Byulleten Pochvennogo instituta im. V.V. Dokuchaeva. 2015. Vol. 78.

THE ROLE OF ORGANIC AND ORGANOMINERAL COMPONENTS IN THE FORMATION OF THE PHOSPHATE REGIME IN PLOUGH HORIZONS OF EROSION-DEGRADED AGRO SODDY-PODZOLIC SOILS

Z. S. Artemieva

V.V. Dokuchaev Soil Science Institute, 119107 Moscow, Pyzhevskii 7, bld. 2

The soil organic matter is one of the factors affecting the phosphate ionic sorption of soils. Of special interest is the study of sorption characteristics of organomineral relationship products in soil. The organic-clayey (clay fractions) and organic (light fractions) complexes play the most important role in developing the soil phosphate regime. Under study was the phosphate state in plough horizons of erosion-degraded agro soddy-podzolic soils as based upon the parameters of the phosphate-ionic sorption in different components of the organic matter. The organic and organomineral fractions of plough horizons in soils that were not subjected to water erosion are characterized by a high level of phosphorus mobility and the capacity to provide a constant amount of phosphates available for plants (P_{mob} is 17.95±2.06 mg/kg of soil), the low sorption capacity to phosphate-ions (P_{sorp} is 96.06±0.53 mg/kg of soil). Agro-ecological peculiar features of eroded soils are the increased sorption of phosphate-ion (P_{sorp} becomes higher by more than 2 times) and the low level of available phosphorus (P_{mob} is declined almost by 2 times) as compared to those in uneroded soils. The processes of sediment accumulation promote some improving the soil sorption parameters, what is manifested in increasing the amount of mobile phosphorus in the soil solution and in decreasing the phosphorus sorption by the soil solid phase. In this case P_{mob} is increasing by more than 20% in washed-out soils, whereas P_{sorp} becomes decreased by 1%.A set of parameters for the phosphate-ionic sorption of organomineral components in the studied soils with different elementary soil structures may serve as an informative system for estimating the phosphate regime in erosion-degraded agro soddy-podzolic soils.

Keywords: organic and organic-clayey complexes of soil, one-point isotherm of phosphorus sorption, soil erosion.

INTRODUCTION

The total content and forms of nutrient compounds in soil and the phosphate compounds in particular are closely associated with soil formation processes and can serve as a diagnostic feature of the soil development degree [1, 11].

The problem relating to changes in the nutrient state of soils subjected to erosion processes and determination of diagnostic features for assessing their level remains very acute in agriculture [1]. It is known that the organic matter is considered as one of the factors affecting the phosphate-ionic sorption in soil. However, the role of some factors and mechanisms responsible for the sorption properties in soils intensively used in agriculture is open so far to discussion [6].

The study of sorption characteristics for products of the organomineral interaction in soil is of great interest. The organic-clayey (clay fractions) and organic (light fractions) complexes play the most important role in the formation of the phosphate regime in soil. The light fractions are slightly stable to binding the phosphate-ion as compared to the organic-clayey complex [3, 15]. Organic and organic-clayey complexes provide a vital soil property – the fertility, being the most important component of the soil absorbing complex (SAC). Just SAC as a *system of organomineral particles* is a significant chain in determining the soil stability to different adverse effects including erosion, inappropriate management of soils, etc. [16]. In view of this, it is promising to use the characteristics of organomineral fractions in eroded soils as additional diagnostic features of erosion processes. The heterogeneous soil cover on different relief elements serves as evidence of varying indices for the phosphate regime in soils on slopes.

The available extraction techniques to determine the phosphorus supply in soils are found to be insufficiently informative because they do not allow taking into complete account peculiar features of soils connected with the nutrient fixation [1, 3, 9]. A great diversity of such methods presents some difficulties for comparative assessing the nutrient content in soils of different genesis and evolution stages in anthropogenesis. These shortages are especially manifested in using a landscape approach to the estimate of the soil fertility because the soil cover reveals a combination of soils with quite different properties. The diagnosis improvement of the phosphate regime in soil may be reached by means of physical-chemical methods including the study of sorption kinetics of phosphate-ion exemplified by isotherms of phosphorus sorption. This method has an advantage over extraction techniques and permits to compare the soils with different properties but it is rather labor-intensive. By this reason, Jones and Fox (1977) suggested a single point sorption test. This is a very simplified procedure to create the sorption isotherm using two points, one of which is zero. The isotherm of phosphorus sorption makes it possible to determine a set of parameters including the concentration of the equilibrium solution C_{equal} to characterize the phosphorus amount available for plants; the amount of absorbed phosphorus P_{sorb}; the negative part of the sorption isotherm shows a quantity of labile phosphorus P_{mob} in the equilibrium solution as well as the soil buffering capacity (SBC^{P}) with respect to phosphate-ions that characterizes the soil ability to support the P concentration in the solution at a constant level (it is detected by tangent of inclination angle to abscissa axis). Thus, the single point sorption isotherm should be considered as an informative express-test for routine determination of phosphate-ion sorption parameters [7, 8].

The present paper is aimed to show the investigation results of the phosphate regime in agro soddy-podzolic soils using the physical-chemical methods.

OBJECTS OF RESEARCH

The objects of research in the phosphate regime of soils developed on different relief elements are agro soddy-podzolic soils at the territory of Zelenogradskiy experimental station of the V.V. Dokuchaev Soil Science Institute. 3 key sites were taken along transect of agro soddy-podzolic soils on slopes, the profiles of which have been earlier described in detail [12, 14]. The key sites are located in the north-eastern part of the Moscow region, in the centre of the Russian plain within the Moskva river basin.

The modification of granulodensimetric method was used to extract the organic and organic-clayey complexes [5, 13]. The fine fractions from soil samples were extracted according to the simplified scheme by means of bromoform-ethanol mixture of 2.0 g/cm^3. The clay was removed from soil samples preliminary treated by ultrasound for 15 min. The carbon content was determined by wet combustion method

[2]. The single point sorption test was used for determination of phosphorus. To create a single point sorption isotherm, two air-dry soil bases were mixed with 0.01 M $CaCl_2$ (1 : 100) in 2 test-tubes, one of which was added with KH_2PO_4. The given express-method was approbated and specified for determining the different groups of organic and organomineral components in soil. To create the second point of isotherm for phosphate-ion sorption, some experiments were carried out to find an optimal concentration of the added phosphorus equaled to 15 mkg P/ml [3].The soil suspension treated by ultrasound for 3 min remained for 12 hours and centrifuged for 10 min at the velocity of 3000 revs per min. The colorimetric analysis was made to determine the P concentration in the soil equilibrium solution. The amount of absorbed phosphorus was calculated according to the difference of its content in initial and equilibrium solutions. Two pints were taken to create the isotherm, the first of which is zero to detect the amount of labile phosphorus in the equilibrium solution.

RESULTS AND DISCUSSION

The amount of components in the soil absorbing complex (SAC) makes up 16.87± 0.6% in the studied soils (Table 1), the share of clay fractions is estimated at 15.0 ± 0.87% and light fractions – 1.87 ± 0.4%. The SAC components are represented by fine-dispersed particles as compared to the residue fraction, in which the coarse-dispersed and crystalline oxides are dominant to be a limitation for their absorbing capacity. The study of sorption parameters for SAC components and the residue fraction showed that the equilibrium concentration C_{equal} of phosphorus in 0.01 M $CaCl_2$ accounts for 1.01 ± 0.1 mkg P/ml in organic-clayey SAC components (clay fractions) of noneroded agro soddy-podzolic soils. The development of erosion processes promotes decreasing C_{equal} to 0.16 mkg P/ml, whereas this value becomes increased to 0.8–0.85 mkg P/ml in strongly eroded soils. There is a direct dependence between the P concentration in equilibrium solution and carbon concentration in clay fractions: $r = 0.94$ at $P = 0.006$ (Fig.1).

Thus, the clay fractions of the studied soils reveal a sharply expressed decrease in the equilibrium phosphorus concentration due to the development of denudation processes. This is explained by the fact that the intensity of these processes leads to exposing the deep soil

Table 1. Content, properties and parameters of phosphate-ion sorption by soil components

Soil components	Content of soil components, % from the soil mass	C org, % from the fraction mass	C_{equal}, mkgP/ml	P_{mob}	P_{sorp}	SBC^p, ml/g
				mkgP/g		
			Eroded soils			
Clay fractions	15.0 ± 0.87	3.76 ± 0.25	1.01 ± 0.1	45.0 ± 5.8	378.3 ± 11.5	0.91
Light fractions	1.87 ± 0.40	20.58 ± 4.30	3.2 ± 0.5	60.0 ± 5.0	81.25 ± 8.8	0.21
Residues	82.47 ± 1.25	0.41 ± 0.09	1.37 ± 0.3	13.8 ± 2.5	38.2 ± 0.9	0.11
			Washed-out soils			
Clay fractions	20.73 ± 3.42	2.23 ± 0.49	0.16	10	756	1.60
Light fractions	0.88 ± 0.13	16.11 ± 5.6	2.76 ± 0.08	55	105	0.47
Residues	78.18 ± 3.64	0.27 ± 0.10	0.77	7.3 ± 0.1	65	0.16
			Washed-out – in-washed soils			
Clay fractions	15.45 ± 1.06	3.29 ± 0.44	0.8	35.0 ± 7.1	457.0 ± 15.5	1.00
Light fractions	1.45 ± 0.46	19.54 ± 3.16	Non			
Residues	83.1 ± 1.16	0.40 ± 0.20	1.0 ± 0.1	9.0 ± 1.4	57.5 ± 5.6	0.12
			In-washed soils			
Clay fractions	14.0 ± 0.57	4.04 ± 0.08	0.85	47.5 ± 3.5	422.5 ± 6.4	1.15
Light fractions	2.35 ± 0.5	22.14 ± 7.97	3.61 ± 1.06	75	85	0.47
Residues	83.65 ± 1.06	0.71 ± 0.15	1.1	15	61.5	0.16

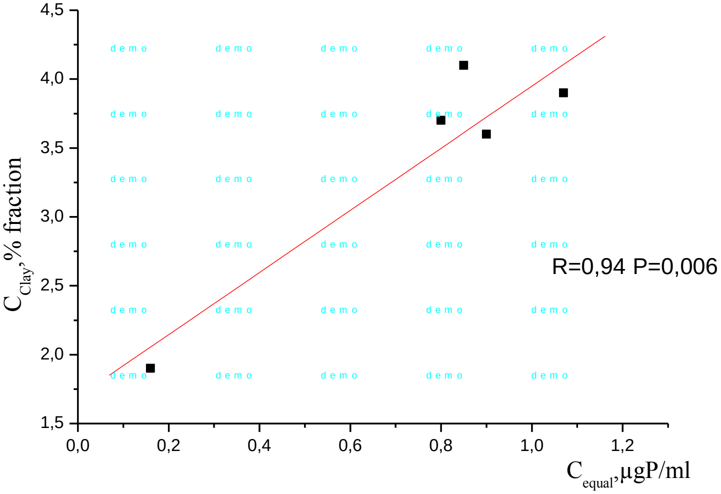

Fig.1. The dependence graph of C_{equal} and C_{clay} (% fraction)

horizons which are low in humus and enriched with smectite components, Fe and Al sesquioxides to increase the P-fixing capacity of soil. The higher is the soil outwash degree the lower is the value of phosphorus equilibrium concentration. The regularities in distribution of labile P in clay fractions are identical to those inherent to C_{equal} in differently sloping soils.

The P amount accumulated in the solid phase from the fertilized soil was calculated using 5 mkg/ml of the equilibrium concentration. The clay fractions of noneroded soils as well as those subjected to out- and inwash revealed the P_{sorb} amount accounting for 375.0 ± 14.14, 457.0 ± 15.55 and 422.5 ± 64.35 mkg P/g respectively. The clay fractions of eroded soils averaged 820.5 ± 91.22 mkg P/g. The amount of phosphorus absorbed by the solid phase of clay fractions is well correlated with the carbon concentration in the soil clay fraction ($r = –0.92$ at $P = 0.009$) (Fig. 2). The soil buffering capacity (SBC^P) is rather low in clay fractions of noneroded soils (0.91ml/g) being reached its maximum (1.6 ml/g) in eroded ones. The soils subjected to out-and in-wash are characterized by SBC^P values ranging from 1 to 1.15 ml/g respect-

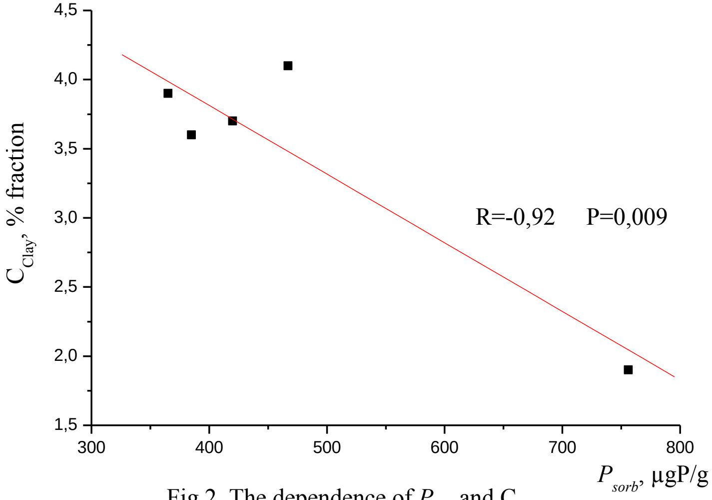

Fig.2. The dependence of P_{sorb} and C_{Clay}.

tively. The parameters for sorption-desorption of phosphate-ions in organic SAC components (light fractions) in which the organic matter has no stable chemical links with clay minerals differ from those for organic-clayey components and display a higher C_{equal} value as compared to that in clay fractions. In noneroded soils it makes up 3.2 ± 0.5 mkg P/ml, being decreased to 2.76 ± 0.08 mkg P/ml in washed-out soils and increased to 3.61 ± 1.06 mkg P/ml in soils subjected to in-wash. The P_{mob} value in light fractions of noneroded soils averages 60.0 ± 5.0 mkg P/g and decreases to 55 mkg P/g due to intensifying the erosion processes, thus reaching 75 mkg P/g in in-washed soils. The P amount accumulated in the solid phase of light factions was determined using 5 mkg P/ml of equilibrium concentration. The P_{sorb} value was 81.25 ± 8.8 mkg P/g in unwashed-out soils and increased to 105 mkg P/g in washed-out ones. It results from this that the light fractions are characterized by SBC^{p} values which are rather low as compared to those in clay fractions (0.21 in noneroded soils and 0.47 in washed-out soils). Consequently, as distinct from clay fractions the light fractions enable to remove phosphate-ion into the solution and have no capability to their sorption.

The C_{equal} value in the residue fraction of noneroded soils is estimated at 1.37 ± 0.3 mkg P/ml being decreased to 0.77 mkg P/ml in washed-out soils. In soils subjected to out-and in-wash it accounts for 1.0 ± 0.1 and 1.1 mkg P/ml respectively. The residue fraction reveals the lowest P_{mob} value, makes up 13.8 ± 2.5 mkg P/g in noneroded soils and decreases to 7.3 ± 0.1 mkg P/g due to erosion process. The P_{sorb} value in this fraction is also low and reaches 38.2 ± 0.9 mkg P/g in noneroded soils being somewhat increased to 65.0 mkg P/g in washed-out soils. The SBC^{P} value in the residue fraction of noneroded soils is 0.11 mkg P/g and 0.16 mkg P/g in soils subjected to outwash.

Thus, the study showed the clay and light fractions possess a higher absorbing capacity and enable to remove phosphorus into the solution as compared to the residue fraction, the latter being characterized by low values of soluble P, the low level of P accumulation in the solid phase, its buffering capacity is rather low as well.

The SAC components have a variable discharge capable to absorb anions, i.e. these components are responsible for governing the phosphate regime in soils as based upon sorption-desorption [3, 15]. This is evidenced by a high correlation between the phosphate-ion sorption and the organic matter content. It is worth emphasizing that the clay fractions are capable to retain phosphate-ions and incapable to remove them into the solution as compared to light fractions. In contrast to these components the changes in parameters characterizing the sorption isotherms of the residue fraction are not correlated with changing the sorption factors. Probably, when the quantity of light fractions is insufficient the distribution of soil phosphorus between the solid phase and the solution is predominantly regulated by precipitation-dissolution processes.

Having assessed the role of some soil components in the formation of soluble phosphates, it seemed reasonable to conclude that the contribution of SAC components is approximately equal to that inherent to the residue fraction and accounts for ≈44% from the amount of soluble P accumulated in soil (Table 2). It is worthy of note that the content of soluble phosphates in noneroded soils is governed by desorption from the SAC components and dissolution processes of their mineral compounds.

Table 2. The content of dissolved (P_{mob}) and sorbed phosphorus (P_{sorb}) in components of the studied soils

Soil components	P_{mob}		P_{sorb}	
	mg/kg of soil	% from P_{mob}	mg/kg	% from P_{mob}
Noneroded soils				
Clay fractions	6.53 ± 1.02	37.23 ± 10.41	54.37 ± 2.05	56.61 ± 2.44
Light fractions	0.98 ± 0.13	5.49 ± 1.02	2.57 ± 1.36	3.2 ± 0.66
Residue	10.44 ± 2.98	57.28 ± 10.38	38.61 ± 1.93	40.19 ± 1.78
Soil on the whole	17.95 ± 2.06		96.06 ± 0.53	
Washed-out soils				
Clay fractions	2.20 ± 0.36	20.59 ± 4.20	179.28 ± 9.48	78.03 ± 1.51
Light fractions	0.97 ± 0.64	4.44 ± 0.76	1.16 ± 0.74	0.51 ± 0.34
Residue	7.57 ± 0.16	70.46 ± 1.41	49.24 ± 1.05	21.46 ± 1.17
Soil on the whole	10.75 ± 0.44		229.97 ± 7.69	
Washed-out-in-washed soils				
Clay fractions	5.49 ± 0.72	32.69 ± 8.10	72.12 ± 2.71	59.65 ± 1.34
Light fractions	0.98 ± 0.13	7.34 ± 2.05	1.08 ± 0.01	0.89 ± 0.05
Residue	10.38 ± 2.91	61.04 ± 8.92	47.77 ± 4.54	39.45 ± 1.39
Soils on the whole	16.85 ± 20.30		120.98 ± 7.26	
In-washed soils				
Clay fractions	6.95 ± 0.22	34.02 ± 1.54	67.69 ± 8.83	56.40 ± 3.22
Light fractions	1.06 ± 0.53	5.65 ± 1.52	1.05 ± 0.13	0.89 ± 0.18
Residue	12.44 ± 0.3	60.84 ± 0.98	51.01 ± 0.13	42.70 ± 3.03
Soil on the whole	20.45 ± 0.28		119.76 ± 8.83	

The soil erosion is conducive to declining the role of SAC components (clay and light fractions) in accumulation of soluble phosphorus in soil (to 25% and more than by 1.7 times). The share of the residue fraction increases to 70% in noneroded soils. Due to agrogenically intensified erosion the amount of soluble phosphorus in soil is controlled by dissolution of mineral compounds to a greater extent as compared to desorption from the SAC components.

So, as distinct from clay fractions the light fractions are capable to restore the reserves of soluble phosphates to a considerable extent. This is explained by the fact that the phosphates are associated with the surface of their adsorbed phase by bond energy which is rather low for all the SAC components [4, 15]. However, their share in accumulation of soluble phosphates is not high and makes up only 13% from all the SAC components (Table 2).

Having estimated the role of definite soil components in P sorption, it follows that the contribution of SAC components in noneroded soils accounts for 59% from the total content of phosphorus absorbed by soil but due to erosion this contribution becomes increased to 78% and the share of the residue fraction is decreased to 21% against 40% in noneroded soils. It is possible to state that the phosphorus is accumulated in the solid phase of noneroded soils due to sorption processes which become considerably increased in the course of the erosion development because the exposed lower horizons of soils are low in the organic matter and enriched with the smectite component. The light fractions take part in P sorption to a lesser extent (from 0.5 to 3.2%) and contribute only to phosphate desorption.

Thus, the products of organomineral interaction provide a significant part of soil phosphates available for plants. The organic SAC components (light fractions) provide available phosphates due to soluble compounds which are released in the course of mineralization process to a lesser extent at the expense of exchange of ions in soil solution by ions of functional groups. The organomineral SAC components (clay fractions) take part in accumulation of available P due to sorption-desorption processes, whereas the residue fraction – due to dissolution-precipitation of mineral compounds.

The parameters for sorption of the phosphate-ion in organomineral fractions used ascriteria for assessing the phosphate regime serve as evidence of a high P mobility in noneroded soddy-podzolic soils: the P_{mob} value is averaged as 17.95 ± 2.06 mg/kg and P_{sorb} – 96.06 ± 0.53 mg/kg. They are characterized by a higher capability to support a constant level of phosphates available for plants. These soils can be regarded to those resistant to degradation [4]. The soils subjected to erosion are characteristic of unfavorable phosphate regime, high sorption with respect to phosphate-ion and their sorption characteristics are changed towards increasing the fixation of phosphate-ions and decreasing the amount of available P: P_{mob} – 10.75 ± 0.44 mg.kg, P_{sorb} – 229.97 ± 7.69 mg/kg. This is conditioned by exposed lower soil horizons which are low in humus content and the clay fractions of which are enriched with the smectite component promoting the increased amount of P absorbed by the soil solid phase. Consequently, the eroded (washed-out) soils are resistant to a lesser extent and the P turnover in them is not energetically balanced.

The processes of sedimentation promote the improvement of soil sorption parameters; this is manifested in increasing the amount of labile P in the solution and declining the P amount absorbed by the soil solid phase: P_{mob} in soils subjected to outwash and inwash – 16.85 ± 20.30 and 20.45 ± 0.28 mg/kg respectively and P_{sorb} – 120.98 ± 7.26 and 119.76 ±8.83 mg/kg. It is worth emphasizing that the soils con light d to lower part of slopes are often wet what is conducive to accumulation of the organic matter that exceeds the ecologically conditioned one. By this reason, although the studied soils are regarded to those resistant to degradation but they can threaten the environment and destroy the ecological equilibrium in landscape.

CONCLUSION

The organic and organomineral fractions of plough horizons in noneroded soils are characterized by a high level of P mobility and the capability to support a constant level of phosphates available for plants (P_{mob} – 17.95 ± 2.06 mg/kg) as well as by the low sorption with respect to phosphate-ion (P_{sorb} – 96.06 ± 0.53 mg/kg). Agro-ecological peculiarities of eroded soils are the increased sorption of phosphate-ion (P_{sorb} increases by more than 2 times) and the low level of P available for plants (P_{mob} decreases almost by 2 times) as compared to noneroded soils.

Thus, a set of parameters for phosphate-ion sorption in organomineral fractions of the studied soils with different elementary structures is a rather informative system for assessing the phosphate regime in erosion-degraded agro soddy-podzolic soils.

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