Intrasoil dispersed phosphogypsum utilization in a small aggregate chernozem system

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Abstract. Unregulated accumulation of phosphogypsum leads to dangerous geochemical flows with an avalanche effect. As a new option for the application of phosphogypsum, its dispersed placement in the small aggregate chernozem system at a depth of its modern anthropogenic illumination was described. A milling method for treating a soil layer of 30–60 cm was developed. Phosphogypsum and soil interact and agrophysical soil properties can be improved. The anthropogenic eluvial-illuvial structure of the soil profile can be eliminated. The morphological, agrophysical properties and soil moisture conditions, thermodynamic processes with Pb\(^2+\), Cd\(^2+\) ions, the morphological parameters of the root system and the yield of sunflower after application of phosphogypsum during its utilization by dispersing in the soil layer of 30–60 cm were studied. Improved soil properties and conditions for development of the rhizosphere, passivation of heavy metals as a result of the carbonate-calcium equilibrium in the soil solution were described. The ecosphere and the agricultural production effect of phosphogypsum utilization in chernozem were substantiated.

1. Introduction

The chemical technology for producing phosphorus fertilizers involves the disposal of large volumes of waste, including phosphogypsum. Sludge collectors of phosphogypsum located in the sea, river deltas, on land are an ecological, recreational, landscape disaster. Unregulated accumulation of phosphogypsum leads to the formation of dangerous geochemical flows with an avalanche effect [9, 12]. It is necessary to find new ways of phosphogypsum utilization.

The possibility of phosphogypsum utilization is due to the fact that it contains 85–90 % of gypsum, up to 5 % of phosphorus compounds, and up to 1.5 % trace elements [14]. The use of phosphogypsum for irrigation and drainage purposes was substantiated by applying phosphogypsum on the soil surface and/or introducing it into the arable layer [3–6, 8, 11]. The use of phosphogypsum for irrigation and drainage purposes was substantiated by applying phosphogypsum on the soil surface and/or introducing it into the arable layer [3–6, 8, 11].

As a result of the use of sulfuric acid in the production process, the reaction of phosphogypsum is acidic – pH 2.8–3.2, and phosphogypsum exhibits buffering acid properties, which the neutralization technology used before sending the product to the tailing dump cannot eliminate. The acidity of phosphogypsum is dangerous for soils with an acid reaction and low buffering of agrophysical and physico-chemical properties. On the contrary, for soils with a neutral and alkaline reaction, characterized by buffering properties, the parameters of phosphogypsum are favorable. Such soils include solonetzes, drained soils, as well as most soils that have been in agricultural crops for a long time, including chernozems. Properties of many soils change that can be described in terms of...
solonetzic pedogenesis on the basis of ideas about the anthropogenic eluvial-illuvial structure of the soil profile as a result of dump primary cultivation of the upper soil layer.

Due to the acid reaction of phosphogypsum, the availability of phosphorus contained in plants is higher than using standard phosphorus fertilizers.

In soils, the process of illusion is being developed. Solonetzic and fused horizons at a depth of 20–40 to 30–60 cm are developing. The process is occurring in chernozems. The modern approach to the introduction of phosphogypsum into the soil upper layer seems impractical, and is due to the lack of technical means for the dispersed introduction of phosphogypsum into the crushed illuvial soil horizon [11].

The methodological basis of the present work is the dispersion of phosphogypsum in black soil at a depth of 30–60 cm. The milling method of mixing ensures the best contact of phosphogypsum and soil and good agrophysical properties of the treated soil.

The novelty of the work is that the dispersion of phosphogypsum in chernozems at a depth of modern anthropogenic illumination of the soil with rotational mixing of phosphogypsum and soil in a layer of 30–60 cm was chosen as a methodological basis.

The research objectives are as follows:

- ensuring the soil-reclamation effect from the introduction of phosphogypsum into chernozem, which will reduce the size of sludge collectors of phosphogypsum as a source of environmental pollution;
- thermodynamic substantiation of the introduction of phosphogypsum into the illuvial horizon of black soil.

2. Methods and materials

The object of research is carbonate chernozem of the southern European facies of the northern zone of Krasnodar Territory.

The soil-agrotechnical station which studies the ecological and recreational utilization of phosphogypsum in chernozem is located in Agrochemist Company, Kanevsky district of Krasnodar Territory.

The research methods are as follows: stationary field, laboratory, mathematical thermodynamic modeling.

The scheme of a long stationary experiment is as follows:

1. Dump soil tillage at a depth of 22–25 cm (agricultural technology standard), control;
2. Milling tillage in a layer of 30–60 cm, simultaneous application of phosphogypsum at a dose of 10 t/ha and its rotational mixing with soil in a layer of 30–60 cm (Fr + FG 10 t/ha);
3. Milling tillage in a layer of 30–60 cm, simultaneous application of phosphogypsum at a dose of 20 t/ha and its rotational mixing with soil in a layer of 30–60 cm (Fr + FG 20 t/ha);
4. Milling tillage in a layer of 30–60 cm, simultaneous application of phosphogypsum at a dose of 30 t/ha and its rotational mixing with soil in a layer of 30–60 cm (Fr + FG 30 t/ha);
5. Milling tillage in a layer of 30–60 cm, simultaneous application of phosphogypsum at a dose of 40 t/ha and its rotational mixing with soil in a layer of 30–60 cm (Fr + FG 40 t/ha).

The number of experiments is one. After the experiment, in subsequent years, standard agricultural techniques were used in all variants of milling tillage and the application of phosphogypsum.

The experiment was performed in four replicates. The placement of options was sequential, repetitions were regular, the control was parallel to the strip of options. The area under the experiment was 0.4 ha, the size of the plot was 400 m * 10 m.

The crops cultivated were corn and sunflower.

The field research methodology.

Soil sampling – GOST 28168-89; soil moisture – GOST 134964-84: the aggregate composition of the soil – by the dry sieving method; soil density – by the cutting ring method; biological productivity – by the method of trial plots; development of the root system – by counting the number of roots crossing the site of 25 cm² in the soil profile in layers with a step of 5 cm.
The laboratory part of the research was based on the general requirements – GOST 29269-91, the generally accepted analytical methods for studying soil properties [10]; mathematical thermodynamic modeling according to [1], mathematical processing of research results in Excel 10.

3. Results

3.1. Morphological properties of the soil

The differences in the morphological properties of experimental soils are significant. The standard dumping used on the chernozems of Krasnodar Territory does not change the properties due to the nature of soil formation. The vertical differentiation of soil horizons is increasing. In the control option, the upper eluvial horizon of the soil has a rough structure. The transition to the illuvial horizon of the soil is sharp. The illuvial horizon has a dense structure, poorly permeable to the roots of plants. The entire rhizosphere is concentrated in the upper 25 cm soil layer. After mechanical treatment, the soil has a clumpy structure, reflecting signs of the solonetz process and slitogenesis in the soil profile.

3.2. Agrophysical properties of the soil

Compared with the control option, in all experimental options where phosphogypsum was applied, there are significant differences in the agrophysical properties of the soil. The entire soil layer of 0–60 cm contains soil aggregates, the soil is loose, easily amenable to mechanical treatment, no lumps were found in the soil profile after treatment. After the introduction of phosphogypsum into a layer of 30–60 cm, the morphological characteristics and agrophysical properties were stable during the observation period. The data on the aggregate composition of the soil (Table 1) show that the soil profile develops so that the blocks of the illuvial horizon of chernozem destroyed by treatment have a structure that is permeable to moisture and roots of cultivated plants. The soil becomes homogeneous and consists of small uniform aggregates; there are no signs of eluvial-illuvial differentiation of the soil profile, as well as signs of its restoration during the years of observation. The effect of transformation of the interaction of the upper soil layers with the illuvial horizon, transition horizon, and parent rocks can be observed (Table 1).

| Table 1. Agricultural composition of soil (mm), depending on treatment for some experimental options, % |
| --- | --- | --- | --- | --- | --- | --- |
| Option | Soil layer, cm | >30 | 30–10 | 10–3 | 3–1 | 1–0.25 | <0.25 |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Beginning of the experiment | 0–30 | 15 | 19 | 32 | 19 | 12 | 3 |
| K | 30–60 | 13 | 19 | 29 | 21 | 14 | 4 |
| Ph+PG 10 t/ha | 0–30 | 3 | 15 | 34 | 24 | 17 | 5 |
| | 30–60 | 3 | 17 | 36 | 24 | 14 | 6 |
| Ph+PG 40 t/ha | 0–30 | 2 | 12 | 31 | 29 | 18 | 8 |
| | 30–60 | 4 | 15 | 37 | 26 | 10 | 5 |
| Stagnation of the agroecosystem | 0–30 | 18 | 20 | 30 | 16 | 13 | 3 |
| K | 30–60 | 9 | 24 | 32 | 18 | 11 | 6 |
| Ph+PG 10 t/ha | 0–30 | 1 | 11 | 37 | 34 | 17 | 0 |
| | 30–60 | 3 | 12 | 38 | 36 | 10 | 1 |
| Ph+PG 40 t/ha | 0–30 | 2 | 5 | 29 | 42 | 18 | 4 |
| | 30–60 | 8 | 26 | 47 | 13 | 6 |
| HCP_{lo}, % | | | | | | | 3.3 |

In the control option, soil density at a depth of 22–25 cm was high, especially in the illuvial horizon – up to 1.35–1.45 g/cm³, which negatively affected the moisture penetration into the soil, its lateral distribution, stability of the soil structure and crop yields. The best density values were obtained in the options with rotational treatment and application of phosphogypsum. The values were 1.05–1.25 g/cm³ (Table 2).
Table 2. Soil density depending on treatment for some experimental options, t/m³

| Option | Soil layer, cm | Beginning of the experiment | Stagnation of the agroecosystem |
|--------|---------------|-----------------------------|-------------------------------|
| K      | 0–30          | 1.26                        | 1.29                          |
|        | 30–60         | 1.44                        | 1.41                          |
| Ph+PG 10 t/ha | 0–30         | 1.05                        | 1.19                          |
|        | 30–60         | 1.15                        | 1.21                          |
| Ph+PG 10 t/ha | 0–30         | 1.11                        | 1.14                          |
|        | 30–60         | 1.12                        | 1.25                          |
| НСР   | 05            | 0.11                        |                               |

HCP₅₀, t/m³ 0.11

3.3. Soil moisture regime

Under the standard agricultural techniques, in the control option, the moisture regime repeats the well-known laws of the natural-territorial complex of the north of Krasnodar Territory. There is a difficult penetration of moisture into the illuvial horizon of the soil, its lateral redistribution, evaporation from the soil surface. This negatively affects the soil moisture regime during the growing season.

After milling and applying phosphogypsum, the evaporation component is reduced. It creates the possibility of developing the root system with less energy and water, the biomass synthesis with the same amount of precipitation (Table 3).

Table 3. Volume of accessible moisture in the soil depending on treatment for some experimental options, mm

| Option    | Soil layer, cm | Beginning of the experiment | Stagnation of the agroecosystem |
|-----------|----------------|-----------------------------|-------------------------------|
|           |                | Beginning of vegetation     | End of vegetation              | Beginning of vegetation | End of vegetation | |
| K         | 0–30           | 99                          | 27                            | 82                       | 39               | |
|           | 0–60           | 180                         | 66                            | 171                      | 75               | |
| Ph+PG 10 t/ha | 0–30         | 84                          | 22                            | 103                      | 31               | |
|           | 0–60           | 172                         | 59                            | 195                      | 63               | |
| Ph+PG 40 t/ha | 0–30         | 105                         | 31                            | 88                       | 18               | |
|           | 0–60           | 190                         | 55                            | 181                      | 56               | |
| HCP₅₀, mm |                | 27.3                        |                               |                           |                   | |

A positive result of changes in the agrochemical properties of the soil is a good contact between the soil and phosphogypsum, as well as an improved soil moisture regime. Artificial small soil aggregates are a comfortable substrate for the development of the root system of plants and biota. In the first year, soil properties accelerate metabolic reactions in PPC, facilitating the transition of nutrients to accessible forms.

The forms of heavy metal ions Pb²⁺, Cd²⁺ in the soil after phosphogypsum application were determined using the mathematical thermodynamic model of the calcium carbonate – the calcium system of the soil solution, taking into account the association and complexation of ions. As a result of the calculations, it was found that after the application of phosphogypsum, the soil acidity decreased by 0.2–0.4 units. This is due to the buffering acidic properties of phosphogypsum, which develop after mixing it with the soil.

The calculation showed that the equilibrium concentration of Pb²⁺ increased from 4.99 to 11.4 %, that of Cd²⁺ increased from 59.08 to 67.44 %. Given the inhibition of the movement of free ions by other charged particles, the active concentration of free Pb²⁺ was 6.76 %, that of Cd²⁺ was 40.93 %. Mathematical modeling of the complex formation of heavy metals shows that the fraction of mobile forms of heavy metals in leached chernozem is small and does not pose a great threat to plants [2] (Fig. 1).
The calculated content of heavy metals in the soil after the application of phosphogypsum does not exceed the MPC [7, 13] (Fig. 2).

3.4. Morphological parameters of the sunflower root system

In the control option of the zonal agricultural technology, the sunflower root system is in the surface soil layer. In the plane of the soil section, a 25 cm² area was crossed by no roots in a layer of 0–5 cm 35 pcs, in a layer of 25–30 cm 1–2 pcs, in a layer of 35–40 cm (HCP05 = 3.5 pcs).

The soil structure after milling of the soil layer of 30–60 cm and applying phosphogypsum contributes to a deeper and more uniform penetration of the roots into the soil. The architecture of the root system is characterized by a fairly uniform distribution over the treated layer, thin roots predominate, the rhizosphere has an optimal habitus. The deep loose soil layer has aggregates corresponding to the scale of the architecture of the root system of steppe plants. The root system maintains the reaction of pH 7.0.

At a dose of phosphogypsum of 20 t/ha in the plane of the soil section, a 25 cm² area was crossed by 15 sunflower roots in a layer of 0–5 cm 27 pcs, in a layer of 25–30 cm 12 pcs, in a layer of 35–40 cm. The negative properties of phosphogypsum caused by the presence of strontium, lead, and cadmium are manifested to a small extent [2, 7, 13].

3.5. Agricultural production and recreational effect

The yield of sunflower (5.73 t/ha) and corn (12.44 t/ha) when phosphogypsum is applied is higher than in the control option by 4.65 and 10.72 t/ha, respectively, HCP05 increased the yield by 0.47 and 0.98 t ha, respectively. The recreational effect of the phosphogypsum unitilization option is due to the fact that accelerated utilization of phosphogypsum sludge collectors is achieved with subsequent reclamation of the alienated lands.

4. Conclusion

Based on the developed methodology, non-waste production of phosphorus fertilizers can eliminate environmental disasters, including in water systems of Krasnodar Territory.
Phosphogypsum utilization was tested simultaneously with milling subsoil agromeliorative cultivation of a soil layer of 30–60 cm. The recreational and agricultural production effect of phosphogypsum in carbonate Chernozem of the southern European facies of the northern zone of Krasnodar Territory was substantiated. The need for a new environmental protection strategy and measures for safe utilization of chemical waste, increasing soil fertility and improving quality of the ecosphere was justified.

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