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SPATIAL DISTRIBUTION OF PHOSPHORUS ON THE SOIL CATENA OF CHROMIC CAMBISOLS COMPLEX

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Abstract

The present study aims to establish the influence of the processes of secondary pedogenesis on the content and distribution of mobile forms of phosphorus in Chromic cambisols complex formed on a silicate base. Phosphorus is not a major nutrient in pedogenesis and is not clear its natural redistribution in the range of soils with general geological origin of terrigenous materials, but located differently in terms of their eluvial-deluvial transfer within a common long soil catena. The size of the total sample is 15 soil sampling points, and at each point samples are taken from the layer 0-25 and 25-50 cm. The sampling points are selected in the middle of a characteristic slope, without manifestation of local linear erosion forms or accumulation zones. Based on the study, it was found that the content of P_2O_5 in the top soil layer did not depend on the location, and the deeper horizon should be considered as diagnostic one in terms of its distribution.

Key words: *soil catena, phosphorus, topographic factors, variogram.*

INTRODUCTION

The complex of Chromic cambisols in Bulgaria is very heterogeneous in terms of genesis, composition and properties. This is due to the true genetic heterogeneity of this group of soils for which in the Bulgarian classification, based mainly on their color and zonal affiliation, a common genetic taxon has been determined at the of the soil type level. Nevertheless, they occupy common areas and in terms of their distribution on Bulgarian territory are zonal, despite the fact that their "zonation" is considered on one side from the European moderately continental and Atlantic soil zones, and on another side from the soil zones in the Mediterranean. In this sense, they are specific without being homogeneous in their range. Their internal type diversity is based on the factors and conditions of soil formation, but covers not only the main type determining pedogenesis (climate, macro relief, vegetation, etc.), but also much more modern conditions, such as denudation or erosion in general, contemporary vegetation, humidification conditions and others. The second group of factors strongly influences the composition and properties of the soil complex, but at the same time they are not "genetic", in the sense that they are not soil-forming at the level of the soil type. The influence of these factors is logically predictable with respect to some components of the soil composition. For example, those accepted at some taxonomic level as eroded or shallow Chromic cambisols have the expectation to establish a lower content of organic carbon and nitrogen, lighter soil texture, weakly manifested biogenic accumulation processes on the surface of the profile. For other elements of the soil composition these dependencies are not obvious, and at the same time some of them are important for the general functionality and for the agricultural suitability of the soil complex. These conditions are met by the content of absorb phosphorus and its distribution in the active part of the soil profile.

As all terrestrial ecosystems, temperate forest ecosystems rely on the availability of phosphorus from the soil, which is related to site parameters as precipitation, bedrock, soil pH, material, and stage of pedogenesis. Many soils in central Europe are young, the phosphorus status of forests is often low or insufficient (Ilg et al., 2009; Jonard et al., 2015). Soil acidification, intensified by anthropogenic deposits, additionally reduces plant available phosphorus (Mohren et al., 1986).

Strong phosphorus sorption, onto humic-mineral-complexes, by Al and Fe oxides and hydroxides, or clay minerals, increased formation of short-range order Al or Fe phosphate, as well as decreased mineralization of organic phosphorus may limit forest growth in many ecosystems (Gerke & Hermann, 1992; Violante & Pigna, 2002; Richardson et al., 2004; Sims & Pierzynski, 2005; Laliberté et al., 2012).

Humic mineral phosphate complexes may increase plant available P and can account for 50-80% of the phosphorus in solution (Gerke, 2010).

Studying phosphorus availability in soil therefore implies accounting for the distribution of different P proportions, in addition to the total P status in soil, as it is assessed by wet-chemical fractionation of soil, and by advanced spectroscopic techniques (Kruse et al., 2015).

Different phosphorus fractions exhibit different properties in soils and chemical P resources in soils change during pedogenesis (Walker & Syers, 1976; Sims & Pierzynski, 2005). The soils accumulate organic P compounds during the first 500 years of pedogenesis (Turner et al., 2007; Prietzel et al., 2013). The geosequence is characterized by a P status gradient, resulting from different bedrock and soil age. In addition to the phosphorus binding form, spatial heterogeneity of P has been identified as an important factor controlling P availability for plants and for an alpine treeline (Jackson & Caldwell, 1993; Liptzin et al., 2013). Phosphorus depth distributions in most cases were assessed only unidimensional (Ferro Vázquez et al., 2014).

Phosphorus is not an essential nutrient in pedogenesis, but at the same time it is very important from an economic point of view. It is not clear its natural redistribution in the area of soils with common geological origin of terrigenous materials, but located differently in terms of their eluvial-deluvial transport within a common long soil catena.

According to Ibrahim et al. (2021) excessive input of phosphorus (P) in agricultural production and its finite resources is becoming a global concern for sustainable P management and more research is needed about the main factors influence on P available.

This study aims to establish the influence of the processes of secondary pedogenesis on the content and distribution of mobile forms of phosphorus in Chromic cambisols complex formed on a silicate base.

MATERIALS AND METHODS

As a basis for the study was used an area of leached, eroded and accumulated (but not meadow) Chromic cambisols in the Eastern slopes of Sakar mountain and in the conditions of dissected hilly terrain. The study was conducted in the period 2019-2021. Soil samples with a sufficiently well-developed contemporary profile were collected and at the same time some of them were strongly eroded. The soil samples were located on the sloping part of a long soil catena, as the height of the sampling points varied from 65 to 200 m above sea level, and the sampling points are grouped in a total of three zones. In each of the altitude zones more than one soil samples were taken at depths of 0-25 and 25-50 cm.

The coordinates of the wide soil catena are in the Universal Transversal Mercator N35 system, with a horizontal resolution of 5 m and a vertical resolution of 1 m, using a height correction from a ground station. The topographic conditions are distinguished by three indicators - altitude with an accuracy of 1 m. In the Baltic altitude system, meter latitude and longitude by Mercator, slope of the terrain in degrees of azimuth and in rhombuses in 90° distributions. It is assumed that in the conditions of the limited area of the soil catena, the climatic conditions and the vegetation are constant factors. The size of the total sample is 15 soil sampling points, and at each point samples are taken from the layer 0-25 and 25-50 cm. The sampling points are selected in the middle of a characteristic slope, without manifestation of local linear erosion forms or accumulation zones. On the basis of the soil samples collected in this way, the soil texture was determined by the photosedimentographic method (Trendafilov et al., 2017) and the total content of mobile phosphorus by the double-lactate method of Egner-Reim, (GOST 26209-91/01.07.93).

The statistical methods used in the study were Pearson correlation analysis, Test of normality - Shapiro-Wilk, Package program - SPSS Statistics.

RESULTS AND DISCUSSIONS

The surveyed soil differences are represented by strongly, moderately and slightly eroded to poorly accumulated profiles. Genetically, the soils have a differentiated profile, but with strongly and moderately eroded differences, the two-membered character of the profile is "masked" not only due to the erosive pedoturbation of the surface horizon with lighter layers lying above and below it.
Studies of phosphorus transformations have mainly focused on P cycling processes resulting in the transformation of original P to other forms. In the early stages of soil development, parent materials contain mainly inorganic phosphate (Cole & Heil, 1981; Smeck, 1973; 1985; Stewart & Tiessen, 1987). The relative proportion of different P fractions is determined by the activities of calcium, iron and aluminum in the soil which, in turn, are greatly influenced by weathering processes (Williams & Walker, l969a; 1969b).
In the described diversity in terms of soil genetic factors (basic and contemporary), was assumed that a relatively stable and reproducible starting point of the modern characteristic could fulfill the topographic factor. Moreover, that it was fundamental to the erosion process, and the latter in the given case determined the modern pedogenesis not only in the specific studied area but also in the area of distribution of the complex eroded, non-eroded and accumulated Chromic cambisols with a common geological basis. The location of the soil sampling points on the topographic basis of the locality is shown in Figure 1.

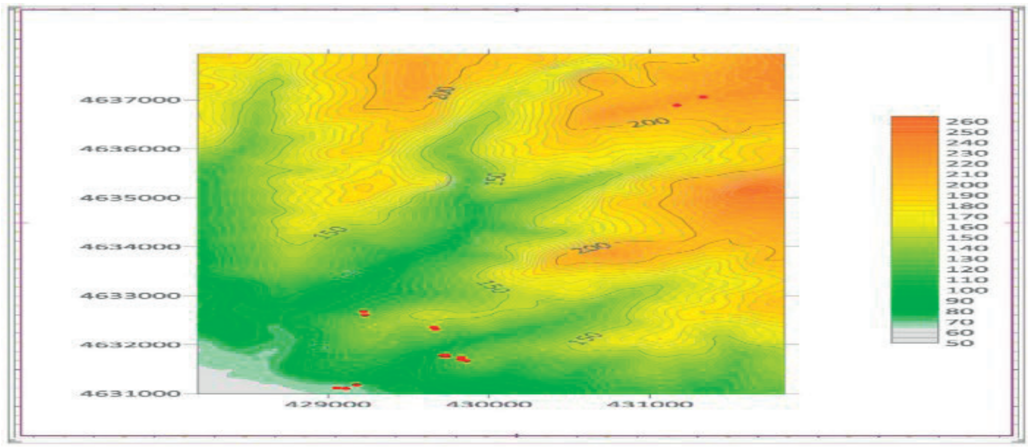

Figure 1. Location of soil sampling points

Total phosphorus content and distribution
The organic and inorganic forms and distribution of phosphorus in the soil vary with different processes as: natural processes that determine soil mineralogy and phosphorus sorption characteristics, as well as human-controlled processes such as the application and timing of phosphorus containing fertilizers, lime and organic material (Batjes, 2010). Under natural conditions, the weathering and dissolution of rocks andrelatively insoluble phosphorus containing minerals is a slow process. This weathering is only capable of supporting slow-growing vegetation and crops adapted to low phosphorus availability. In acid soils, various forms of iron, aluminum and manganese oxides strongly bind phosphorus, while in calcareous soils phosphorus is mainly found in the form of calcium compounds of varying solubility (Dabin, 1980; Fairhurst et al., 1999; Ryan & Rashid, 2006). Clay mineralogy and clay content directly affect phosphorus retention (Sanchez, 1976). The form of phosphorus in the soil will influence phosphorus availability to the plant. Phosphorus uptake is determined by soil water conditions, temperature, crop type and growth rate, root morphology and plant specific characteristics to extract soil phosphorus through excretion of exudates (Hoffland et al., 1992).

Mycorrhizal fungi may also be important in this respect (Smith et al., 2003; Li et al., 2006).
The average P_2O_5 content of the test sample for both depths was 12.9 ± 0.6 mg/kg, and ranged from 8.8 to 21.2 mg/kg. P_2O_5 levels were most commonly found in the range of 10 to 12 mg/kg. In the surface layers of the profile the content of P_2O_5 was on average 14.4 mg/kg, and in the subsoil 11.7 mg/kg. Depends on their location in the soil catena and taking into account the morphology of the soil profile, soil samples were divided into five groups. The characteristics of the soil differences in the individual groups are given in Table 1.

Table 1. Characteristics of the location, the degree of erosion and the soil texture of the soils in the survey groups formed by location

Soil group	Degree of erosion	Soil texture (%)	Elevation zone (m)
1	**Non-eroded and slightly accumulated Chromic cambisols, undifferentiated**	Surface horizon 51.4 Subsoil horizon 43.6	65
2	**Slightly eroded and non-eroded Chromic cambisols, undifferentiated**	Surface horizon 46.6 Subsoil horizon 44.6	117
3	**Moderately eroded Chromic cambisols, undifferentiated**	Surface horizon 35.0 Subsoil horizon 32.0	125
4	**Strongly eroded Chromic cambisols, differentiated**	Surface horizon 40.3 Subsoil horizon 47.3	127
5	**Strongly eroded Chromic cambisols, undifferentiated**	Surface horizon 47.4 Subsoil horizon 45.9	212

In the soils of all groups, the content of P_2O_5 in the surface horizons exceeded that one in the subsoil. In groups 1 and 5, i.e. in non-eroded to slightly accumulated Chromic cambisols, as well as in the Strongly eroded and shallow Chromic cambisols, the difference in the content of P_2O_5 on the soil surface and in depths was statistically proven (Figure 2). At the same time, no statistically proven difference in terms of P_2O_5 content in the total sample was observed.
The mobility of phosphate anions in soil depend on the nature of the mineral surfaces and oxide coatings since phosphate anions are strongly adsorbed by mineral constituents such as sesquioxides and clays (Parfitt, 1978). Organic phosphate compounds differ greatly in their form and in the number of reactive phosphate groups which they possess. Some of theme has the potential for movement, especially mono-phosphate esters (Rolston et al., 1975).
Phosphorus may move with other nutrients in surface flow, as run off, particularly in areas where snow melts before the surface soil thaws and water could infiltrate (Timmons et al., 1977).

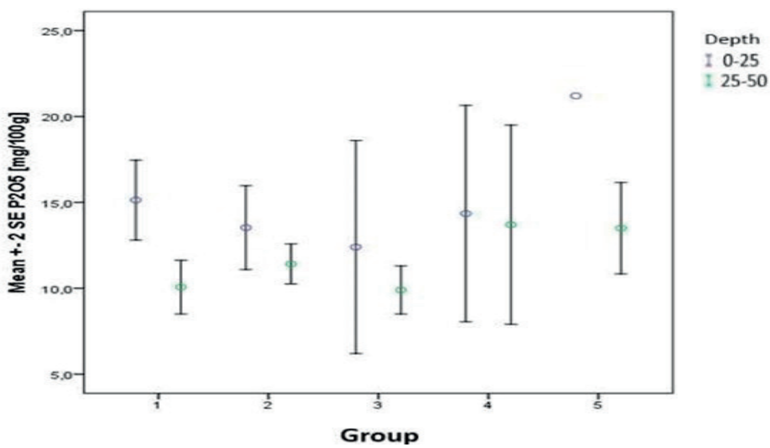

Figure 2. Phosphorus content by depth in the individual soil groups

Influence of the topographic factors of the terrain on the distribution of P_2O_5 in the soil

The influence of the topographic factor was studied by altitude, slope and exposure (location of the soil sampling point).

The influence of altitude within the boundaries of the soil catena is expressed in meters above sea level and was established by regression analysis (Goovaerts, 1992). A tendency to exceed the P_2O_5 content in the total statistical sample is considered to be proven at a probability level of 95% (F. 6.9), as the sampling depth normalizes nearly a quarter (24.2%) of P_2O_5 variation into the studied soils in total. This was the reason for further study in the dynamics of the main studied feature, the samples collected from different depths to be considered as separate statistical subsamples. In order to determine the representativeness of the subsamples normalized from the soil samples, collected at a depth of 0-25 and 25-50 cm, it was necessary to study their frequency distribution, as a preliminary mathematical expectation was that they were distributed in the normal frequency range. The results are shown as frequency histograms in Figure 3.

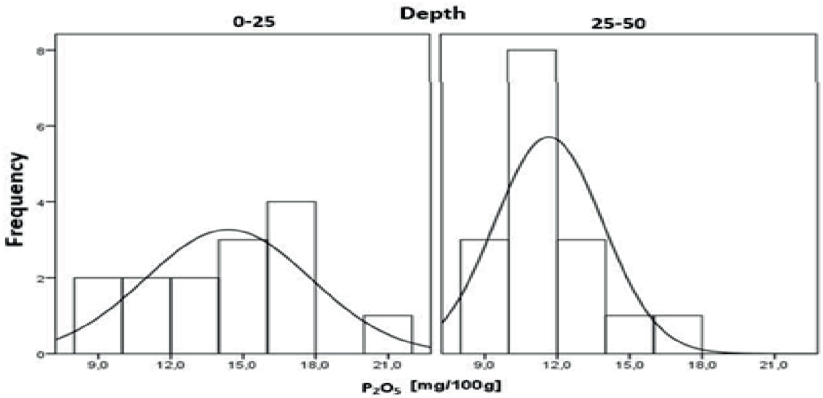

Figure 3. Histogram of the frequency distribution of phosphorus in the individual depths

Although the histogram for the frequency distribution of the amount of P_2O_5 at a depth of 50 cm showed more convincingly the approximation of the experimentally established frequency distribution to a normal frequency distribution, according to the results of the nonparametric K-S test, both distributions in the subsamples at depth 0-25 and 25-50 cm were reliably approximated to normal frequency distributions with a probability level of 95%.

Table 2. Pearson Correlation analisys - groupped mean for depth 0-25 cm

Correlations[a]

		P_2O_5 [mg/100 g]	OZ	OX	OY
Pearson Correlation	**P_2O_5 [mg/100 g]**	1.000	0.623	0.579	0.660
	OZ	0.623	1.000	0.875	0.940
	OX	0.579	0.875	1.000	0.859
	OY	0.660	0.940	0.859	1.000
Sig. (1-tailed)	**P_2O_5 [mg/100 g]**	.	0.009	0.015	0.005
	OZ	0.009	.	0.000	0.000
	OX	0.015	0.000	.	0.000
	OY	0.005	0.000	0.000	.
N	**P_2O_5 [mg/100 g]**	14	14	14	14
	OZ	14	14	14	14
	OX	14	14	14	14
	OY	14	14	14	14

a. Weighted Least Squares Regression - Weighted by Group

Table 3. Pearson Correlation analisys - ungroupped mean for depth 0-25 cm

Correlations

		P_2O_5 [mg/100 g]	OZ	OX	OY
Pearson Correlation	**P_2O_5 [mg/100 g]**	1.000	.348	.354	.487
	OZ	0.348	1.000	0.866	0.886
	OX	0.354	0.866	1.000	0.812
	OY	0.487	0.886	0.812	1.000
Sig. (1-tailed)	**P_2O_5 [mg/100 g]**	.	0.111	0.107	0.039
	OZ	0.111	.	0.000	0.000
	OX	0.107	0.000	.	0.000
	OY	0.039	0.000	0.000	.
N	**P_2O_5 [mg/100 g]**	14	14	14	14
	OZ	14	14	14	14
	OX	14	14	14	14
	OY	14	14	14	14

Table 4. Pearson Correlation analisys - groupped mean for depth 25-50 cm

Correlations[a]

		P_2O_5 [mg/100 g]	OZ	OX	OY
Pearson Correlation	**P_2O_5 [mg/100 g]**	1.000	0.465	0.289	0.415
	OZ	0.465	1.000	0.940	0.970
	OX	0.289	0.940	1.000	0.940
	OY	0.415	0.970	0.940	1.000
Sig. (1-tailed)	**P_2O_5 [mg/100 g]**	.	0.035	0.139	0.055
	OZ	0.035	.	0.000	0.000
	OX	0.139	0.000	.	0.000
	OY	0.055	0.000	0.000	.
N	**P_2O_5 [mg/100 g]**	16	16	16	16
	OZ	16	16	16	16
	OX	16	16	16	16
	OY	16	16	16	16

a. Weighted Least Squares Regression - Weighted by Group

Table 5. Pearson Correlation analisys - ungroupped mean for depth 25-50 cm

Correlations

		P_2O_5 [mg/100 g]	OZ	OX	OY
Pearson Correlation	**P_2O_5 [mg/100 g]**	1.000	0.509	0.355	0.460
	OZ	0.509	1.000	0.931	0.939
	OX	0.355	0.931	1.000	0.923
	OY	0.460	0.939	0.923	1.000
Sig. (1-tailed)	**P_2O_5 [mg/100 g]**	.	0.022	0.088	0.037
	OZ	0.022	.	0.000	0.000
	OX	0.088	0.000	.	0.000
	OY	0.037	0.000	0.000	.
N	**P_2O_5 [mg/100 g]**	16	16	16	16
	OZ	16	16	16	16
	OX	16	16	16	16
	OY	16	16	16	16

Dependence of P_2O_5 content on the location of the sampling points was determined by stepwise linear regression, in which the meter coordinates by OH (East-West), OU (North-South) and OZ (height) were successively entered as steps of the regression analysis (Cressie, 1993).
Measurements of the linear square grid as a result of the design of the mercator were neglected due to the small area of the object (Yost et al., 1982).
The statistical scattering of the sampling points along the OX axis was 1021 m, and along the OU-2867 m axis.

The Pearson correlation coefficients are shown in Tables 2-5. The complex influence of the location of the sampling point on the value of the studied indicator was studied with the help of variograms (Oliver & Webster 1986; Webster & Oliver, 1992), as the direction of the axis of the variogram coincides with the direction of the soil catena on the three axes.
The resultant direction of the soil catena was 150° in azimuth and it was set on the variograms of the studied P_2O_5. The results for the surface and subsoil horizons are shown in Figure 4 and Figure 5.

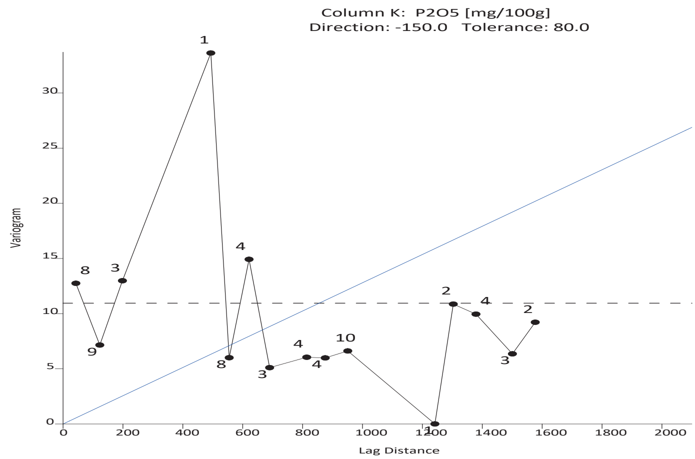

Figure 4. Variogram of the phosphorus content in the surface horizon

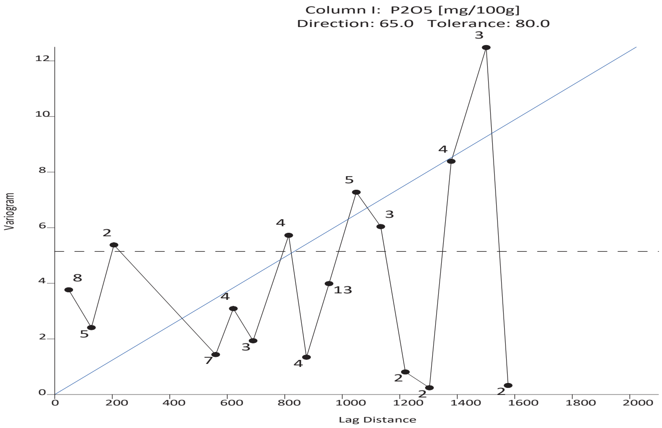

Figure 5. Variogram of the phosphorus content in the subsoil horizon

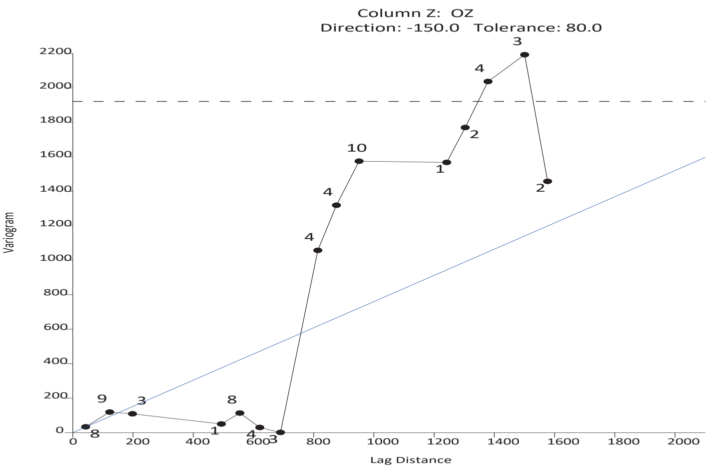

Figure 6. Variogram of the relief from the sampling points

Figure 6 shows the variogram of the relief, as along the Y axis is plotted the altitude at the sampling points and on average for the cluster groups. The increase of the variogram was interpreted as Gaussian, but with the increased of the sampling points it was more probable to be approximated to linear, as within the limits of X-Y there was no equalization of the function.

The distribution of P_2O_5 content within the same X-Y limits also showed a significant dispersion, but in all its other characteristics differs from the distribution of the hyxometric levels. It was studied at two depths 0-25 and 25-50 cm. The only thing between the variograms for the distribution of P_2O_5 in the two studied depths was the length of the log. It was the same for both variograms, about 800 m and represented about 1/3 of the length of the long axis of the X-Y polygon, in which the studied soil catena fits. In their other characteristics, the variograms for the distribution of P_2O_5 differ. The variogram of Figure 4 for the distribution of P_2O_5 in the surface soil layer showed angiotropicity and a certain tendency for cyclical distribution, which however was not proven. It can be argued with the greatest certainty that the content of P_2O_5 in the surface layer did not depend on the location, but at the same time it changes strongly, probably due to other factors. In the deeper layer, regardless of the high dispersion, closer results were found at closer points at a total length of the logs up to 800 m. At a total log over 800 m the total dispersion increased, but some observations were not in accordance with this conclusion, saturation was not established. Probably, with the increase in the number of observations, the variogram for the deep soil layer will be able to be approximated as Gaussian and thus to be identified by type with a variogram showing the change of the hyxometric levels. The influence of the topographic factor within the soil catena was studied by multiple stepwise linear regression, as independent variables were introduced the height, the slope (in any direction expressed as əh/ə (x, y), at the point of sampling and exposure in degrees around the azimuth circle.

Significance for the change in P_2O_5 content was only the height of the terrain from which the sample was taken, at a level of extrapolability to the limits of the soil catena. The data did not differ for the surface and the subsoil horizon. The results are presented in Table 6.

Table 6. Linear regressions for the change of phosphorus content depending on the height, slope and exposure in the surface and subsoil horizon

Model Summary[b,c]

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics					Durbin-Watson
					R Square Change	F Change	df1	df2	Sig. F Change	
1	0.623[a]	0.388	0.337	5.0246	0.388	7.607	1	12	0.017	1.993

a. Predictors: (Constant), OZ
b. Dependent Variable: P_2O_5 [mg/100 g]
c. Weighted Least Squares Regression - Weighted by Group

ANOVA[a,b]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	192.056	1	192.056	7.607	0.017[c]
	Residual	302.963	12	25.247		
	Total	495.019	13			

a. Dependent Variable: P_2O_5 [mg/100 g]
b. Weighted Least Squares Regression - Weighted by Group
c. Predictors: (Constant), OZ

CONCLUSIONS

Based on the study, the main conclusions that can be formulated were that the content of P_2O_5 in the surface layer did not depend on the location, but at the same time changes greatly under the influence of a number of other factors. As diagnostic in terms of the distribution of naturally assimilate phosphorus in the soil should be considered the deep subsoil horizon, in which the geological distribution of P_2O_5 was not affected by its biological dynamics. In order to build a reliable distribution model, soil samples must be taken in a geographical network at equal distances along the X-Y axis and taking into account the height of the sampling point.

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