BEHAVIOR OF MINERALS IN AGRO-SODDY PODZOLIC SOILS RESULTED FROM DIFFERENT RATES OF ORGANIC FERTILIZERS

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The experimental results showed the influence exerted by different rates of organic fertilizers in the kind of poultry excrements on crystallochemical parameters of minerals containing in the fine-dispersed fractions (less than 1, 1–5, 5–10 mkm). The considerable changes induced by increased rates of organic fertilizers take place in the ratio between the basic mineral phases and the crystallochemistry of minerals of the clay fraction as the most functional part of soil. One should indicate that the content of the clay fraction decreases, the layered silicates are destroyed and transformed as affected by higher rates of potassium and ammonium, fixed by mixed-layered formations with smectite pockets. The functionally inert minerals such as quartz, feldspar, plagioclase and mica of dioctahedric type are accumulated.

Keywords: minerals, feldspar, organic fertilizers in the kind of poultry excrement

INTRODUCTION

The mineralogical and petrographic composition, the structural peculiar features of minerals practically control over all properties of soils [12, 18].

Gorbunov (1978) has offered a differentiated assessment of mineral reserves in soils that was later supplemented with the materials permitting to show a real picture of distribution of several element reserves both in different-sized fractions and also the main mineral phases [19]. The latter is conditioned by crystallochemical peculiarities of minerals and their capacity to release nutrient elements so vital for plants.

The problem relating to the behavior of minerals has been arisen because of the intensified agricultural production (agromineralogy of soils). Under study were changes in the crystallochemistry of minerals taken place due to fertilization in different forms and rates as well as irrigation with water of different quality, what made it possible to assess the reaction of soil minerals to different human interventions [3, 5, 7, 17, 13]. It is worth of note that the study of changes in the behavior of the petrographic-mineralogical composition of soils is urgently required to solve the problems of the modern agricultural production and to make the monitoring of soils and forecasting of changes in the environment better organized.

However, the influence of different rates of organic fertilizers on the behavior of minerals in soil hasn't been insufficiently studied up to now. The field investigations carried out earlier were oriented to experiment variants with the aim at studying the effects exerted by mineral fertilizers and sometimes in admixture with organic ones. But the clay minerals possess catalytic properties with respect to organic substances. Being dependent on the structure, chemical composition and the link between the elements in the crystalline lattice of minerals containing in the clay they are manifested in different way. The clay serves as a catalyst in reactions and transformations of a great number of organic substances (dehydration, etherification, polymerization, depolymerization, numerous reactions of condensation, oxidation, reduction and hydration). Robertson indicated that "there is no common explanation for catalytic effects of the clay. Every reaction should be considered separately" [20]. The model experiments permitted to study the role of clay minerals in the humus formation and conservation [22]. An attempt was made to compare the influence of humification process of plant residues on different mineral substrata (sand, loam) with the different content of clay minerals in them. Due to the increased adsorbing and catalytic capacity of clay minerals the transformation products of plant residues are intensively accumulated in soil and lead to the formation and conservation of newly formed humus substances.

The higher rates of organic fertilizers and poultry manure in particular change the soil properties to a considerable extent. This is conditioned not only by increasing the amount of biophile elements including N, P, K but also transforming the soil pH into acidic one.

Under use are various technologies to transform the poultry manure into a valuable substance for soil fertilization. The most promising is the organic fertilizer consisting of poultry manure combined with different admixtures of peat, straw, sod mat, etc. Such fertilizers possess good physical-mechanical properties to be friable, transportable, to have neutral pH and a high amount of N, P, K [2]. They increase the soil fertility but cause the contamination of the environment and soil degradation [24]. The data obtained in model experiments showed that the humus state is highly dependent on acidic-based properties of soils, the potassium amount in them, the content of mobile forms of heavy metals and a number of water-physical soil properties. For instance, the content of potassium mobile forms is increased to 500 mg/kg, being conducive to increasing the humus mobility, dispersing the soil mass and deteriorating the optimal Ca: K ratio, what leads to excessive compaction of the topsoil. The higher rates of organic fertilizers combined with the poultry manure lead to increasing the content of mobile phosphates to 1500 mg/kg and mobile potassium to 500 mg/kg. The selectivity of the organic matter to calcium becomes declined as compared to manganese; the amount of nitrogen compounds gets increased as well. These changes are associated with the reaction of mineral fine-dispersed fractions and in the first place with the easy weathered components capable to release the nutrient elements.

Special attention should be paid to irreversible changes in the mineral part of soils under the influence of management practices, what has been proved by experimental results obtained in the study of the behavior of mineral fine-dispersed fractions [6, 7, 8, 11]. It is necessary to control over changes in the soil acidity taking place due to aggressively acidic fertilizers or non-composted forms of organic fertilizers of agro soddy-podzolic soils. The further neutralization of the topsoil by different amendments doesn’t lead to the expected effect because the actively functioning components – the minerals of the fine-dispersed part have been partially destructed.

The objective of the given study is to show the behavior of minerals in the fractions less than 1 mkm, 1–5 mkm and 5–10 mkm, separated from the topsoil and subsoil horizons of the agro soddy-podzolic soil. This is the result of a long-term field experiment aimed to study the influence of higher rates of organic fertilizers contained the poultry manure upon the behavior of minerals in soil.

OBJECTS OF RESEARCH AND METHODS

The objects of research are mineral fine-dispersed fractions extracted from the topsoil and subsoil horizons of the soddy-podzolic soil fertilized by different rates of the poultry manure in admixture with sawdust (experimental fields in Odintsovo district of the Moscow region).

Under use was the organic fertilizer combined the poultry manure with the sawdust to be friable and to have the C: N ratio equaled to 15–18. This mixture was wet (25%) and had N, P, K in the amount of 1.7%, 0.3% and 1.2% respectively. In this experiment the middle (100 t/ha), high (500 t/ha) and super-high (1000 kg/ha) rates of the above organic fertilizer were applied. The super-high fertilizer rate was used to create a highly cultivated soil by its grassing for 3–4 years for inactivation of the pathogenic microflora.

To determine the soil mineralogical composition, the clay fraction (< 1 mkm), the fractions of fine (1–5 mkm) and middle (5–10 mkm) silt were extracted using the method after Gorbunov (1963) and analyzed by the X-ray diffractometer XZG-4A (Carl Zeiss Jena, Germany). The main characteristics of this device are the following: tension in tube – 30 kV, anode current – 30 mA, the rotation speed of goniometer – 2^{o}/min, copper radiation is filtered by nickel. The X-ray diffractograms were obtained for the air-dried samples saturated with ethylene glycol and ignited at 550^{o}C for 2 hours. The Biscaye method was performed to determine the content of mineral phases in the fraction less than 1 mkm. The relative area of the diffracted maximum in the range of 7.0, 10.0 and 17.0–18.0 was measured in X-ray diffractograms of the soil samples saturated with ethylene glycol what corresponded to the intensity of basal reflexes for kaolinite and chlorite, hydromica and mixed-layered formations with the smectite pocket. The calculation coefficients were taken as 4 for hydromica, 7.0 for Á reflex of kaolinite and chlorite and 1 – for mixed-layered formations. The content of mineral phases in the fractions of 1–5 and 5–10 mkm was determined by Cook method.

RESULTS AND DISCUSSION

The obtained results permitted to detect a sharply expressed decrease in the content of the clay fraction (< 1 mkm) in the topsoil from 17% in the experimental variant with the middle rate of organic ferti-

Table 1. The content of particle-size fractions, separated from the samples of topsoil and subsoil horizons of agro soddy-podzolic soils with different rates of organic fertilizers (according to N.I. Gorbunov), %

Depth, cm	Horizon	The content of fractions in soil, %			
		<1	1–5	5–10	>10
The middle rate of organic fertilizers					
0–23	P	17.0	10.1	7.5	65.5
23–40	EL	16.6	12.0	6.5	64.9
The high rate of organic fertilizers					
0–23	P	12.3	11.1	7.0	69.5
23–40	EL	11.4	11.6	6.4	70.7
The super-high rate of organic fertilizers					
0–23	P	9.6	11.1	6.2	73.2

lizers to 9.6% in the topsoil of the variant fertilized by super-high rates. The distribution of fractions of fine and middle silt revealed small changes (11–12% and 6–7% respectively).

The mineralogical composition of the fraction <1 mkm extracted from the topsoil and subsoil of the agro soddy-podzolic soil is represented by the following components: imperfect kaolinite, magnesium-iron chlorite, hydromica of trioctahedric type in admixture with dioctahedric structures and a number of unordered complicated mixed-layered formations (Table 2, Fig.1). The latter have been diagnosed with a higher and a lower content of smectite pockets. Among the clastogenic minerals the fine-dispersed quartz, feldspar and plagioclase were found in this fraction. These components are frequently met in this fraction separated from the soddy-podzolic soils used for agricultural purposes for a long period of time [4]. The most informative is the behavior of mixed-layered formations that are different both in the type of pocket stratification in crystallites and in their belonging to a definite type of minerals. The ratio between the above minerals is changed in dependence on the rate of the applied organic fertilizer and the ge netic soil horizon. The clay material extracted from the agro soddy-podzolic soil with the small rate of the organic fertilizer consists of mixed-layered formations, which are dominant there.

Among the mixed-layered formations the mica-smectite with a higher content of smectite pockets (33.1%) is prevailed; the mica-vermiculite formations show 23.8% and mica-smectite formations with

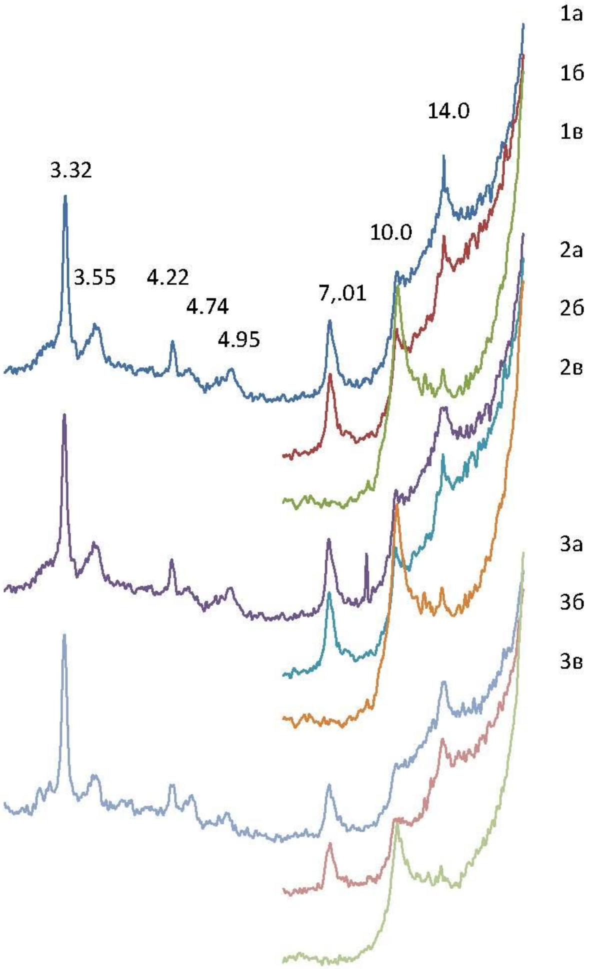

Fig. 1. X-ray diffractograms of the fraction < 1 mkm extracted from topsoil of agro soddy-podzolic soil: 1 – middle rate of organic fertilizers combined with the poultry manure; 2 – high rate of organic fertilizers combined with the poultry manure; 3 –super-high rate of organic fertilizers combined with the poultry manure; а – an air-dried sample; б – after salvation by ethylene glycol; в – after ignition at 550ºC for 2 hours.

a low content of smectite pockets make up less than 50%. It is more than 60% in the sum. The hydromica of trioctahedric type in admixture with dioactehedric pockets is 33.0%, the kaolinite in the sum with chlorite – 7.4%. The fine-dispersed quartz, feldspar and plagioclase are also present. The above minerals are characterized by the increased intensity of reflexes, the major part of which has acute picks (Fig. 2). This fact serves as evidence of the well-expressed structure of their crystallinity and a small amount of amorphic components as compared to the study of clay fractions in soils with the high rates of organic fertilizers.

The clay material in the agro soddy-podzolic soil with middle rates of organic fertilizers differs from that considered above according to the composition of minerals and their crystallochemical parameters. The reflex intensity of all the components in the clay is considerably decreased as resulted from declining the crystallinity degree of minerals, the presence of X-ray-amorphic substances, in the first place, the destruction products of the plant residues and decomposition of the

Table 2. The ratio between the main minerals phases of the fraction < 1 mkm in samples of topsoils and subsoil horizons of the agro soddy-podzolic soil with different rates of organic fertilizers, %.

Depth, cm	Horizon	Content of the clay fraction	Kaolinite + chlorite	Hydromica	Mixed-layered formations, Å		
					mica-smectite with the low content of smectite pockets	mica-vermiculite	mica-smectite with the high content of smectite pockets
					12	14	17
The middle rate of organic fertilizers							
0–23	P	16.9	7.4	33.0	2.8	23.8	33.1
23–40	EL	16.6	8.5	38.7	10.5	18.4	24,0
The high rate of organic fertilizers							
0–23	P	12.3	9.4	37.5	11.9	21.4	19.8
23–40	EL	11.4	10,0	44.2	7.3	18.0	20.6
The super-high rate of organic fertilizers							
0–23	P	9.6	8.2	71.1	6.3	9.3	5.1

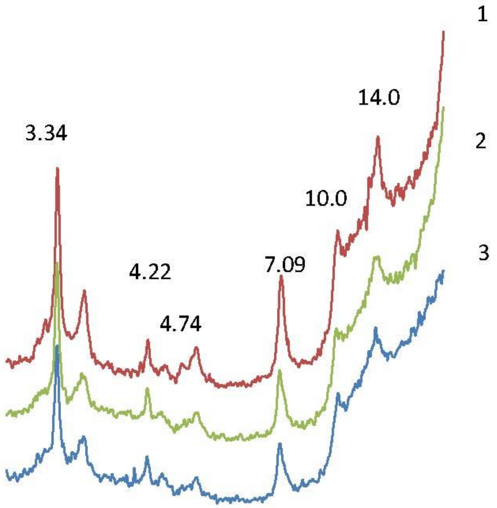

Fig. 2. Comparison of the intensity of mineral reflexes on X-ray diffractograms of air-dried samples of the fraction less than 1 mkm separated from the topsoil of agro soddy-podzolic soil.

organic matter. The ratio between the main mineral phases changes as well towards increasing the share of chlorite in the sum with kaolinite to 9.4% and hydromica – 37.5%. The sum of mixed-layered formations gets declined; the pockets in crystallites are reorganized due to their reaction to the components of substances applied with the organic fertilizers

Their amount with a low content of smectite pockets becomes significantly increased by 3 times as a result of two processes: (1) fixation of potassium and ammonium introduced together with the fertilizers and (2) activation of degradation processes affected by aggressive organic substances; hydromica is transformed into mixed-layered mica-smectite formations with a low content of smectite pockets. Two different processes take place – agradation and degradation resulting in the increased amount of mica-smectites with the low content of smectite pockets and in the decreased amount of mica-smectites with the high amount of smectite pockets. It is necessary to notice that the quantity of fine-dispersed quartz becomes higher. The identical picture has being observed in the clay fractions of soils suffered from anthropogenic loads to a considerable extent. Based upon these observations a concept of "silication of the soil clay fraction" was proposed, due to which the functioning of the fine-dispersed material is changed in the topsoil of human-modified soils [6]. The amount of mica-vermiculite formations is somewhat declined. However, the change in the content of this component plays an insignificant role as compared to the mica-vermiculite formations with the high amount of smectite pockets.

The highest changes in the ratio between the main mineral phases and in the behavior of mixed-layered formations are observed in the clay fraction of the soil with the super-high rate of organic fertilizers. A significant decrease of the reflex intensity of layered silicates is fixed, whereas the amount of quartz, feldspar and plagioclase increases. The presence of the reflex at 4.4 Á and its highest intensity as compared to that in the clay fractions of soils with the low rate of organic fertilizers serves as evidence of a higher content of the X-ray-amorphic substances (destruction products of minerals and the organic matter) in the clay fraction. The latter is characterized by a dominant amount of trioctahedric mica (71.1%). The mixed-layered formations play an insignificant role (5.3 + 9.3 + 5.2%), among them are dominant the mica-vermiculite formations with the high amount of vermiculite pockets. The smectite phase represented by mica-smectites with the high content of smectite pockets makes up only 5%. Such transformations in the clay fraction of the given soil may be considered as a result of the following processes. The presence of X-ray-amorphic substances and the decreased intensity of reflexes of layered silicates testify the destruction of layered silicates and mixed-layered formations with the high amount of smectite pockets in particular. Their content in the clay fraction extracted from the topsoil with the middle rate of organic fertilizers accounts for 33.1%, whereas it makes up 5.2% in the clay fraction of the soils excessively fertilized.

The soils revealed an increased amount of potassium and ammonium. In the period of their fixation by the unordered mixed-layered formations with the high content of smectite pockets in the crystalline lattice the process of agradation takes place when the smectite pockets are transformed into the mixed-layered formations with the low content of smectite pockets and then into the hydromica, the amount of which becomes increased in the clay fraction of the topsoil (71%).This phenomenon is well known as a process of potassium fixation by soil [23]. The increase of the amount of water-soluble potassium that was fixed in the experiment variant with the super-high rates of organic fertilizers led to intensive agradation with the formation of hydromica structures.

In the case of modeling with labeled nitrogen it was shown that the crystallochemical parameters of mixed-layered minerals with smectite pockets are changed as resulted from the fixation of ammonium radical [21]. The decrease in the reflex intensity of layered silicates in the clay fraction of soils is also an evidence of degradation process affecting by the substances applied with the organic fertilizers.

The mineralogical composition of the 1-5 mkm fraction is varying from 10 to 12% (Table 3). The composition of minerals in this fraction differs from that in the clay fraction to a considerable extent. Quartz is dominant (25–27%), K-feldspar makes up 17–21%, mica – 19–28% and plagioclase – 11–12%. Among layered silicates are present kaolinite (5–6%), chlorite (3–6%), trioctahedric mica (19–28%) and vermiculite (8–10%) (Fig. 3, 4).

The crystallochemical state of the above minerals changes insignificantly with the exception of silt fractions extracted from soils with the super-high rate of organic fertilizers. Under change is also the ratio

Table 3. The content of minerals in the fraction of fine silt (1–5 mkm) extracted from the topsoil and subsoil of agro soddy-podzolic soil, %

Depth, cm	Horizon	Content of the fraction	Minerals, Å							$\frac{I_{10}}{I_5}$*
			verminculite	mica	kaolinite	chlorite	quartz	K-feldspar	plagioclase	
			14	10	7	4.74	3.31	3.22	3.18	
The middle rate of organic fertilizers.										
0–23	P	10.1	10.3	28.1	5.3	2.9	25.5	16.7	11.4	3.2
23–40	EL	12.0	10.5	19.7	5.1	6.1	25.9	19.9	12.9	2.7
The high rate of organic fertilizers										
0–23	P	11.1	8.0	19.6	6.1	6.1	26.8	21.0	12.5	2.0
23–40	EL	11.6	9.4	23.9	5.8	3.7	26.9	20.0	10.3	2.2
The super-high rate of organic fertilizers.										
0–23	P	11.1	9.6	21.0	6.3	5.7	24.7	20.1	12.6	2.8

* Ratio between reflex intensities of mica.

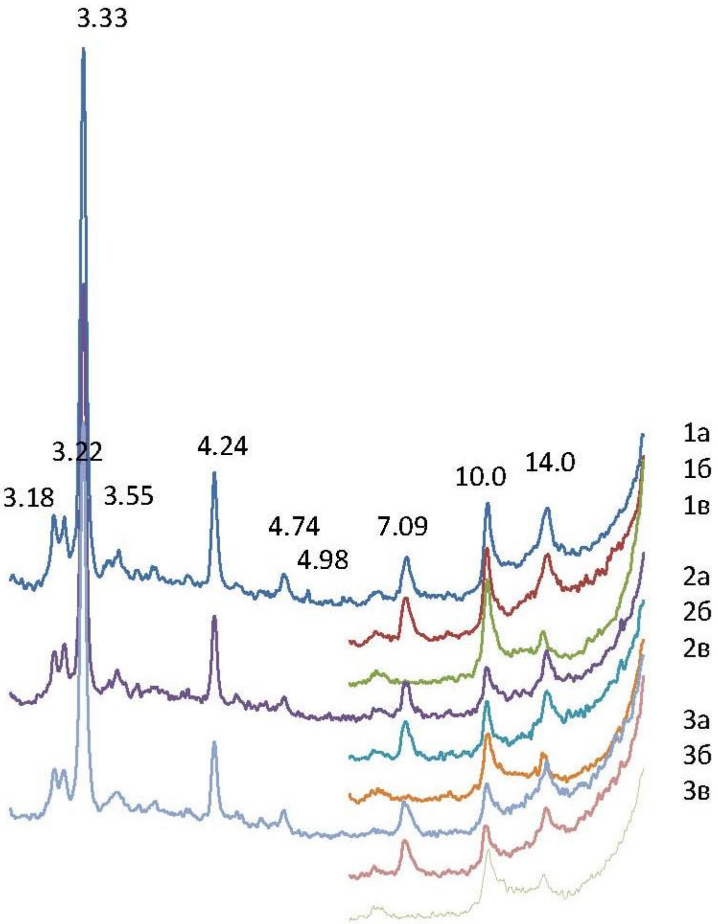

Fig.3. X-ray-diffractograms of the fractions of the fine silt (1–5 mkm), extracted from the topsoil of agro soddy-podzolic soil.

between dio-and trioctahedric micas. The high and super-high rates of organic fertilizers contribute to increasing the amount of dioctahedric mica, which is more stable and incapable to release the nutrients for plants.

The mineralogical composition of the 5–10 mkm fraction, extracted from the subsoil horizons of the agro soddy-podzolic soil. The amount of middle silt is insignificant – 6%, its fluctuation enriches only 1% within the soil profile.

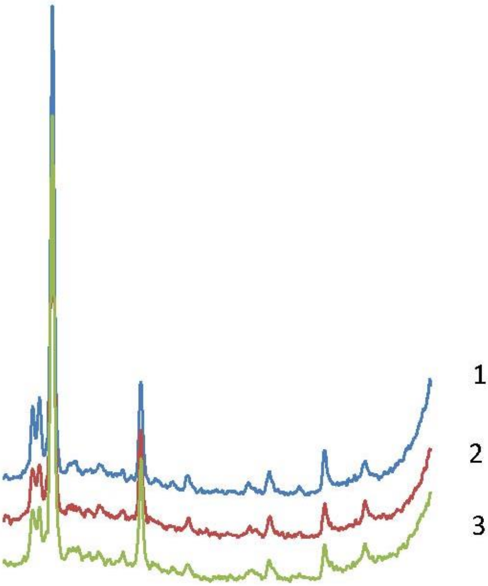

Fig. 4. The comparison of reflex intensities of minerals in the fraction of middle fraction (5–10 mkm) extracted from air-dried samples of the topsoil in the agro soddy-podzolic soil.

Table 4. The content of minerals in the fraction of middle silt (5–10 mkm) from the topsoil and subsurface horizons of agro soddy-podzolic soil, %

Depth, cm	Horizon	Content of the fraction	Minerals, Å							$\frac{I_{10}}{I_5}$*
			Vermiculite	mica	kaolinite	chlorite	quartz	K-feldspar	plagioclase	
			14	10	7	4.74	3.31	3.22	3.18	
The middle rate of organic fertilizers										
0–23	P	7.5	3.6	14.8	3.4	3.8	31.2	27.3	16.1	2.0
23–40	EL	7.1	4.9	14.3	3.7	3.3	31.1	26.5	16.3	2.4
The high rate of organic fertilizers										
0–23	P	6.2	4.8	13.4	3.1	3.8	35.9	23.4	15.1	1.9
23–40	EL	6.5	3.1	13.2	2.0	3.6	33.6	27.6	16.9	2.6
The super-high rate of organic fertilizers										
0–23	P	6.4	5.1	16.1	3.4	3.4	31.2	24.0	16.9	2.2

* Ratio between reflex intensities of mica

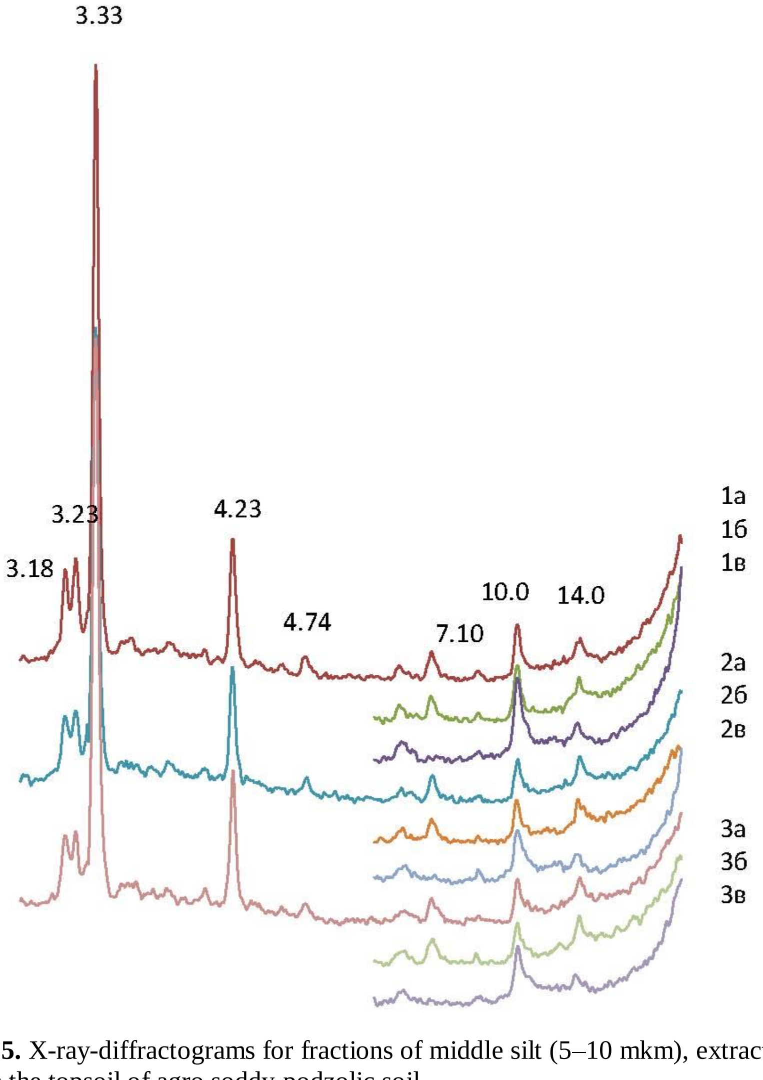

Fig. 5. X-ray-diffractograms for fractions of middle silt (5–10 mkm), extracted from the topsoil of agro soddy-podzolic soil.

The composition of minerals in this fraction is identical to that in the fraction of fine silt, i.e. quartz is dominant and makes up 31–35%, K-feldspar – 23–27%, plagioclase – 15–16%. Among the layered silicates

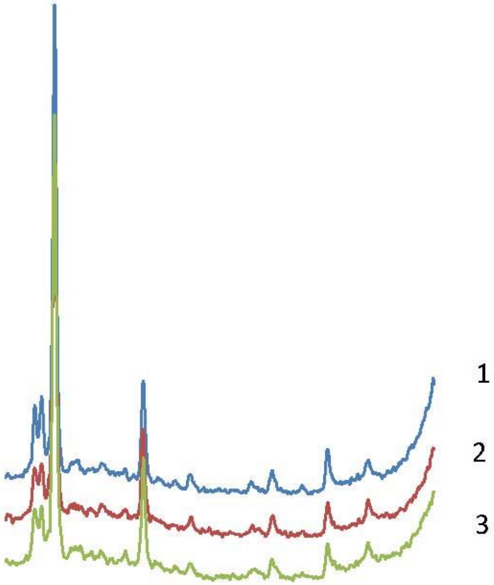

Fig. 6. Comparison of reflex intensities of minerals in X-ray-diffractograms of air-dried samples used for extraction the fraction of middle silt (5–10 mkm) from the topsoil of agro soddy-podzolic soil.

the mica of di-, and trioctahedric type (13–16%), kaolinite (2–3%) and chlorite (3–4%) are present (Table 4, Fig. 5). The reflex intensity of layered silicates in the soil with the low rate of organic fertilizers is the highest (Fig.6). The quantity of minerals changes insignificantly. Hence, the minerals in the fraction of middle silt seemed resistant to the organic fertilizers to a greater extent.

CONCLUSION

The obtained data serve as evidence that the fraction < 1 mkm, the amount of which was decreased by 2 times, is the most informative component in agro soddy-podzolic soils. The mineralogical composition of this fraction is represented by mixed-layered formations with different stratified pockets (mica-smectite with the high and low content of smectite pockets, mica-vermiculite), hydromica of di-, trioctahedric type, imperfect kaolinite, magnesium-iron chlorite. The clay material contains the fine-dispersed quartz, K-feldspar and plagioclase.

The input of organic fertilizers together with the poultry manure to the soil was conducive to the following processes taken place in minerals of the clay fraction.

Destruction of mixed-layered formations of mica-smectite type with the high amount of smectite pockets;

Transformation of hydromica and chlorite together with removal of potassium cations from the crystalline lattices of minerals.

Agradation of mixed-layered formations with the high amount of smectite pockets in crystallites as a result of potassium and ammonium fixation, introduced into the soil with the applied organic fertilizers.

Mechanical disintegration of clastogenic minerals resulted in increasing the amount of quartz, K-feldspar and plagioclase fixed in the clay fraction of soils obtained the high and super-high rates of organic fertilizers.

Transformations of minerals in the silt fractions are not significant as compared to those in the clay fraction.

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