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Integrated assessment of the influence of shungite-containing fertilizer on physical and chemical properties of typical chernozem in Rostov region

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Abstract. The aim of the presented research was to study the impact of the shungite-containing fertilizer on elemental composition and physical and chemical properties of typical chernozem in Rostov region, Russia. The trial was conducted under conditions of a model experiment with application of laboratory and instrumental methods of soils analysis in accordance with established procedures. The novelty of the study is that it defines the influence of the shungite-containing fertilizer on the content of humus, exchangeable base in the soil, active soil acidity, intensity of processes of nitrogen, phosphorus and potassium transformation in typical chernozem.

1. Introduction

One of the most significant issues of any state's national security is the quality of life of its population, which is directly linked to food safety. It is possible to provide the population of the country with national safe and high-quality food only if farming is carried out on fertile soils with the use of new agrochemical technologies, which provide balanced plant nutrition with macro- and microelements. High-quality vegetable crops are even harder to grow due to widespread degradations of soils, decreasing level of fertilizers' application and environmental pollution. That is why it is necessary to conduct constant monitoring of soil fertility status when applying nonconventional agricultural chemicals.

The aim of the research was to conduct a laboratory-scale study of the influence of the shungite-containing fertilizer on the elemental composition and physical and chemical properties of typical chernozem in Rostov region.

The tasks of research were:

- to study the influence of the shungite-containing fertilizer on the elemental composition of typical chernozem.
- to define the influence of the shungite-containing fertilizer on the content of humus and exchangeable bases in the soil, as well as active soil acidity.
- to define the influence of the shungite-containing fertilizer on the content of nutrients in soil: ammonium and nitrate nitrogen, labile phosphorus and exchange potassium.



2. Materials and methods

The object for the study of the influence of the shungite-containing fertilizer on physical and chemical properties of soils is typical calcareous medium-deep heavy-loam chernozem on loess-like loam in the Botanical garden of Southern Federal University (47°14'7.6" N, 39°38'36.8 E).

The object of the research is typical calcareous South-European facies (North-Azov) chernozem in the Botanical garden of SFU. It was chosen due to the following reasons:

- It is located in the conservation area and is almost uncontaminated.
- This subtype of chernozem is rather widespread on the territory of Rostov region.

The climate of the region is moderately continental. It is characterized by the combination of excessive heat and relative lack of moisture. Average year-round temperature ranges from + 7° to + 10°. The coldest months are January and February. Average January temperature is –6.0°. July is the hottest month with the highest temperature at noon, above 40 degrees. The vegetational season lasts for 180 – 200 days, effective heat sum is about 3000°, normal frost danger period lasts 100 – 120 days [1]. Average annual precipitation is 474 mm. Predominant winds are eastern and north-eastern; their average velocity is 5 m/s.

The main soil-forming materials are loess-like loam, which covers watershed and slopes in thick mass. Outcrops at the northern rim of the garden show that the thickness of loess-like loams here reaches 12-15m. They are of a pale-yellow color, porous, and can be characterized by significant calcareousness, the amount of coarse dust fraction (0.05-0.01 mm) there reaches 38-45%.

Morphological profile of typical South-European facies chernozem is characterized by medium-deep humus horizon (40-80cm). Effervescence is registered either on the surface or at the bottom of the humus horizon. Carbonate emanations primarily in the form of rare carbonate veins appear a little lower the effervescence line, their maximum (white-eye) is concentrated in the lower part of transitional Bk or BCK horizon.

A characteristic morphological mark of typical chernozem is the dark-grey color of humus horizons, which gradually turns into brownish and pale-yellow in the lower horizons. A and AB horizons are overgrown with roots; there are many earthworm funnels which are rich in humus; they have a grainy-lumpy structure. Considering their grain-size distribution, these horizons are light and middle loamy. Transition to lower horizons is gradual. Horizons B, BC and C have a dark-brownish and brownish-pale-yellow color. Their structure is lumpy-nuciform and lumpy. According to their grain-size distribution, they are heavy loam. They contain carbonates in the form of mould, veins, and white-eye.

According to its grain-size distribution, typical chernozem is attributed to silty coarse clay heavy loam. Typical carbonate chernozems of the Botanical garden are rich in dust fractions (0.05-0.001 mm), which amount to 60-80%. There is very little sand larger than 0.25 mm, the share of fine grade sand is insignificant as well.

The research was carried out through laboratory-scale trials. The trials scheme was as follows:

- Control (no fertilizers)
- 2.5 tons/ha
- 5.0 tons/ha
- 7.5 tons/ha
- 10.0 tons/ha

The trials were conducted three times. 500 ml vessels were used in the trials. Each vessel was loaded with 400.0 g of soil, which preliminary had been passed through a 3mm sieve. The fertilizer in question, Shungite, was applied as powder. Before the vessels were loaded, the fertilizer and the soil had been thoroughly mixed. The composts' moisture was 60.0% of field moisture capacity; the temperature was 25 °C. The soil was tested in 2 weeks, one month, 2 and 3 months of the fertilizer/soil interaction.

Before the trial establishment, the soil had the following characteristics: 2.73% of humus; pH 7.6;

exchange base composition (mg-eq/100g): 30,1 Ca²⁺ , 3,7 Mg²⁺ ; N-NO₃ concentration was 3,85 mg/kg, N-NH₄ – 2,93 mg/kg, P₂O₅ – 3,42 mg/100 g, K₂O – 30,5 mg/100 g.

Laboratory tests were carried out three times; the final result was the average of three results.

Organic matter was determined by Turin's method in Simakov's modification, water extract pH – by potentiometry, hygro-moisture – by thermostatic-weight method, exchange calcium and magnesium – by Gissing's method in Aleshin's modification, nitrate nitrogen – by the method of Grandval-Lajoux, ammonium nitrogen – with Nessler's reagent, labile phosphorus and exchange potassium – by Machigin's method [2,3].

3. Results

3.1 The influence of the shungite-containing fertilizer on the elemental composition of typical chernozem

The elemental composition of soils is the content and quantitative ratio of chemical elements in soils. The synonym to “the elemental composition” is the term “bulk chemical composition of soils”. Bulk or elemental composition of soils is the first and essential chemical characteristic of soils, which is the basis for understanding soils' qualities, their genesis and fertility. It is used for assessment of soils' potential fertility.

Generally, elemental composition of soil is inherited from parent rock, which transforms during the soil-formation process, enriches with chemicals of organic substances, as well as mineral elements, biophiles. In case of man-induced impact, significant changes in soil elemental composition take place sometimes.

The data on the shungite-containing fertilizer's bulk composition showed higher concentrations of almost all elements compared to typical chernozem. The excess is from 1.17 (for Pb) to 3 times (TiO₂, V, Cr, MnO, Ni, Cu, Zn, As, Sr, Al₂O₃, MgO), Fe₂O₃ concentration is 3.92 times higher, and Co concentration is 9.37 times higher. This coincides with literature data of other researchers. However, concentrations of CaO (1.19 times) and SiO₂ (1.3 times) are lower in Shungite, than in the soil in question.

Conducted research showed that when applying different doses of the fertilizer, there are no verifiable differences in elements' total forms concentrations against control (see table 1). It was observed that concentrations of Ni, Cu, Zn and Pb slightly increased, when doses of applied Shungite were increased. Some elements tend to decrease in concentration, when doses of the applied fertilizer increased: V, Cr, Mn. With Sr, statistically verifiable concentration decrease was identified, which is apparently explained by the fertilizer's adsorption properties.

Table 1. The influence of shungite-containing fertilizer on the elemental composition of typical chernozem.

Element	Control, average	2.5 tons/ha		5 tons/ha		7.5 tons/ha		10 tons/ha	
		average	t empir	average	t empir	average	t empir	average	t empir
TiO ₂ (%)	0.85	0.82	3.0	0.58	0.1	0.83	1.0	0.84	0.5
V (ppm)	116.47	112.43	1.7	113.47	0.7	108.66	4.0	108.00	4.0
Cr (ppm)	121.13	117.14	0.4	120.81	0.1	129.82	0.7	118.29	0.3
MnO (ppm)	927.51	903.88	1.1	903.88	1.1	920.64	1.0	919.42	0.8
Fe ₂ O ₃ (%)	4.95	4.92	0.4	5.03	2.0	5.00	2.5	5.01	2.0
Co (ppm)	27.90	24.78	1.2	28.8	0.4	29.29	0.9	28.62	0.5
Ni (ppm)	54.67	54.33	0.2	58.22	1.0	56.73	1.2	55.19	0.3
Cu (ppm)	51.50	49.31	0.3	53.38	0.6	51.64	0.1	52.08	0.3
Zn (ppm)	101.21	98.39	1.0	103.53	1.5	105.61	3.2	102.35	0.6
As (ppm)	11.22	11.27	0.1	10.31	2.8	10.23	1.5	11.48	1.0
Sr (ppm)	150.46	143.99	1.7	143.94	1.9	141.98	2.7 ^{*a}	141.15	5.5 [*]
Pb (ppm)	35.19	35.59	0.2	29.53	2.8	29.35	1.6	36.55	1.1
CaO (%)	1.48	1.56	2.7	1.50	2.0	1.48	0.1	1.48	0.1
Al ₂ O ₃ (%)	12.01	11.87	0.7	12.09	2.0	12.10	1.5	12.02	0.1

SiO ₂ (%)	67.52	66.75	2.1	67.48	0.2	67.63	0.8	67.50	0.1
P ₂ O ₅ (%)	0.15	0.16	0.1	0.16	0.3	0.16	0.2	0.16	0.2
K ₂ O (%)	2.15	2.14	0.3	2.14	0.1	2.15	0.1	2.16	0.3
MgO (%)	1.24	1.23	0.5	1.26	2.0	1.22	0.3	1.20	2.0

^a Notice: * shows statistically relevant differences at 95 % level of probability (t empir.>t theor.)

3.2 The influence of the shungite-containing fertilizer on humus content in typical chernozem

Humus is the basic organic substance in soil, containing nutritious elements, which are necessary for higher plants. Humus amounts to 85-90% of organic substance in soil; it is an important criterion for assessment of its fertility.

Humus contributes to creation of an agronomical healthy structure and soil conditions favorable for plant life. Humus contains basic nutritious elements for plants (N, P, K, S, Ca, Mg), as well as various microelements. During the process of humus substances' gradual mineralization, these elements become available for plants.

Humus substances in soil provide food for heterotrophic soil microorganisms. Humus content in soil defines intensity of biological and biochemical processes, which determine accumulation of nutritious elements necessary for plants.

The soil under investigation can be attributed to medium-humic soils according to humus content. When the shungite-containing fertilizer was applied, during the first two terms of composting, an increase in humus content was identified at all investigated doses, but this was not statistically confirmed. However, in 2 and 3 months of soil/fertilizer interaction (correspondingly, the doses were 7.5; 10 tons/ha and 5, 7.5, 10 tons/ha), a verifiable increase in humus content was identified. The content increase at shungite dose of 10 tons/ha reached 1.4 times (5.33%) against control.

3.3 The influence of the shungite-containing fertilizer on exchangeable base status in typical chernozem

Exchange absorbability of soil is the ability of soil to absorb and exchange ions, which appear on the surface of colloidal particles, clay minerals and bounded functional groups of humus substances, into an equivalent number of ions of the solution interacting with solid soil. This is one of soil's most important characteristics; to a great extent, it determines soil fertility and the character of soil-formation processes. Exchange absorbability defines and regulates the nutrient status of soil, contributes to accumulation of multiple elements of mineral plant nutrition; it regulates soil reaction, and its water-physical properties.

Due to diversity of environmental conditions and peculiarities of the soil-formation process, the content of exchangeable cations in different types of soils is different. Exchangeable cations in chernozems are primarily calcium and magnesium.

The study of the shungite-containing fertilizer's impact on absorbability of soil and adsorbed cations in typical carbonate chernozem revealed a statistically verifiable increase in concentration of exchangeable calcium and the total of exchangeable calcium and magnesium at the applied dose of 10 tons/ha in the first term of the trial (2 weeks). Other variants showed only the tendency of increase in adsorbed cations. One month after the incubation, a certain decrease in exchangeable cations concentration was identified against control; in later terms (2 and 3 months) a minor increase could be traced. The mentioned changes are not confirmed statistically.

3.4 The influence of the shungite-containing fertilizer on active acidity of typical chernozem

Active soil acidity is conditioned by the presence of hydrogen ions (protons) in the soil solution; their activity depends on characteristics (ionic strength) of the solution, which define the ion activity coefficient. According to the content of the dissolved substances and the character of their interaction with the solid phase of soils, defining the balance between concentrations of hydrogen and hydroxyl ions in the soil solution, soils can have neutral (pH 7), acid (pH<7), or alkaline (pH>7) reaction.

Soil reaction depends on a combination of factors: chemical and mineral composition of the mineral part of soil, presence of unbound salts, content and quality of the organic substance, soil air composition, soil moisture, and organisms' activity. The most important regulator of soil reaction is the salts which

are present in the soil. When neutral, acid, alkaline salts change from solid phase to solution during moistening and back while drying, they have a corresponding impact on reaction of the soil solution, which influences soil's fertility as well.

Active acidity of the soil under investigation, typical carbonate chernozem, is weak-alkaline, ranging from 7.6 to 7.8, which can be explained by the presence of carbonates.

When different doses of shungite were applied, no significant impact of the fertilizer on active acidity of the chernozem in question was identified. Only the first term of the trial (2 weeks) showed certain pH increase up to 7.83, which was statistically proved for the doses of 2.5 and 7.5 tons/ha. During the interval of 1-3 months of the fertilizer/soil interaction, pH values were ranging from 7.60 to 7.80, which did not differ from control.

3.5 The influence of the shungite-containing fertilizer on concentration of mineral nitrogen in typical chernozem

Nitrogen is the most important nutritious element for all plants. According to trial results, as composting time for soil under optimal conditions (60 % of field moisture capacity and 25° C) increased, the intensity of ammonification process increased as well. The maximum concentration of ammonium nitrogen in typical chernozem was reached in 3 months. The revealed regularity was identified in all variants of the trial.

It should be noted that the increase in ammonium nitrogen concentration in soil after application of shungite could be traced during the whole incubation period (2 weeks, one month, 2 months, 3 months). During the 1st term of sample collection, a statistically proven increase in ammonium nitrogen concentration was indicated at the fertilizer dose of 7.5 tons/ha, during the 3rd term – at all investigated doses, and during the 4th term – at shungite doses of 5.0 and 7.5 tons/ha, which is apparently connected to the prolonged activity of the fertilizer in question.

High nitrification capacity of typical chernozem was identified in all variants of the trial. Nitrate nitrogen concentration in soil in 2 weeks of incubation was ranging from 16.63 to 19.73 mg/kg, which was 4.7 times higher than before the trial (3.85 mg/kg). Higher intensity of nitrification was detected in one month and in 2 months of incubation. Later, the rate of nitrate nitrogen accumulation started to slow down due to immobilization by microorganisms and increasing ammonification.

The use of the shungite-containing fertilizer increases nitrification intensity. Statistical analysis showed a proven increase of nitrate nitrogen in two weeks of composting at the dose of 2.5 tons/ha, and in one month and two months of fertilizer/soil interaction it was detected at all doses of the fertilizer in question.

3.6 The influence of the shungite-containing fertilizer on labile phosphorus and exchange potassium concentration in typical chernozem

The influence of phosphorus on life of plants is diverse. With normal phosphorus nutrition, yields rise considerably, and their quality improves. Without phosphorus, just like without nitrogen, life is impossible.

The level of labile phosphorus concentration in the trial is elevated and high.

Analysis of samples in 2 months showed lower labile phosphorus concentrations against earlier terms. Thus, chemical and biological fixation of labile phosphorus took place. In the laboratory environment, with humidity and temperature optimal for microbiological activity, biological fixation of phosphorus can happen at a much greater rate than in nature.

When different doses of shungite were applied, in 2 weeks of fertilizer/soil interaction, the concentration of labile phosphorus was verifiably lower, which is explained by absorbing characteristics of the fertilizer and its chemical composition. It is believed that the main mechanism of phosphates' absorption and fixation in soil is chemical reactions of subsidence. However, a significant role in phosphate fixation is attributed to the mechanism of their surface sorption.

During the fertilizer application in trials, an increase in the concentration of labile phosphorus was determined in a month of composting. Shungite application at the doses of 5.0, 7.5, 10.0 tons/ha provides a statistically verifiable increase in the concentration of labile phosphorus in soil. Meanwhile,

availability index in the variants mentioned above is characterized as very high. This happens due to the processes of phosphorus mobilization in the soil and fertilizer. During the further fertilizer/soil interaction (2 and 3 months) labile phosphorus concentration was at the control level.

4. Conclusions

The laboratory-scale study showed that the use of the shungite-containing fertilizer based on Karelian shungite from Turastamozerskoe field had a positive effect on physical and chemical properties of typical chernozem in question. Generally, according to the research, its impact depends on the time of interaction between the fertilizer and the soil, as well as the fertilizer's dose.

It was observed that the use of the shungite-containing fertilizer does not have a significant influence on total forms of elements (V, Cr, Co, Ni, Cu, Zn, As, Sr, Pb, TiO₂, MnO, CaO, MgO, Al₂O₃, Fe₂O₃, SiO₂, P₂O₅, K₂O), but a statistically significant reduction of Sr concentration was identified.

A verifiably higher content of humus was identified in 2 (dose of 7.5 tons/ha) and 3 months of the fertilizer/soil interaction (doses of 5 tons/ha, 7.5 tons/ha and 10 tons/ha).

When shungite is applied to soil, it increases the exchangeable base status.

The use of the shungite-containing fertilizer does not have a significant influence on active soil acidity of typical chernozem.

It has been established that the use of shungite intensifies the processes of ammonification and nitrification in typical chernozem. A statistically-valid increase in ammonium nitrogen concentration was identified in two months of composting at all investigated doses and in three months when applying 5.0 tons/ha and 7.5 tons/ha of shungite. A significant increase in nitrate nitrogen was identified in one month of the fertilizer/soil interaction at all investigated doses.

The use of shungite has a significant impact on the processes of phosphorus and potassium transformation in soil. In two weeks of composting, statistically significant decrease in labile phosphorus was detected in the samples with shungite, and in a month, an increase was identified. It was established that shungite causes a decrease in concentration of exchange potassium within a month of the fertilizer/soil interaction, and later a steady balance is settled between exchange and fixed forms of potassium.

It is necessary to continue studying active forms of macro- and microelements in typical chernozem, as well as microbiological values of soil fertilized with shungite. It would also be necessary to continue studying the impact of shungite in model and field trials with plants. Moreover, it would be useful to study shungite as an ameliorant for remediation of soils contaminated with metals.

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