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PHOSPHATE ADSORPTION ON SOILS IN THE GURGHIU AND HARGHITA MOUNTAINS, ROMANIA

György FÜLEKY* & Sámuel JAKAB**
**Szent István University, 2103 Gödöllő, Páter Károly u. 1., Hungary*
fuleky.gyorgy@mkk.szie.hu
***Sapientia EMT, Tg. Mureş, Romania* jakab.bocskai@rdslink.ro

Abstract: Phosphate adsorption on soils in the Gurghiu and Harghita Mts., Romania. Ten soil profiles from the Mezőhavas region of the Gurghiu Mountains and ten from the Vf. Madarasi Tető region of the Harghita Mountains were investigated by taking samples from the various horizons of each profile, leading to a series of 39 soil samples from Gurghiu and 37 from Harghita. In the course of the work the rate of phosphate adsorption on the soils was determined, and correlations were sought between chemical soil properties and the rate of adsorption. The maximum adsorption rate was calculated with the help of the Langmuir isotherm, and numerous other soil properties were examined in order to determine which parameters were correlated with the rate of phosphate adsorption. Among the soil properties, the oxalate-soluble Al and Fe contents, i.e. the non-crystalline Al and Fe oxyhydroxides, proved to be in close, positive, approximately linear correlation with the phosphate adsorption rate for both groups of soils. In addition, phosphate adsorption exhibited a close, negative, exponential correlation with the quantity of exchangeable cations, and a positive linear correlation with the pyrophosphate-soluble Al, i.e. that bound to organic matter.

Key words: Soil profiles, Gurghiu Mts., Harghita Mts., Phosphate adsorption, Exchangeable cations, Organic matter, Langmuir isotherms

1. INTRODUCTION

Within the framework of the COST 622 European volcanic soils project and a Sapientia research project, investigations were made on soils formed on andesite rock in the Gurghiu and Harghita Mountains, including the occurrence of various soil types and factors causing changes in the soil cover. In both locations soil series consisting of ten soil profiles were sampled, and it was found that acidic, non-podzolic, brown forest soils were most frequently formed at heights of below 900 m above sea level, while andosols were generally formed above this height, (Jakab et al. 2005). These latter soils were formerly thought to be formed mostly on young volcanic rocks, so the discovery of typical andosols in the present work was somewhat surprising. Various criteria have been recorded for the existence of this soil type, including the adsorption of at least 70% of the substantial 5000 mg/kg phosphorus load. Previous studies showed that the high rate of phosphate adsorption in andosols could be attributed primarily to allophane, but a substantial role was also thought to be played by the oxalate-soluble Fe and Al contents and by the pyrophosphate-soluble Al content, bound to organic matter, (Füleky, 2004). It is a well-known fact that $H_2PO^{-}_4$ and HPO^{2-}_4 ions have a great affinity for soil components, to which they are specifically adsorbed. Consequently, in the course of the present work phosphate adsorption was examined in a higher concentration range in order to give a more accurate estimation of the phosphate adsorption capacity of the soils. A further aim was to investigate the role of chemical soil properties in phosphate adsorption.

2. METHODS

Ten soil profiles taken from the Mezőhavas region of the Gurghiu (Görgényi) Mountains and ten from the Vf. Madarasi Tető region of the Harghita (Hargita) Mountains at heights between 700 and 1800 m were investigated in the present work. A total of 39 samples were taken from the various horizons of the Gurghiu profiles and 37 from the Harghita profiles for chemical and physical analyses. Measurements were made on the following parameters: pH_{H2O}, pH_{KCl}, pH_{NaF}, humus, loss on ignition, exchangeable cations, oxalate-soluble, pyrophosphate-soluble and dithionite-soluble Si, Fe and Al, clay, sand and silt fractions, and bulk density (Mizota & Reeuwigh, 1989).

To measure phosphate adsorption, 1 g soil samples were shaken with 0, 50, 100, 500, 1000, 3000, 5000 and 10,000 mg kg^{-1} P solution for 24 hours. After filtration and centrifugation the phosphorus content was determined with a spectrophotometer. The following Langmuir equation was fitted to the data: $P_{ads} = P_{max} \cdot kc/1+kc$, where P_{max} is the maximum quantity of adsorbable phosphate, k the equilibrium constant and c the concentration of the equilibrium solution in mg dm^{-3}.

3. RESULTS

The major soil properties are presented in Table 1. The highest and lowest values recorded for a total of 76 samples are included in the table.

Table 1. Minimum and maximum values of soil properties recorded for soil series from the Gurghiu and Harghita Mountains (n = 76)

	Min.	Max.	Mean values		
			Arithmetic	Geometric	Median
Oxalate-soluble Al %	0.21	6.41	2.13	1.50	1.90
Oxalate-soluble Fe %	0.10	4.68	1.19	0.95	1.01
Pyrophosphate-soluble Al %	0.01	4.83	1.40	0.93	1.18
Pyrophosphate-soluble Fe %	0.01	5.05	1.07	0.67	0.83
Dithionite-soluble Al %	0.16	5.85	1.97	1.45	1.79

Dithionite-soluble Fe %	0.08	5.70	2.13	1.87	1.97
Oxalate 1/2Fe+Al %	0.43	7.09	2.73	2.18	2.76
Exchangeable K cmol/kg	0.03	0.75	0.30	0.27	0.27
Exchangeable Na cmol/kg	0.01	0.98	0.22	0.04	0.02
Exchangeable Mg cmol/kg	0.025	5.19	0.60	0.21	0.18
Exchangeable Ca cmol/kg	0.01	13.89	1.82	0.57	0.61
Exchangeable cations cmol/kg	0.28	19.99	2.87	1.44	1.41
CEC cmol/kg	11.33	82.08	36.2	32.2	31.8
pH_{H20}	3.13	6.02	4.62	4.58	4.64
pH_{KCl}	2.81	5.07	4.16	4.13	4.24
pH_{NaF}	6.66	12.25	9.82	9.69	10.1
Organic C %	0.41	35.74	8.31	5.54	5.62
Pmax mg/kg	1593	13800	6876	6131	7349

All the soil properties listed were used to classify the soils. It is clear from the table that the maximum quantity of adsorbable phosphate exhibited an extremely wide range of values (1593–13800mg P/kg soil). Considering the fact that extreme analytical values were found for both soil series, it is obvious that very diverse soil types occurred among the samples tested.

Table 2 presents the maximum values of adsorbable phosphorus content. Together with the three series of data that had the greatest influence on the quantity of phosphorus that could be adsorbed.

Table 2. Maximum phosphate adsorption capacity of the Gurghiu and Harghita soils

Harghita	P_{max}	Al p.	ox. 1/2Fe+ Al	Exchange cations	Gurghiu	P_{max}	Al p.	ox1/2 Fe+Al	Exchange cations
	mg/kg	%	%	cmolkg^{-1}		mg/kg	%	%	cmolkg^{-1}
Au	5316	0.6	0.8	3.33	Au	5448	1.2	2.0	2.40
Bv	13800	4.8	7.1	0.46	AB	9218	2.4	3.8	1.35
Au	8699	2.3	3.4	0.33	Bs	9045	2.1	4.1	1.34
A/B	9752	3.6	4.4	0.28	Au	6406	1.0	1.7	2.24
Bv	8021	0.1	3.4	0.28	Bs	9907	4.3	5.4	2.03
A0	8490	1.2	2.1	2.54	Bv_1	7367	1.7	3.6	1.96
Au	7348	1.6	3.1	0.60	Bv_2	7181	1.1	3.7	2.21
A/B	8673	2.2	1.0	0.49	Au	12600	2.7	4.0	2.77
Bv	8490	1.3	3.7	0.63	AC	8950	2.1	4.9	2.20
A0	3521	0.4	0.6	6.44	C/R	5601	0.9	3.6	2.07
Au	6482	1.2	2.4	0.51	Au	3994	0.6	0.8	4.57
A/B1	9101	3.0	4.1	0.32	Au	6551	1.4	1.8	1.91

A/B2	8127	2.1	3.3	0.35	Ao	8396	2.7	3.2	1.13
BR	12700	1.0	2.7	0.34	AB	7901	1.4	3.2	1.06
Au	5130	0.6	1.1	1.37	Bv_1	7351	0.1	3.2	0.58
A2	6911	1.6	2.7	0.43	Bv_2	6532	0.6	2.4	1.22
B1	8071	2.1	3.1	0.34	Au	1054 0	3.6	4.3	1.05
B2	6351	0.9	2.1	0.33	Bv	8941	1.7	5.0	1.13
A0	5099	0.5	1.0	2.06	A	7373	1.9	1.9	5.28
A	4920	0.8	1.4	0.44	Bv	9481	2.3	5.7	2.99
Bv	7236	1.4	2.9	0.35	Bv	7617	1.3	3.3	2.15
Bv2	7645	2.4	3.0	0.34	Au	2146	0.3	0.8	12.57
2A/B2	7157	1.2	2.6	0.34	AB	1983	0.2	0.8	12.41
2Bv	6882	1.2	1.9	0.36	BvR	1594	0.2	0.7	12.29
0	3530	0.7	1.3	1.95	Ao	2879	0.5	0.9	6.38
A	6784	1.6	2.5	0.66	Ao	2749	0.6	0.6	5.03
B1	8243	2.2	3.8	0.38	ABv	1898	0.4	0.7	8.93
B2	5988	1.7	3.7	0.36	Bv	1776	0.3	0.6	11.34
II/B	8071	1.3	3.4	1.71	Au	6900	1.3	1.9	2.45
III/A	7659	1.1	2.8	0.49	Bs	1150 0	3.0	5.6	1.52
III/B	8053	0.6	3.5	0.50	Bv_1	8514	1.2	5.9	1.43
III/R	5429	0.0	0.8	1.48	Bv_2	7958	0.8	5.6	1.04
A	1999	0.2	0.7	8.89	B/R	8047	0.7	5.4	1.62
A/B	1799	0.2	0.6	2.91	Au	8144	1.7	2.1	2.46
B	2345	0.2	0.5	13.21	Bs	1200 0	3.9	4.4	0.95
20-40	2044	0.2	0.4	12.73	Bv	8019	1.0	4.3	1.40
100	2372	0.5	0.5	19.99	Au	5497	0.8	1.3	3.12
					Bs	9237	3.3	3.6	0.37
					Bv	7136	1.2	2.6	0.87

These are the oxalate soluble iron and aluminium contents and the pyrophosphate-soluble Al content and the quantity of exchangeable cations.

It is clear from table 2 that high P_{max} values were generally associated with high pyrophosphate-soluble Al contents and high oxalate-soluble Al and Fe contents. The $1/2Fe_o+Al_o$ value must be greater than 2% for classification as andosol. The table shows that this condition was satisfied by the soils with high phosphate adsorption capacity. In the case of pyrophosphate-soluble Al there is no limit value for andosol, but it is clear that samples with andic properties, i.e. high phosphate adsorption capacity have high values of this parameter (Fig. 1).

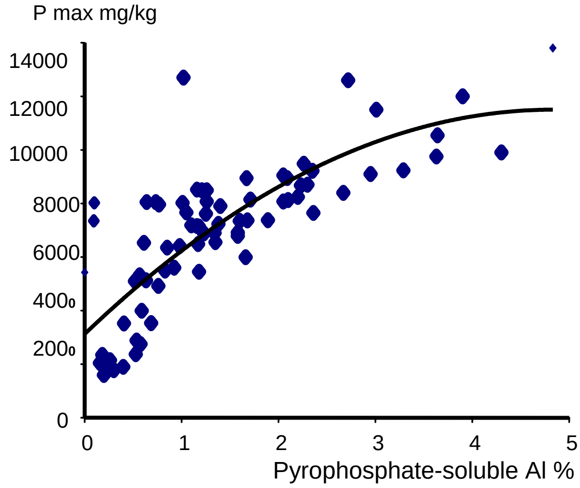

Fig. 1. Correlation between the phosphate adsorption capacity of the soil and the pyrophosphate-soluble Al content (polynomial)

These samples also have high values of organic C% and low quantities of exchangeable cations (Fig. 2).

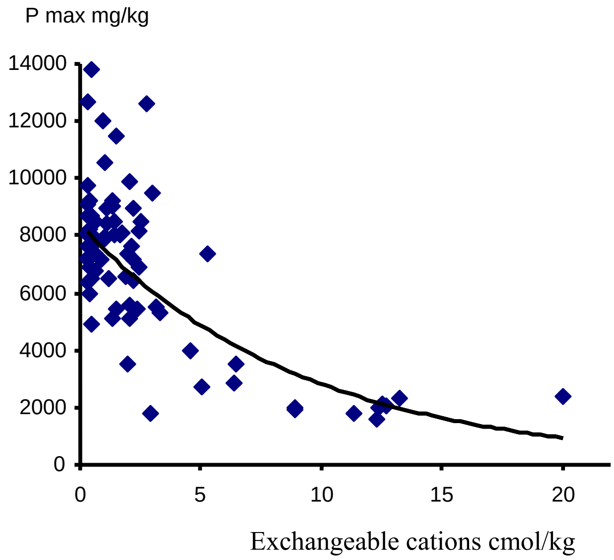

Fig. 2. Correlation between the phosphate adsorption capacity of the soil and the quantity of exchangeable cations (exponential)

Figure 2 indicates that there is a great increase in the level of phosphate adsorption at exchangeable cation values below 2 cmol kg^{-1}. In such cases the exchangeable cations are replaced by H^{+} and Al^{3+} ions. thus increasing the affinity of the soil for phosphate. Figure 3 illustrates the correlation between the parameter that provides proof of andic properties ($1/2Fe_o+Al_o$ %) and the phosphate adsorption capacity of the soil.

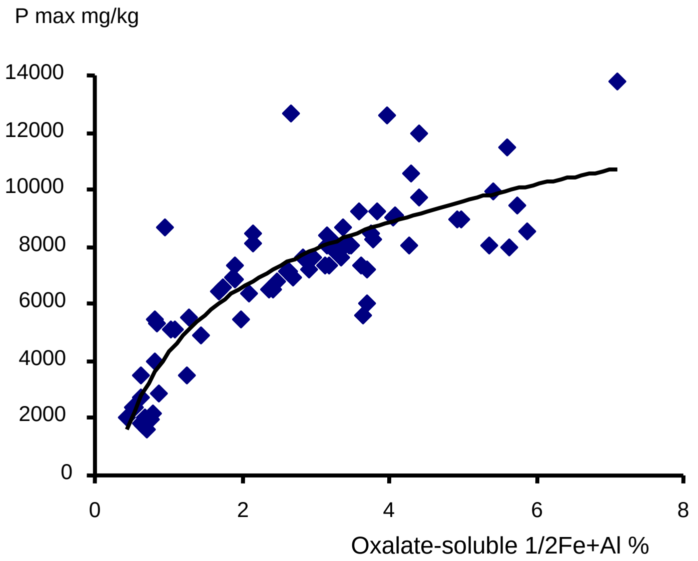

Fig. 3. Correlation between the phosphate adsorption capacity of the soil and the oxalate-soluble Fe and Al content (logarithmic)

It is clear from the figure that most of the soils exceeded the 2% limit, with the exception of the acidic. non-podzolic brown forest soils. A linear correlation also gave a good description of the correlation between the two parameters. but the R^2 value was higher. It can be concluded from the figures that the 5000 mg/kg value prescribed for phosphate adsorption analyses was exceeded by many of the soils; the greater the oxalate-soluble Fe and Al content of the soil and the quantity of pyrophosphate-soluble Al bound to organic matter, and the smaller the quantity of exchangeable cations. the greater the level of phosphate adsorption. If the correlations between other soil properties and the phosphate adsorption capacity are considered (Table 3). it can be seen that in general there was a negative correlation not only with the total quantity of exchangeable cations. but also with the individual cations.

Table 3. Correlations between phosphate adsorption and chemical soil properties

Soil property	Correlation	R^2
Exchang. K	Linear	0
Exchang. Na	Linear	0
pH_{KCl}	Linear	0.0062
CEC	Logarithmic	0.0507
pH_{H2O}	Linear	0.0635
Pyr. Fe	Linear	0.0903
Dith.Fe	Linear	0.0953
Organic C %	Linear	0.0114
Ox. Fe	Linear	0.126
Exchang.cations	- Power	0.5243
pH_{NaF}	Linear	0.5421
Exchang. Mg	- Power	0.5567
Ox. Al	Linear	0.5585
Pyr. Al	Linear	0.5959
Exchang. Mg	- Exponential	0.6222
Pyr. Al	Polinomial	0.6306
Exchang.cation	- Exponential	0.6433
Exchang. Ca	- Exponential	0.6586
1/2Fe+Al	Linear	0.6689
Ox. Al	Logarithmic	0.6829
Dith Al	Logarithmic	0.7114
Ox. 1/2Fe+ Al	Logarithmic	0.7461

In addition to the oxalate-soluble and pyrophosphate-soluble Al and Fe contents, the dithionite-soluble Fe and Al contents, which are generally correlated with the former, also exhibited a close positive correlation with the level of phosphorus adsorption. It was interesting to note that in general pH was not correlated with phosphate adsorption. If these correlations are considered for the separate regions, for example for the Gurghiu soils alone, a substantial correlation could also be observed for organic C. The dithionite-soluble Al content also exhibited the closest correlation with phosphate adsorption for these soils.

4. Conclusions

With the help of Langmuir adsorption isotherms it was concluded from phosphate adsorption analyses that andosols were capable of adsorbing substantial quantities of phosphorus. Sometimes in excess of 10000 mg/kg. Members of the soil series found at lower altitudes, which were acidic, non-podzolic brown forest soils, generally adsorbed smaller quantities of phosphate, similarly to the volcanic soils found on arid regions of Hungary (Füleky, 2004). The andosols generally formed under wetter conditions at higher altitudes adsorb larger quantities of phosphate. The maximum adsorbable phosphorus quantity for the volcanic soils of the Gurghiu and Harghita Mountains, calculated using the Langmuir isotherm. was in close positive correlation with the quantities of pyrophosphate-soluble Al and oxalate-soluble Al and Fe. A close non-linear negative correlation was also found between the phosphate adsorption of the soil and the total quantity of exchangeable cations. In summary, it can be stated that soils in the higher regions of the Gurghiu and Harghita Mountains are able to adsorb substantial quantities of phosphate due to their andic properties. This high rate of adsorption can be attributed chiefly to the quantity of oxalate-soluble, non-crystalline and organically bound pyrophosphate-soluble iron and aluminium oxyhydroxides. but Al and Fe ions on the surfaces of crystal lattices are also involved in adsorption.

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