Effect of meliorative doses of phosphogypsum on the agrochemical properties of the soil and the yield of sunflower

K Denisov, D Upolovnikov, I Poletaev and A Linkov
Saratov State Agrarian University named after N.I. Vavilov, Saratov, Russia
E-mail: konpetrov@yandex.ru

Abstract. The influence of meliorative doses of phosphogypsum application on agrochemical soil properties and sunflower yield was studied. The results of experiments carried out in the Volga region on light chestnut soils are presented. It was revealed that the content of heavy metals for all variants of the experiment did not exceed the approximate permissible concentration; application of phosphogypsum shifted the reaction of the soil environment towards neutral. The use of this agricultural technique increased the content of nutrients in the soil and labile organic matter, most of all, this was noted in the variant with a phosphogypsum dose of 8 t/ha. It was concluded that the combined application of mineral fertilizers and phosphogypsum at a dose of 4 t/ha leads to a significant increase in yield by 0.65 t/ha. The use of phosphogypsum as an ameliorant solves the environmental problem of utilizing wastes after the production of mineral fertilizers accumulated in the Russian Federation in the amount of about 50 million tons. The studies carried out have confirmed the soil-improving and fertilizing properties of phosphogypsum, as well as its environmental safety.

1. Introduction
Phosphogypsum is a product, the use of which in agriculture as an additive to mineral fertilizers is becoming more widespread today. More precisely, phosphogypsum is a product of the production of phosphoric acid. According to its composition, it can be characterized as a chemical ameliorant, as it contains up to 94% CaSO4, as well as a calcium-phosphorus-sulfur fertilizer [1-2]. Phosphogypsum is almost identical to natural gypsum, but with the correct organization of technological processes, its cost is 15-20% lower than of natural gypsum.

In addition, in the composition of non-fractional heparin, residues of phosphates, phosphoric acid (2-4%, including up to 1.5% water-soluble), sesquioxides, silicon compounds, trace impurities of rare earth elements are present as impurities [3-5].

The problem of using and storing phosphogypsum is relevant for many countries where natural phosphorites are processed. The degree of use of phosphogypsum in Russia is no more than 2-4% per year, while in Germany, Belgium, Japan it is about 100%.

Phosphogypsum is used on soils with high water content to reduce stickiness and prevent the formation of a waterproof crust. Phosphogypsum contains calcium, which displaces sodium from the soil and normalizes water permeability.

Phosphogypsum is applied to the soil as fertilizer once every few years in large quantities. It contains calcium and sulfur, that increases the yield of agricultural crops. In addition, it does not require cleaning before being introduced into the soil, since the phosphorus it contains is absorbed by plants [6-7].
Therefore, with the systematic use of non-fractional heparin, the accumulation of heavy metals in soil and plants is quite possible. This will determine the need for strict control over changes in the content of the latter in the soil and their entry into plant products.

In this regard, an urgent task is the agrochemical assessment of neutralized phosphogypsum, as well as the development of a technology for its use in agriculture.

The problem of the dosages of neutralized phosphogypsum and the frequency of its application is the main one in solving the problem of realizing the potential productivity of agricultural crops, optimizing the reaction of the environment, etc. Despite the fact that long-term experiments with phosphogypsum were carried out in Russia and their results were repeatedly generalized, the problem of determining the optimal doses of ameliorant in the conditions of the Volga region has been extremely insufficiently studied.

Our research is devoted to an important problem for agriculture - the study of the effect of phosphogypsum in combination with mineral fertilizers on the productivity of oilseeds and the production of high quality plant products, the agrochemical properties of soils and the identification of the possibility of using phosphogypsum as an ameliorant, phosphorus and sulfur fertilizer.

2. Materials and methods

Experiments were carried out in 2018 at the experimental field of the Saratov State Agrarian University named after N.I. Vavilov (Saratov Region, Engelsky District, Stepnoye).

The soils of the experimental site are dark chestnut, heavy loamy, coarse silty clay with a humus content of 2.8%.

The thickness of the humus horizon is \(A + B_1 = 41\) cm, the lower boundary \(B_C\) is 92 cm, boiling at a depth of 46-75 cm, the \(pH\) of the aqueous extract is 6.73. Exchangeable calcium predominates in the absorbed base. The share of these cations is 77.4–85.8% of the sum of bases, the share of magnesium cations is 12.1–20.0%. Down the profile, its amount increases. The sodium content is low, 1.0–1.7%.

The soil is moderately supplied with phosphorus, poorly supplied with nitrogen. The content of heavy metals is shown in (table 1).

| Index    | Lead | Cadmium | Zinc | Arsenic | Nickel |
|----------|------|---------|------|---------|--------|
| Content  | 90.5 | 0.31    | 64.2 | 2.5     | 17.65  |
| Approximate permissible concentration | 130.0 | 2.0 | 220.0 | 10.0 | 60.0 |

Horizon A is dark chestnut, of lumpy structure, depth of horizon is 25-30 cm.

Horizon AB is dark gray with a brownish tint, the total thickness of the horizons \((A + AB)\) is 70-130 cm, effervescence is observed in the lower part of B.

In general, the weather conditions in 2018 were not favorable for the growth and development of cultivated plants. An increase in air temperature above 30 °C and a lack of precipitation during critical periods of plant development did not allow a high yield to be formed.

The hydrothermal coefficient for the growing season was 0.62.

The scheme of the experiment included 4 options:

- Control (without phosphogypsum);
- Fertilized ground N12P52 – application of ammophos in a dose of 150 kg/ha;
- Fertilized ground + application of phosphogypsum in a dose of 4 t/ha;
- Fertilized ground + application of phosphogypsum in a dose of 8 t/ha.

Phosphogypsum was used in the spring for cultivation, the experiment was repeated 4 times, the plot area was 25 m², plots were randomized. The total area of the experimental site is 400 m².
Sunflower cultivation technology is generally accepted for the Saratov region. A hybrid of Machaon sunflower was sown.

During the experiment, the soil was analyzed according to the following indicators: the content of N, P, K, humus, and acidity.

Nitrate nitrogen was determined by the disulfophenol method with the Lunget-Griss reagent. Mobile forms of phosphorus and exchangeable potassium were determined according to the Machigin method in the modification of TsINAO GOST 26205-84. Humus content was determined according to the method of I.V. Tyurin in the modification of TsINAO GOST 26213-84.

The content of heavy metals in the soil was determined according to the “Guidelines for the determination of heavy metals in soils of agricultural land and crop production” (Moscow, 1992).

Heavy metals in sunflower seeds were determined according to the “Guidelines for the determination of heavy metals in forages and plants and their mobile compounds in soils” (Moscow, 1993).

The analysis of the structure of the yield and the biological yield of sunflower was carried out according to the Methodology of the state variety testing of agricultural crops (1989).

Acidity was determined according to GOST 26597-89 Sunflower. Oil content was determined according to GOST 10857-64 Oil seeds.

3. Results and Discussions

Keeping a soil fertility is an urgent task for the soils of the Volga region. The application of phosphogypsum dehydrate, that can improve the nutritional regime of agricultural crops, is one of the method for solving this problem.

According to the results of the experiment, the application of mineral fertilizers and phosphogypsum increased the content of nutrients in the soil, influenced its acidity and the content of labile organic matter (table 2).

| Variants                                      | NO₃  | P₂O₅  | K₂O  | PH   | Organic matter, % |
|----------------------------------------------|------|-------|------|------|------------------|
| Control                                      | 3.6  | 30.6  | 280  | 6.38 | 1.9              |
| Fertilized ground                            | 4.1  | 37.4  | 285  | 5.88 | 2.0              |
| Fertilized ground + phosphogypsum in a dose of 4 t/ha | 4.8  | 39.2  | 320  | 6.90 | 2.2              |
| Fertilized ground + phosphogypsum in a dose of 8 t/ha | 5.1  | 43.9  | 349  | 7.20 | 2.1              |

The content of nitrate nitrogen in the topsoil layer increased after application both of mineral fertilizers and phosphogypsum. After 8 t/ha of phosphogypsum, the content of nitrate nitrogen was 5.1 mg/kg, which exceeded the control by 41.7%. The dose of phosphogypsum of 4 t/ha increased the nitrogen content in the soil to 4.8 mg/kg, which exceeded the control by 33.3%. The application of only mineral fertilizers increased the content of this macroelement by only 13.8%.

Relating available phosphorus in the soil, its’ content increased in all variants of the experiment. Most of all it was marked after combined application of mineral fertilizers at a dose of 150 kg/ha and phosphogypsum at a dose of 8 t/ha. It averaged 43.9 mg/kg, exceeded the control variant with a content of 30.6 kg/ha by 43.5%. Slightly smaller increase was at the dose of phosphogypsum application of 4 t/ha, it was 28.1%. After application of mineral fertilizers without phosphogypsum, this figure reached 37.4 mg/kg, which also exceeded the control.

Having studied the average values of exchangeable potassium content in the soil, there has been marked an increase in all variants of the experiment. The difference in the potassium content in the soil according to the experimental variants was insignificant and ranged from 280 mg/kg in the control variant to 349 mg/kg in the variant with the combined application of mineral fertilizers and...
phosphogypsum at a dose of 8 t/ha. After application of fertilizers and phosphogypsum, the excess over the control variant was from 1.7 to 24.6%.

It has been established that the application of chemicals in sunflower cultivation had a significant effect on soil pH. In all variants with the application of phosphogypsum, soil deoxidation occurred. It was the highest in the variant with the application of phosphogypsum at a dose of 8 t/ha (7.2 units), while applying a dose of 4 t/ha it was 6.9 units. That exceeded the control by 0.82 and 0.52 units, respectively. These values fit into the optimum acidity values for sunflower.

The content of labile organic matter in the soil also increased in all variants of the experiment, due to the better development of plants, which was a consequence of an improvement in mineral nutrition.

The content of heavy metals in the soil did not exceed the approximate permissible concentration (APC) for all variants of the experiment (table 3).

### Table 3. Heavy metals content in sunflower crops by experimental variants, topsoil layer, mg/kg.

| Variants                              | Lead | Cadmium | Zinc  | Arsenic | Nickel |
|---------------------------------------|------|---------|-------|---------|--------|
| Control                               | 7.63 | 0.28    | 41.70 | 4.0     | 28.42  |
| Fertilized ground                     | 7.85 | 0.29    | 42.09 | 3.9     | 29.06  |
| Fertilized ground + phosphogypsum in a dose of 4 t/ha | 8.39 | 0.31    | 45.52 | 4.1     | 32.47  |
| Fertilized ground + phosphogypsum in a dose of 8 t/ha | 8.95 | 0.30    | 47.23 | 3.9     | 33.76  |
| APC                                   | 130.00 | 2.00    | 220.00 | 10.00   | 60.00  |

Having studied the cadmium content in the soil, it varied slightly according to the variants of the experiment and fluctuated within 0.28-0.31 mg/kg, which is about 15% of the APC. Arsenic content did not depend on the application of mineral fertilizers and phosphogypsum and in all variants of the experiment was not more than 41% of the APC; in the control, its content was 40% of the APC.

The lead content varied according to the experimental variants, but did not exceed the APC. When mineral fertilizers were applied, its content in the soil practically did not change. When phosphogypsum was applied, it increased by 17.3 and 14.0% at doses of 8 and 4 t/ha, respectively.

The zinc content also varied slightly according to the variants of the experiment. When applying phosphogypsum together with mineral fertilizer, it was 9.2-13.3%. The same trend was observed for nickel content. After combined application of mineral fertilizers and phosphogypsum, the excess did not exceed 18.7% in comparison with the control variant.

The most important factor in assessing any agronomic technique is yield. After application of mineral fertilizers and phosphogypsum, the yield of sunflower, depending on the dose, showed a significant increase in all variants (table 4).

### Table 4. Sunflower yield by experimental variants, t/ha.

| Variants                              | Yield | Yield increase |
|---------------------------------------|-------|----------------|
| Control                               | 1.63  | -              |
| Fertilized ground                     | 2.05  | 0.42           | 25.8 |
| Fertilized ground + phosphogypsum in a dose of 4 t/ha | 2.28 | 0.65           | 39.9 |
| Fertilized ground + phosphogypsum in a dose of 8 t/ha | 2.33 | 0.70           | 42.9 |
| LSD<sub>0.05</sub>                    | 0.071 |                |
| F<sub>fact</sub>                      | 207.9 |                |
| F<sub>theor</sub>                     | 3.86  |                |

In the control variant, the yield was 1.63 t/ha. The application of ammophos at a dose of 150 kg/ha increased the yield of sunflower seeds by 25.8% and was 2.05 t/ha. After application of mineral fertilizers together with phosphogypsum at a dose of 4 t/ha during cultivation, the increase to the control was 0.65 t/ha, and at a dose of 4 t/ha - 0.70 t/ha, respectively.
It should be noted that the variants with different doses of phosphogypsum did not differ significantly, the difference was 0.05 t/ha.

Product safety is also very important index. Within the framework of the Customs Union, the content of toxic elements in crop products is determined by the technical regulation of the Customs Union 015/2011 “On grain safety”, which defines the maximum permissible limit (MPL) of heavy metals.

According to table 5, the content of heavy metals in plant raw materials did not exceed the maximum permissible level in all variants of the experiment.

**Table 5.** The content of heavy metals in sunflower according to the variants of the experiment, mg/kg of dry matter.

| Variants                        | Lead  | Cadmium | Arsenic |
|--------------------------------|-------|---------|---------|
| Control                        | 0.34  | 0.052   | 0.015   |
| Fertilized ground              | 0.36  | 0.054   | 0.011   |
| Fertilized ground + phosphogypsum in a dose of 4 t/ha | 0.41  | 0.069   | 0.016   |
| Fertilized ground + phosphogypsum in a dose of 8 t/ha | 0.57  | 0.086   | 0.017   |
| MPL                            | 1.0   | 0.1     | 0.3     |

The application of fertilizers and phosphogypsum did not affect the arsenic content in sunflower oil seeds. This indicator ranged from 0.11 to 0.17 mg/kg of dry matter.

The lead content after the application of phosphogypsum was 20.6-67.6% higher than in the control variant. The application of mineral fertilizers increased the lead concentration in plant raw materials to 0.36 mg/kg of dry matter, which is 5.8% higher than in the control.

Most of all, the application of phosphogypsum increased the cadmium content in sunflower seeds, it was 0.086 mg/kg of dry matter after application of 8 t/ha of phosphogypsum and 0.069 mg/kg of dry matter after application of 4 t/ha of phosphogypsum. That exceeds the control variant by 65.4 and 32.7 %, respectively. Application of only mineral fertilizers practically did not affect the cadmium content in sunflower oil seeds.

4. Conclusion

The application of phosphogypsum and mineral fertilizers increased nutrients content in the soil, as well as the content of organic matter, and led to the soil deoxidation.

After combined application of mineral fertilizers and phosphogypsum in a dose of 8 t/ha, the greatest increase in the content of nitrogen, phosphorus and potassium was observed in comparison with other variants of the experiment. After application of the maximum dose of phosphogypsum exceeded the control variant, the application of mineral fertilizers and phosphogypsum at a dose of 4 t/ha, nitrogen content in the soil was higher by 41.7; 24.4 and 6.25%, phosphorus content – by 43.5; 14.8 and 11.9%, and potassium content – by 24.6; 22.5 and 9.1%, respectively.

The reaction of the soil medium shifted towards neutral after phosphogypsum application., The value of the indicator increased with an increase in the application dose, so at a dose of 4 t/ha, the difference with the control variant was 0.52 units, after application of 8 t/ha it was 0.82 units.

The application of mineral fertilizers and phosphogypsum increased the amount of organic matter in the soil from 0.1 to 0.3%. Most of all, it increased in the variant after application of 4 t / ha of phosphogypsum (2.2%). The content of heavy metals in the soil in all variants of the experiment did not exceed the APC.

The application of mineral fertilizers at a dose of 150 kg/ha significantly increased the yield of sunflower by 25.8%. Application of mineral fertilizers and phosphogypsum at a dose of 4 t/ha also led to a significant increase in yield by 0.65 t/ha. Nevertheless, increasing the dose of phosphogypsum to 8 t/ha did not significantly increase the yield of sunflower.
Thus, the application of phosphogypsum dihydrate during spring cultivation can increase the yield of agricultural crops, while the content of heavy metals both in the product and in the soil does not exceed the APC. The use of phosphogypsum as an ameliorant can solve the environmental problem of utilizing wastes after the production of mineral fertilizers accumulated in the Russian Federation in the amount of about 50 million tons. Thus, the studies carried out have confirmed the soil-improving and fertilizing properties of phosphogypsum, as well as its environmental safety.

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