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APPLICATION OF MULTIVARIATE STATISTICAL ANALYSIS FOR THE ESTIMATION OF THE PHOSPHORUS STATUS IN CALCAREOUS SOIL

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SYNOPSIS

Available (Olsen-P) and total phosphorus (TP) of highly calcareous soil under vineyards were determined. In order to provide a more reliable basis for the estimation of phosphorus status, principal component analysis was applied. The differences between upper (0-30 cm) and underlying layer of soil (30-60 cm) were evident, in sense of pH (8.08±0.05 and 8.25±0.09, respectively), the contents of total carbonates (41.9±7.2% and 66.3±11.4% $CaCO_3$) and organic matter as C_{org} (3.0±0.6% and 1.5±0.8%), as well as in the content of acid-soluble metals. Also, the contents of Olsen-P and TP differed greatly between soil layers. In underlying soil layer, the soil characteristics, which define the retention of the main part of total P i.e. ΔP = TP − Olsen-P are the clay components and organic matter.

INTRODUCTION

The distribution of total P on its particular appearing forms and the manner of its binding to certain substrates, as well as P availability to plant uptake depend on the ecochemical characteristics of soil (Makarov, 1997; McDowell & Sarpley, 2001; Chardon & Schoumans, 2002). Consequently, the transformations of P added through fertilizers also depend on the ecochemical characteristics of soil (Samadi & Gilkes, 1998). Therefore, the associations of phosphorus-species with the constituents of soils are being one of the main interests of agrochemical and ecochemical investigations several decennia ago. One of the determining factors in the formation of P-associations with soil constituents is soil pH. Soil organic matter and oxides or hydroxides of Al, Fe and Mn have a very important role in the chemistry of P. In calcareous soil, the preferential association of phosphorus with calcium is expected.

The aim of this paper was to clarify the relationships between available P (Olsen-P), as the most important phosphorus fraction for plants, the total P and some ecochemical parameters of soil (pH, total carbonates, total organic carbon, and acid-soluble metals - Ca, Mg, Al, Fe and Mn). These investigations were performed separately for both, the top and the underlying soil layer and the established phosphorus status between those was compared. In order to avoid shortcomings arising from the interpretation of simple relationships between soil parameters, the multivariate statistical analysis was applied.

METHODS

SOIL SAMPLES

The soil type on the sampling sites is rendzine on a mainly calcitic and dolomitic fluvioglacial deposit. The content of soil skeletal material is on average 75% consisting mainly of particles between 0.5 and 2 cm. In the fine soil fraction (< 2 mm), sand content is 50 to 90%, silt 8-35%, and clay ranges between 2 and 15% (Fustic & Djuretic, 2000).

Totally, 44 samples of calcareous soils (under vineyards), i.e. 22 from 0-30 cm (topsoil) and 22 samples from 30-60 cm depth (underlying) were analysed. The samples were air-dried, sieved (< 2 mm) and ground to < 0.15 mm.

CHEMICAL ANALYSES

pH-Value was determined with a combined glass-electrode in soil/deionized water suspensions 1: 2.5 (w/v) (ISO 10390 1994).

Carbonate carbon, C_{carb}, was determined by a standard volumetric method (ISO 10693 1995).

Total organic carbon, C_{org}, was determined by elemental microanalysis after the treatment of samples with 6M HCl in order to eliminate C_{carb}.

The acid soluble total metals (TCa, TMg, TAl, TFe and TMn) were determined in the solutions for TP, by AAS on a Varian SpectrAA 55 instrument.

Total phosphorus, TP, was determined after the treatment of samples with HNO_3 + $HClO_4$ and subsequently with HCl, according to HESSE (1971). In the obtained solutions, total P was determined by inductively coupled plasma spectroscopy (ICPS), on a Shimadzu 7500 instrument.

The available phosphorus or Olsen-P, was extracted with 0.5*M* $NaHCO_3$ (Olsen et al., 1954; Tiessen & Moir, 1993). The P concentration in extracts was spectrophotometrically determined on a Merck 400 instrument.

STATISTICAL ANALYSES

The results were processed by means of the SPSS 10.0 Program. The statistical analyses included descriptive (mean and standard deviation) and factor analysis. By factor analysis the original set of 10-correlated soil parameters (pH, C_{carb}, C_{org}, TCa, TMg, TAl, TFe, TMn, TP and Olsen-P), were transformed into a new set of mutually uncorrelated factors according to MIURA & BADAYOS (1999).

RESULTS AND DISCUSSION

The mean values of investigated soil parameters are given in Table 1. The difference between soil layers is evident. Generally, the soil has an alkaline reaction, a very high content of carbonates and is not rich in organic matter. Ca is the dominant metal in soil because of its mainly calcitic origin. The contents of total P and Olsen-P classify the top soil layer as very rich and the underlying as a lowly to medially supplied by this nutrient.

Table 1: The values (mean and standard deviation) of investigated soil parameters (n=22).

Depth (cm)	0 – 30		30 – 60	
Parameter	Mean	St.dev.	Mean	St.dev.
pH	8.08	0.05	8.25	0.09
C_{carb} (% $CaCO_3$)	41.9	7.2	66.3	11.4
C_{org} (%)	3.0	0.6	1.5	0.8
TP (mg/kg)	1076	261	350	115
Olsen-P (mg/kg)	49	19	7	3
TCa (g/kg)	157	17	276	48
TMg (g/kg)	23	4	18	3
TAl (g/kg)	30	7	15	8
TFe (g/kg)	21	4	10	5
TMn (mg/kg)	603	128	285	142

Based on the factor analysis, 3 factors with Eigenvalues larger than 1 after Varimax rotation were extracted. They account for about 86.5% (Table 2) and 91.3% (Table 3) of the total variance, for top and underlying soil layer, respectively.

TOP SOIL LAYER. As it can be seen (Table 2), **factor 1** is composed from two complementary groups of parameters representing the main constituents of the soil: the hydroxide-oxide-clay pole (TMn, TFe and TAl) and the carbonatic pole of soil (C_{carb} and TCa). Magnesium, because of its associations with carbonates, organic matter and phosphates, Mg is shared between several factors (factor 1, 2 and 3).

Factor 2 is represented by Olsen-P (the potentially source of Ca-P, Al-P and Fe-P), the TP and pH and is expressing the status of phosphorus. One characteristic of the phosphorus status is the inverse proportionality between TP and Olsen-P content and pH, and this could be the effect of either, 1) the competitive exchange between hydroxyl-ions and ions of P-species on binding sites, and/or 2) a gradual increase of negative charge on the potential phosphate-binding species having values of pHzpc > 8.0 (Behra et al., 1999; Stumm, 1992), such as α-Al_2O_3, γ-AlOOH, α-Fe_2O_3, amorphous FeOOH, MgO. An increase of pH thus decreases the amount of phosphorus-species which can be directly bound on these substrates and also mobilizes P bound to dissolved organic carbon (Stumm, 1992; Chardon & Schoumans, 2002). The other characteristic is the absence of TP as well as Olsen-P in factor 1. This feature could be an indication that the operationally determined fractions and sub-fractions which constitute TP and Olsen-P (exchangeable P, Ca-P, Al-P, Fe-P, reducible-bound P, organically-bound P, humic-bound P etc.) are distributed between, i.e. are associated with all the components of factor 1. The relatively high value for TMg indicates that the role of Mg may be also important in binding of P i.e. P accumulation.

Table 2: Factor analysis for top soil layer: Eigenvalues, cummulative of the total variance, factor loading of the 3 factors, and communality estimates of the 10 soil parameters.

	F1	F2	F3	Commun.
Eigenvalue	4.74	2.30	1.60	
Cumulative (%)	47.4	70.5	86.5	
Ccarb	**-0.969**	-0.084	0.106	0.957
TMn	**0.968**	0.085	-0.160	0.971
TFe	**0.967**	0.152	-0.126	0.974
TAl	**0.956**	-0.000	-0.134	0.932
TCa	**-0.894**	0.053	-0.085	0.810
Olsen-P	0.121	**0.852**	0.228	0.793
TP	-0.053	**0.842**	0.316	0.812
pH	-0.132	**-0.784**	0.233	0.686
Corg	-0.027	0.055	**0.931**	0.871
TMg	-0.425	0.457	0.670	0.839

Factor 3 is consisting only from Corg (plant residues, humic substances and low-molecular organic matter) and represents organic matter status. It also has high value on TMg, due to the partly origin of TMg from biomass residues.

UNDERLYING SOIL LAYER. **Factor 1.** The main difference of the underlying layer (Table 3) in comparison with the upper is the strong association total phosphorus with the entire hydroxide-oxide-clay-organic matter pole. Namely, factor 1 is composed from all parameters except TMg (**factor 2**) and Olsen-P (**factor 3**). This feature can be explained by the assumption that in this older and more isolated soil layer an appreciable shift of P-distribution from the more mobile to the more immobile fractions is occurring. Therefore the correlation between TP and Olsen-P is lost. Due to the fact that Olsen-P is separated in a distinct factor, factor 3, the retention of main part of total P i.e. ΔP = TP − Olsen-P is defined by clay components and organic matter of soil.

The differentiation of TMg into a separate factor can be explained in the same way as for the upper layer.

Table 3: Factor analysis for the underlying soil layer: Eigenvalues, cummulative of the total variance, factor loading of the 3 factors, and communality estimates of the 10 soil parameters.

	F1	F2	F3	Commun.
Eigenvalue	6.27	1.45	1.40	
Cumulative (%)	62.7	77.2	91.3	
TMn	**0.962**	0.162	0.158	0.977
TFe	**0.957**	0.200	0.163	0.983
TAl	**0.919**	0.217	0.231	0.945
Ccarb	**-0.919**	-0.292	-0.184	0.964
pH	**-0.910**	-0.002	0.099	0.837
TCa	**-0.904**	-0.174	-0.101	0.858
TP	**0.744**	0.357	0.414	0.851
Corg	**0.701**	0.405	0.341	0.772
TMg	0.196	**0.965**	-0.021	0.970
Olsen-P	0.119	-0.017	**0.977**	0.970

CONCLUSION

In the top soil layer, pH is separated as one of main soil characteristics determining accumulation of phosphorus. In underlying soil layer, the soil characteristics, which define the retention of the main part of total P are clay component and organic matter.

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