5.5	5.0	9.7	-0.5	4.0	0.8	0.1	0.0	2.6	4.8	7.4	204.8	261.1	200.0	1.33
24	1073	45-105	LV	un.	1.3	680	4.5	4.2	10.5	-0.3	0.0	0.0	0.1	1.1	9.1	0.1	9.1	197.1	265.6	172.6	1.26
25	1101	78-97	LV	Monte Alto	0.0	490	6.1	6.9	10.4	0.8	2.0	0.4	0.0	0.0	4.3	2.4	6.6	110.1	273.4	228.6	0.68
26	1107	0-140	LV	Monte Alto	3.7	430	5.2	4.7	10.2	-0.5	1.8	0.7	0.1	0.0	5.8	2.6	8.4	170.0	261.6	328.0	1.10
27	1109	120-150	LV	Monte Alto	0.0	550	6.6	6.4	10.3	-0.2	1.1	0.2	0.0	0.0	2.2	1.3	3.5	120.1	290.7	285.1	0.70
28	1139	100-150	nd.	un.	13.5	340	5.1	4.3	9.7	-0.8	0.1	0.0	0.0	0.7	2.3	0.1	2.4	107.0	127.0	39.0	1.43
29	1143	90-117	LA	Itararé	11.4	340	5.5	4.3	10.0	-1.2	0.1	0.0	0.0	0.6	4.0	0.1	4.1	66.0	116.9	21.0	0.96
30	1144	150-180	LA	Itararé	4.7	380	5.5	4.7	10.2	-0.8	0.1	0.0	0.0	0.1	3.8	0.1	3.9	45.6	134.7	38.5	0.58
31	1145	0-120	FF	Itararé	15.1	310	4.8	3.9	9.4	-0.9	0.1	0.1	0.1	2.8	11.3	0.3	11.6	56.2	106.6	35.5	0.90
32	1146	50-70	CX	Itararé	11.7	270	4.8	4.2	9.9	-0.6	0.1	0.0	0.0	1.0	5.1	0.1	5.2	62.8	108.0	27.0	0.99
33	1148	105-160	LA	Itararé	6.5	290	4.9	4.4	10.2	-0.5	0.1	0.0	0.0	0.5	3.1	0.1	3.2	138.0	108.0	27.0	0.68
34	1149	140-170	LA	Itararé	0.4	430	4.8	4.6	10.4	-0.2	0.1	0.0	0.0	0.4	4.7	0.1	4.8	43.2	136.8	45.0	0.81
35	1193	nd.	nd.	un.	31.6	440	4.4	4.8	9.0	0.4	0.1	0.0	0.0	0.9	2.5	0.1	2.2	116.0	135.0	44.0	1.46
36	1172	106-150	LVA	Cosmópolis	0.0	190	4.8	4.0	10.1	-0.8	0.1	0.0	0.0	0.0	2.1	0.2	2.7	7.8	63.0	18.0	1.24
37	1173	97-140	LV	Cosmópolis	7.7	590	5.2	4.3	10.0	-0.9	0.0	0.1	0.0	0.6	4.6	0.1	4.7	46.0	148.0	71.0	1.45
38	1176	200-240	LV	Salto	44.9	570	4.1	4.1	8.5	0.0	0.0	0.0	0.0	1.3	5.3	0.0	5.3	171.0	177.0	59.0	1.64
39	1299	54-75	F	Ribeirão Bonito	11.9	730	4.5	4.0	9.9	-0.5	0.2	0.1	0.0	1.2	3.9	0.3	4.2	7.6	175.0	72.0	2.33
40	1339	125-240	R	Dourado	44.6	70	4.8	4.1	8.7	-0.7	0.1	0.0	0.0	1.0	3.0	0.2	1.2	16.0	18.0	7.0	1.51
41	1345	60-112	M	Santa Ernestina	4.9	480	6.5	5.3	9.6	-1.2	22.9	9.0	0.4	0.0	1.9	32.3	34.2	290.0	99.0	180.0	4.98
42	1346	24-90	LV	Guariba	0.2	500	5.4	5.3	10.3	-0.1	0.1	0.0	0.0	0.0	3.0	0.1	3.1	34.0	168.0	232.0	0.34
43	1347	120-170	LV	Guariba	3.4	470	5.5	5.5	9.9	0.0	0.6	0.1	0.0	0.0	1.3	0.7	2.0	102.0	150.0	110.0	1.16
44	1349	125-170	LVA	Guataporá	2.7	570	6.0	4.3	10.2	-1.7	0.4	0.1	0.1	0.6	2.6	0.6	3.2	17.7	188.0	142.0	2.25
45	1351	90-130	LVA	Pitangueiras	6.0	350	5.1	4.7	9.9	-0.4	0.2	0.0	0.0	0.1	2.6	0.2	2.8	66.0	120.0	75.0	0.94
46	1352	75-100	R	Dobrada	45.6	60	4.8	4.3	8.6	-0.5	0.2	0.0	0.0	0.3	2.2	0.2	2.4	18.0	24.0	15.0	1.28
47	1391	54-86	LVA	un.	13.1	390	4.8	4.3	9.7	-0.5	0.4	0.1	0.0	0.2	2.3	0.5	2.8	128.0	114.0	50.0	1.91
48	1392	50-93	LVA	un.	20.9	330	4.5	3.8	9.4	-0.7	0.1	0.1	0.0	1.2	3.0	0.2	3.2	113.0	113.0	26.0	2.27
49	1395	88-113	nd.	un.	1.1	500	5.2	5.1	9.8	-0.1	0.5	0.5	0.1	0.1	2.5	1.1	3.6	128.0	107.0	153.0	1.42
50	1397	100-160	LV	un.	4.6	410	4.9	5.1	10.0	0.2	0.0	0.0	0.0	0.0	1.9	0.2	2.1	116.0	171.0	80.0	1.15
51	1409	51-82	T	Votuporanga	42.8	200	5.8	4.8	8.9	-1.0	1.3	0.5	0.1	0.3	1.8	1.9	3.7	69.0	54.0	38.0	2.17

Continua...

Table 1. Cont.

Sample	Profile ⁽¹⁾	Depth	Classification ⁽²⁾	Localization	Prem ⁽³⁾	Clay ⁽⁴⁾	pH ⁽⁵⁾			ΔpH ⁽⁶⁾	cmol.kg ⁻¹			H ⁺ Al ⁽¹¹⁾	SB ⁽¹²⁾	T ⁽¹³⁾	V ⁽¹⁴⁾	g kg ⁻¹			—mol mol ⁻¹ —		
							H ₂ O	KCl	NaF		Ca ²⁺⁷	Mg ²⁺⁸	K ⁺					Al ³⁺¹⁰	SiO ₂ ⁽¹⁵⁾	Al ₂ O ₃ ⁽¹⁵⁾	Fe ₂ O ₃ ⁽¹⁵⁾	Ki ⁽¹⁶⁾	Kr ⁽¹⁶⁾
52	1410	29-42	C	Votuporanga	19.5	240	5.5	4.5	9.4	-1.0	2.4	0.9	0.1	0.4	2.1	3.4	5.5	62.1	92.0	64.0	44.0	2.44	1.70
53	1411	126-160	LVA	Avai	0.0	660	5.3	5.5	10.4	0.2	0.0	0.0	0.0	0.1	3.3	0.0	3.3	0.6	120.0	208.0	94.0	0.98	0.76
54	1412	93-132	LVA	Avai	2.5	530	4.9	4.5	10.1	-0.4	0.1	0.0	0.0	0.2	2.3	0.1	2.4	5.4	159.0	202.0	55.0	1.34	1.14
55	1413	67-97	N	Águas da Prata	1.9	610	6.0	5.3	10.2	-0.7	2.8	0.8	0.2	0.1	3.9	3.8	7.7	49.3	178.0	160.0	153.0	1.89	1.17
56	1415	96-118	PVA	Bauru	1.3	370	5.1	4.1	9.6	-1.0	0.1	0.2	0.1	3.7	4.4	0.4	4.8	8.7	143.0	104.0	33.0	2.34	1.94
57	1416	130-200	LVA	Bauru	30.3	240	5.2	4.4	9.1	-0.8	0.1	0.0	0.1	0.7	1.7	0.2	1.9	9.1	90.0	76.0	25.0	2.01	1.66
58	1417	38-106	PVA	Bauru	7.7	540	5.1	4.5	9.7	-0.6	0.8	0.5	0.1	0.7	2.3	1.4	3.7	37.5	213.0	152.0	69.0	2.38	1.85
59	1418	46-126	T	Bauru	18.1	570	6.2	5.6	9.3	-0.6	2.5	0.5	27.0	0.2	0.8	30.0	30.8	97.4	305.0	204.0	70.0	2.54	2.08
60	1419	44-92	PV	Piratininga	4.9	620	5.4	4.6	9.9	-0.8	1.3	0.4	0.1	0.6	2.8	1.8	4.6	38.9	236.0	207.0	114.0	1.94	1.43
61	1420	160-200	T	Agudos	10.1	340	6.1	6.1	9.6	0.0	1.1	0.4	0.0	0.0	0.2	1.5	1.7	88.4	102.0	104.0	41.0	1.67	1.33
62	1421	260-300	LVA	Agudos	17.7	310	4.8	4.3	9.6	-0.5	0.2	0.0	0.0	0.6	3.1	0.2	3.3	6.3	107.0	108.0	40.0	1.68	1.36
63	1447	51-93	LV	un.	0.0	640	5.2	4.9	9.8	-0.3	0.3	0.1	0.0	0.2	3.1	0.4	3.6	13.4	212.0	209.0	252.0	1.72	0.97
64	1450	33-56	N	un.	11.0	600	5.8	5.2	9.8	-0.6	4.5	0.6	0.0	0.1	2.8	5.1	8.0	64.8	221.0	199.0	143.0	1.89	1.29
65	1453	42-100	LV	un.	0.0	620	5.4	5.3	10.3	-0.1	0.1	0.0	0.1	0.0	2.4	0.2	2.6	6.6	102.0	234.0	258.0	0.74	0.43
66	1457	14-31	L	un.	0.0	330	5.1	5.1	10.0	0.0	0.1	0.0	0.1	0.0	2.2	0.2	2.4	9.1	62.0	96.0	73.0	1.10	0.74
67	1459	115-150	L	un.	0.0	620	5.2	5.5	10.2	0.3	0.0	0.0	0.0	0.3	1.5	0.0	1.5	1.3	169.0	122.0	84.0	2.35	1.63
68	1461	132-200	LV	Oswaldo Cru	8.6	490	5.0	4.5	9.6	-0.5	0.0	0.0	0.0	0.3	1.5	0.0	1.5	1.3	169.0	122.0	84.0	2.35	1.63
69	1474	80-108	LV	Oswaldo Cru	38.1	230	5.2	4.4	8.7	-0.8	0.9	0.2	0.0	0.1	0.8	1.1	1.9	58.6	71.0	56.0	29.0	2.16	1.62
70	1475	99-140	LV	un.	30.4	180	4.6	4.2	9.0	-0.4	0.2	0.0	0.0	0.7	1.4	0.2	1.6	14.6	68.0	55.0	27.0	2.10	1.60
71	1486	64-84	T	Salmourão	29.3	280	6.3	5.1	9.3	-1.2	2.4	1.2	0.3	0.0	0.8	3.9	4.7	83.1	108.0	67.0	33.0	2.74	2.08
72	1492	53-95	LV	Cândido Moa	720	50	4.2	10.0	-0.8	-1.2	4.5	1.1	0.1	0.0	1.0	5.7	6.7	85.0	127.0	248.0	296.0	2.02	0.81
73	1494	39-75	N	Cândido Moa	2.5	670	6.2	5.6	9.8	-0.6	4.5	1.1	0.1	0.2	0.8	4.0	4.8	83.2	244.0	200.0	237.0	2.07	1.18
74	1495	55-77	LV	Cândido Moa	3.4	730	6.4	5.8	10.0	-0.6	3.2	0.7	0.1	0.6	3.7	0.6	4.4	14.9	195.0	200.0	259.0	1.66	0.91
75	1499	104-150	LV	Cândido Moa	0.0	680	4.7	4.4	10.2	-0.3	0.3	0.3	0.0	0.6	3.7	0.6	4.4	14.9	195.0	200.0	259.0	1.66	0.91
76	1501	124-160	R	Cândido Moa	37.7	120	4.6	4.1	9.0	-0.5	0.1	0.0	0.0	0.6	0.8	0.1	0.9	13.0	40.0	43.0	16.0	1.58	1.28
77	1525	95-160	T	Oswaldo Cruz	38.3	230	6.6	5.5	9.3	-1.1	2.7	0.6	0.1	0.0	0.0	3.4	3.4	100.0	92.0	82.0	17.0	1.91	1.68
78	1534	90-130	LVA	Marília	27.6	210	4.4	3.9	9.4	-0.5	0.1	0.1	0.1	1.8	2.5	0.3	2.8	10.1	83.0	65.0	22.0	2.17	1.78
79	1535	68-95	PVA	un.	32.5	190	4.4	3.7	9.1	-0.7	0.1	0.1	0.1	0.0	0.4	0.3	0.7	42.9	34.0	64.0	16.0	0.90	0.78
80	1541	58-105	LV	Jau	24.1	470	5.9	5.3	9.5	-0.6	0.9	0.4	0.1	0.1	0.9	1.4	2.3	60.9	37.0	94.0	44.0	0.67	0.51
81	1542	72-108	N	Jau	10.4	550	6.4	5.6	9.8	-0.8	2.3	0.8	0.1	0.2	1.6	3.2	4.9	67.2	142.0	104.0	86.0	2.32	1.52
82	1543	98-150	G	Jau	35.2	580	7.0	5.5	9.2	-1.5	5.7	2.0	0.1	0.0	1.3	7.8	9.2	85.9	141.0	146.0	34.0	1.64	1.43
83	1544	30-63	N	Jau	6.1	630	6.0	5.1	10.0	-0.9	3.4	0.8	0.1	0.0	2.0	4.3	6.4	68.8	17.8	146.0	227.0	0.21	0.10
84	1545	100-200	LV	Jau	1.5	570	6.8	6.2	10.3	-0.6	2.4	1.0	0.1	0.0	0.2	3.5	3.7	94.6	132.0	151.0	212.0	1.49	0.78
85	1546	30-64	T	Jau	28.0	370	5.4	4.3	9.5	-1.1	0.3	0.6	0.1	0.4	2.2	1.0	3.2	31.3	124.0	104.0	88.0	2.03	1.31
86	1547	75-138	LV	Jau	26.1	300	5.2	4.2	9.5	-1.0	2.9	1.0	0.1	0.6	1.9	4.0	5.9	67.6	84.0	84.0	76.0	1.70	1.08
87	1548	15-49	nd.	un.	11.0	520	5.8	5.0	9.6	-0.8	2.1	0.7	0.2	0.0	1.8	3.0	4.9	63.0	173.0	101.0	134.0	2.91	1.57
88	1559	85-160	RY	Garça	47.3	90	6.2	5.3	8.3	-0.9	2.3	0.7	0.1	0.0	1.2	3.1	4.3	72.4	33.0	24.0	3.0	2.34	2.16
89	1561	68-80	PVA	un.	31.1	290	5.0	3.9	9.5	-1.1	2.2	0.5	0.2	0.4	2.0	2.9	4.9	59.4	111.0	122.0	22.0	1.55	1.39

⁽¹⁾ Reference profile of Agronomic Institute of Campinas. ⁽²⁾ Classification according to Embrapa (2006) - C: Cambissolo, CX: Cambissolo Háplico, F: Plintossolo, FF: Plintossolo Pétrico, G: Gleissolo, L: Latossolo, LA: Latossolo Amarelo, LV: Latossolo Vermelho, LVA: Latossolo Vermelho-Amarelo, M: Chernossolo, N: Nitossolo, NV: Nitossolo Vermelho, P: Argissolo, PA: Argissolo Amarelo, PV: Argissolo Vermelho, PVA: Argissolo Vermelho-Amarelo, R: Neossolo, RY: Neossolo Flúvico and T: Luvisso. ⁽³⁾ Remaining phosphorus (ppm). ⁽⁴⁾ pH measured in water (pH H₂O), 1 mol L⁻¹ KCl (pH KCl) (Embrapa, 1997) and 1 mol L⁻¹ NaF (pH NaF) (Bolland et al., 1996). ⁽⁵⁾ DpH = pH KCl - pH H₂O (Mekaru & Uehara, 1972). ⁽⁶⁾ DpH = pH KCl - pH H₂O (Mekaru & Uehara, 1972). ⁽⁷⁾ (8) (10) (11) Respective values of exchangeable contents of calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺) and aluminum (Al³⁺) and of total acidity (H⁺Al) (Raj et al., 2001). ⁽¹²⁾ Sumo f bases (SB = Ca²⁺ + Mg²⁺ + K⁺). ⁽¹³⁾ Soil cation exchange capacity at Ph 7 (T) [T = Ca²⁺ + Mg²⁺ + K⁺ + (H⁺Al)]. ⁽¹⁴⁾ Base saturation (V%) [V% = 100 (Ca²⁺ + Mg²⁺ + K⁺) / T]. ⁽¹⁵⁾ Soil contents of silicon, aluminum and iron extractable by boiling 9 mol L⁻¹ H₂SO₄ expressed as their respective oxides (Embrapa, 1997). ⁽¹⁶⁾ Weathering indexes given by Ki = 1.7 SiO₂ / (Al₂O₃ + Fe₂O₃). un. = unavailable.

⁽¹⁾ Reference profile of Agronomic Institute of Campinas. ⁽²⁾ Classification according to Embrapa (2006) - C: Cambissolo, CX: Cambissolo Hápico, F: Plintossolo, FF: Plintossolo Pétrico, G: Gleissolo, L: Latossolo, LuA: Latossolo Amarelo, LV: Latossolo Vermelho, LVA: Latossolo Vermelho-Amarelo, M: Chernossolo, N: Nitossolo, NV: Nitossolo Vermelho, P: Argissolo, PA: Argissolo Amarelo, PV: Argissolo Vermelho, PVA: Argissolo Vermelho-Amarelo, R: Neossolo, RY: Neossolo Flávio and T: Luvisso. ⁽³⁾ Remaining phosphorus (Alvarez V. et al. 2000). ⁽⁴⁾ Pipette method (Embrapa, 1997). ⁽⁵⁾ pH measured in water (pH H₂O), 1 mol L⁻¹ KCl (pH KCl) (Embrapa, 1997) and 1 mol L⁻¹ NaF (pH NaF) (Bolland et al., 1996). ⁽⁶⁾ DpH = pH KCl - pH H₂O (Mekaru & Uehara, 1972). ⁽⁷⁾ (8) (9) (10) (11) Respective values of exchangeable contents of calcium (Ca²⁺), magnesium (Mg²⁺) and aluminum (Al³⁺) and of total acidity (H⁺AD) (Raj et al., 2001). ⁽¹²⁾ Sumo f bases (SB = Ca²⁺ + Mg²⁺ + K⁺). ⁽¹³⁾ Soil cation exchange capacity at Ph 7 [T = Ca²⁺ + Mg²⁺ + K⁺ + (H⁺AD)]. ⁽¹⁴⁾ Base saturation (V%) [V% = 100 (Ca²⁺ + Mg²⁺ + K⁺) / T]. ⁽¹⁵⁾ Soil contents of silicon, aluminum and iron extractable by boiling 9 mol L⁻¹ H₂SO₄ expressed as their respective oxides (Embrapa, 1997). ⁽¹⁶⁾ Weathering indexes given by Ki = 1.7 SiO₂ / Al₂O₃ and Kr = 1.7 SiO₂ / (Al₂O₃ + Fe₂O₃). un. = unavailable.

Table 2. Results of the multiple regression analyses relating remaining phosphorus (Prem) to soil pH measured in 1 mol L⁻¹ NaF (pH NaF) and to sum of bases (SB) ($\text{Prem} = a_0 + a_1 \text{pH NaF} + a_2 \text{SB}$) based on different sizes of measured data sets

Parameter	Estimate	Standard error	t value	prob > t
Fitting with 50 % of total measured data				
a_0	260.08	13.81	18.83	0.0001
a_1	-25.24	1.41	-17.85	0.0001
a_2	-0.26	0.11	-2.29	0.0270
	F = 159.35	Prob > F = 0.0001	R ² = 0.8780	n = 45
Fitting with 70 % of total measured data				
a_0	263.60	11.99	21.98	0.0001
a_1	-25.59	1.23	-20.83	0.0001
a_2	-0.28	0.12	-2.44	0.0178
	F = 217.06	Prob > F = 0.0001	R ² = 0.8763	n = 62
Fitting with 90 % of total measured data				
a_0	262.80	11.94	21.99	0.0001
a_1	-25.59	1.23	-20.81	0.0001
a_2	-	-	-	-
	F = 433.16	Prob > F = 0.0001	R ² = 0.8454	n = 80

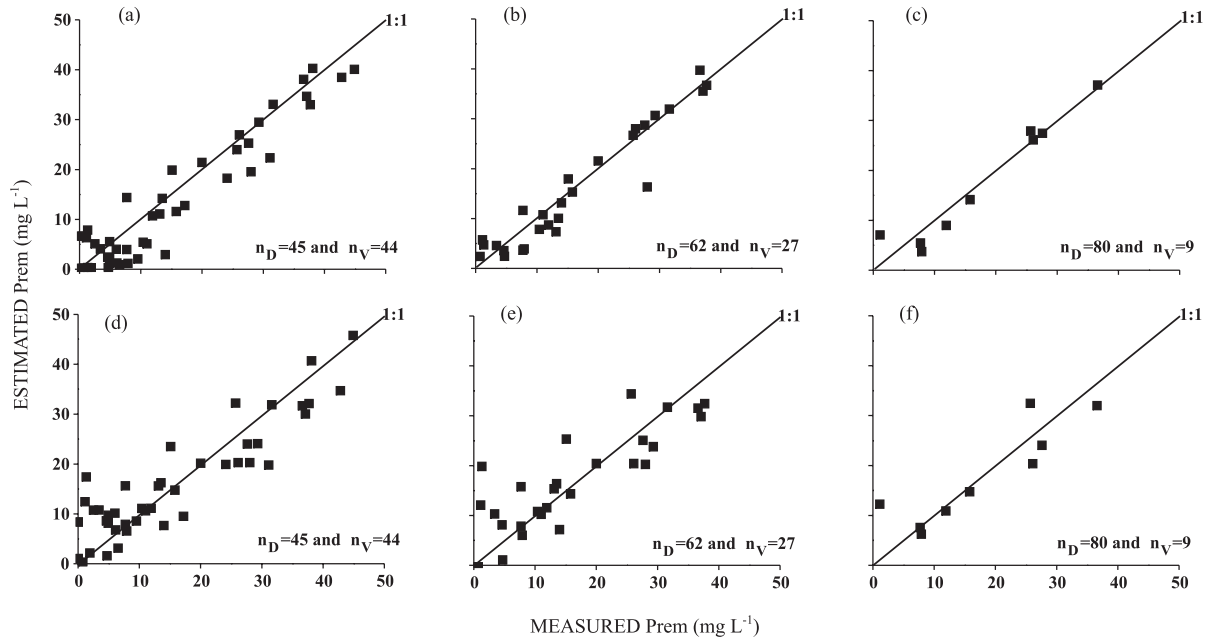


Figure 1. Scatter diagrams relating the measured remaining phosphorus (Prem) to the estimated values by the artificial neural network (a, b, c) and by multiple regression analysis (d, e, f). n_D = dataset size used in the development of the pedotransfer function; n_V = dataset size used in the validation of the pedotransfer function.

The use of Prem as determinant variable for soil stratification in classes of P, S, and Zn availability was presented by Alvarez V. et al. (2000). In this paper, the authors also suggested Prem as an estimator of the soil acidity buffering capacity for the calculation of lime requirements of cropped soils. This Prem use can, for instance, allow for the identification of different buffering capacities in soils with identical clay-sized

particle contents. In this context, soils poor in organic matter and with low Prem values tend, due to their greater oxide contents, to require greater lime amounts for a same pH variation than soils with higher Prem values. The utility of the ANN-based pedotransfer function to estimate the acidity buffering factor Y proposed by Alvarez V. et al. (2000) ($\hat{y} = 4.002 - 0.125901 \text{ Prem} + 0.001205 \text{ Prem}^2 - 0.00000362 \text{ Prem}^3$)

was tested considering the three subsets of training and validation data used in the development of the pedotransfer function. The results (Figure 2) reiterated the higher sensitivity of the ANN-based pedotransfer function to the increase in the test database in relation to the accuracy of the Prem estimates. The comparisons of the Y values calculated from measured with estimated Prem values revealed a progressive decrease in the sum of the squared differences (SSD) between the Y values calculated from measured and estimated Prem values as the ANN was developed from 50 % (SDD = 8.7) to 70 % (SDD = 2.8) and 90 % (SDD = 0.9) of total input data in the training phase.

Despite the simple laboratory determination of Prem, the establishment of Prem estimates by a ANN-based pedotransfer function that are accurate enough for agricultural applications would allow for an additional use of both SB and Al^{3+} values routinely

determined in the different Brazilian soil fertility laboratories. Although the number of samples used in this study did not allow for the development of a definitive pedotransfer function for Prem estimates, it is believed that the formation of a massive database containing Prem, pH NaF, SB, and Al^{3+} values is advisable for the posterior development of an ANN-based pedotransfer function which, once implemented as software, will make an immediate calculation of remaining P values possible.

CONCLUSIONS

1. It was possible to estimate remaining P values with an artificial neural network-based pedotransfer function using soil pH values measured in 1 mol L⁻¹ NaF, soil contents of exchangeable Al, and the sum of soil contents of Ca, K and Mg as predictor variables.

Table 3. Results of the simple linear regression analyses relating measured remaining phosphorus (Prem_m) with estimated values (Prem_e) based on pedotransfer functions developed by artificial neural networks (ANN) and by multiple regression analysis (MRA)

Equation ⁽¹⁾	IC- <i>a</i> ⁽²⁾	IC- <i>b</i> ⁽³⁾	R ²	SSD ⁽⁴⁾
Testing/fitting with 50 % and validation with 50 % of total measured data				
$\text{Prem}_e \text{ ANN} = -0.63 + 0.93 \text{ Prem}_m$	-2.58–1.32	0.83–1.02	0.8993	718.5
$\text{Prem}_e \text{ MRA} = 3.81 + 0.77 \text{ Prem}_m$	-1.47–6.15	0.65–0.88	0.8091	1036.5
Testing/fitting with 70 % and validation with 30 % of total measured data				
$\text{Prem}_e \text{ ANN} = -0.11 + 0.98 \text{ Prem}_m$	-2.54–2.32	0.85–1.10	0.9138	312.1
$\text{Prem}_e \text{ MRA} = 5.72 + 0.69 \text{ Prem}_m$	-1.99–9.44	0.51–0.88	0.6927	733.3
Testing/fitting with 90 % and validation with 10 % of total measured data				
$\text{Prem}_e \text{ ANN} = -0.44 + 1.01 \text{ Prem}_m$	-5.29 – 4.41	0.78 – 1.24	0.9295	73.6
$\text{Prem}_e \text{ MRA} = 4.27 + 0.76 \text{ Prem}_m$	-3.06 – 11.60	0.41 – 1.11	0.7600	168.1

⁽¹⁾ $y = a + bx$. ⁽²⁾ and ⁽³⁾ Respective confidence intervals calculated at 95 % for the intercept *a* and slope *b*. ⁽⁴⁾ Sum of squared differences between the measured remaining phosphorus values of the subset of validation data and the respective values estimated by the pedotransfer function.

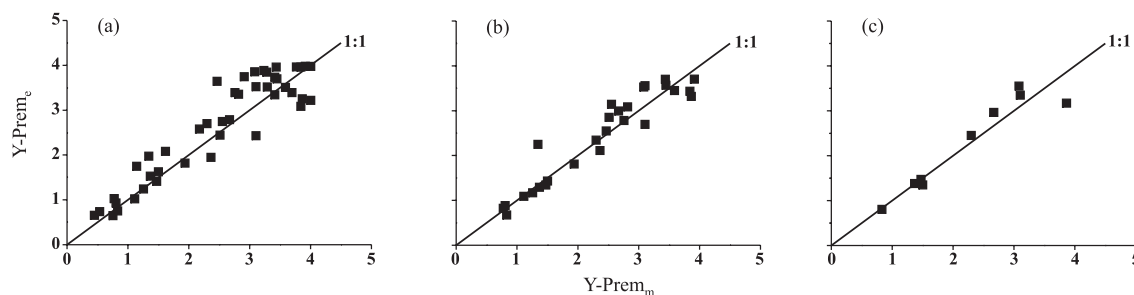


Figure 2. Scatter diagrams relating the soil acidity buffering factor Y calculated from measured remaining phosphorus (Y-Prem_m) to values calculated from remaining phosphorus (Y-Prem_e) estimated by artificial neural network-based pedotransfer functions developed from testing datasets consisting of 50 (a), 30 (b) and 10 % (c) of the total data. $\hat{y} = 4.002 - 0.125901 \text{ Prem} + 0.001205 \text{ Prem}^2 - 0.00000362 \text{ Prem}^3$ (Alvarez V. et al., 2000).

2. The remaining P values estimated by the artificial neural network approach were more accurate than those obtained by multiple regression analysis.

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