Accounting for strontium content in the system ameliorant - soil - plant to establish an environmentally safe dose of phosphogypsum

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Abstract. The strontium content in phosphogypsum, soil and plants has been studied. It has been established that during the processing of phosphate raw materials, most of the strontium passes into phosphogypsum, reaching 1.4–2.3% in it. With the introduction of a single dose of phosphogypsum (23 t / ha), the content of total strontium in the soil increased to 309–364, and a double dose to 402, which is below the maximum permissible level (600 mg / kg). The ratio between calcium and strontium in the medium sodium reclaimed chernozem solonetz was at a good and satisfactory level, and in plants it was more than 100, which is typical for territories with a relatively satisfactory ecological situation. Meliorative (calculated) agronomic and ecologically safe rates of phosphogypsum consumption for soils of solonetzic complexes of the Volga economic region are given.

1. Introduction
The presence of such important nutrients as calcium, phosphorus, sulfur, a number of trace elements in phosphogypsum makes it attractive for use not only as a fertilizer on nutrient-poor soils, but also as an ameliorant. However, the presence of strontium, fluorine, cadmium and other harmful impurities of 1 and 2 hazard classes in it poses a number of questions for agro chemists, ecologists and hygienists, the answers to which may not always be unambiguous. In this regard, we set ourselves the goal of studying the behavior of strontium in the meliorant - soil - plant system and trying, on the basis of the experimental data obtained, to calculate an ecologically safe dose of phosphogypsum.

2. Materials and methods
In the course of the experiment, the use of acid phosphogypsum produced by LLC Balakovo Mineral Fertilizers from the Khibiny apatite concentrate. Mass fraction of the main substance (CaSO4 • 2H2O) in terms of dry dihydrate 92%, hygroscopic water 20%, total phosphorus 1.5%, total strontium 1.4%, water-soluble fluoride compounds 0.24%.

Reclamation of medium sodium chernozem solonetz was carried out in the Volgar farm in Balakovo district. The reclamation dose of phosphogypsum was calculated according to the content of exchangeable sodium in the AUC and amounted to 23 t / ha. It was compared with a doubled dose of 46 t / ha to better reveal the process of migration of strontium in the soil at high doses of the ameliorant. Phosphogypsum for reclamation was brought from different dumps - old and fresh.

The chernozem solonetz was compared with the dark chestnut soil of the Engels district. The strontium content and the ratio of calcium to strontium were determined in the biomass of four solonetz-resistant crops - winter rye, barley, sorghum and alfalfa. The gross strontium and calcium content in...
soils, plants and phosphogypsum was determined spectrometrically with inductively coupled plasma (AES-ICP, ICP-MS). Analyzes were performed at the V.V. Dokuchaeva RAAS.

3. Results
The main factor limiting the fertility of solonetz is their water-physical properties. When wet, the solonetz horizon is highly plastic, viscous, and sticky, swells strongly, and easily pentatizes. When the solonetz horizon dries up, the soil mass is strongly compressed, fracturing and blockiness of soils develop. This leads in some cases to rupture of plant roots. The hardness of the solonetzic horizon increases, which contributes to an increase in soil resistance during processing. The water permeability of alkaline soils is 10-15 times less than that of non-alkaline soils. This leads to the fact that most of the precipitation flows down the surface. Therefore, the total moisture reserve in solonetzes is always lower than in zonal soils. The largest amount of solonetz lands is located in the Volga region and Western Siberia - 11.6 and 10.2 million hectares [1-5].

Scientists SSAU them. N.I. Vavilov [6-8] have significant experience in reclamation and development of solonetz and alkaline soils, the area of which in the Saratov region is 1 million 670 thousand hectares. The positive effect of phosphogypsum on the fertility of solonetz and solonetzic soils has been established, which boils down to the following:

- When phosphogypsum is applied at doses of 2-5 t / ha under non-irrigated conditions, stable forms of humic acids are formed, and the processes of desalinization and desalinization of the soil are enhanced. Its application is most effective on irrigated lands;
- Phosphogypsum, due to the presence of phosphorus in its composition, has a stronger effect on soil fertility and crop yield than ordinary gypsum;
- Mixtures of phosphogypsum are even more effective, especially with phosphate rock. Mixtures with lime, flasks, waste defect from sugar factories are acceptable;
- Phosphogypsum and mixtures based on it have a long-term effect (5-10 years);
- Phosphogypsum is much cheaper than natural raw gypsum;
- The effect of phosphogypsum is enhanced when combined with organic fertilizers. Composting is one of the most important methods for recycling phosphogypsum and protecting the environment from pollution;
- The high ecological efficiency of the use of phosphogypsum and its mixtures with phosphate rock was revealed.

Strontium is close to calcium in its chemical properties and behavior. The coefficient of biological accumulation of strontium by plants is more than 1, which leads to the possibility of its concentration due to biogenic accumulation in the upper soil horizons.

In the samples of phosphogypsum produced at LLC BMU, the content of total strontium is 1.4% on average, reaching in some cases 1.9-2.3%. During the processing of apatite, most of the strontium is converted into phosphogypsum, which can lead to the pollution of reclaimed solonetze and solonetzic soils. The ratio between Ca: Sr in phosphogypsum varies, on average, from 12 to 18.

Possible contamination of soils and plants with strontium began to be discussed back in the 1980s and 1990s [9]. The problem was aggravated by the fact that no normative documents were developed for it regulating its environmental safety. "Criteria for assessing the ecological situation of territories to identify zones of an ecological emergency and zones of ecological disaster" appeared only in 1992 [4]. They show the limits of the ratio between Ca: Sr in plants and forages, taking into account the anomalous area of the landscape. A relatively satisfactory ecological situation is recognized as one in which the ratio between Ca: Sr in plants and feed is more than 100 over the entire area. If it is less than 10-1 on more than 20% of the area, then this indicates an emergency ecological situation.

There are no approved sanitary and hygienic standards for strontium content in soil. V.V. Kowalski [3] believes that the upper harmless limit for strontium content in soils is its concentration of 600 mg / kg. It is this amount of it found in the geochemical provinces, where Urovskaya disease is widespread,
causing disturbances in metabolism in humans and animals, substitution of strontium for calcium in bone tissue, leading to looseness and fragility of bones. Therefore, when applying phosphogypsum to the soil, first of all, one should pay attention to the initial strontium content in the soil.

Our studies have shown that the content of total strontium in the upper layer of soils in the control variant ranges from 119 to 210, averaging 173 mg/kg (table 1).

**Table 1.** The content of total strontium and the ratio of calcium to structure in the soils of the Trans-Volga region.

| No.p/p | Horizon          | Depth, cm | Sr total, mg/kg | Gross CaO,% | Ca: Sr |
|--------|------------------|-----------|-----------------|-------------|--------|
|        | Medium sodium chernozem solonetz |           |                 |             |        |
| 1      | A_PAH           | 0-20      | 196             | 3.2         | 117    |
| 2      | A_PAH           | 0-20      | 210             | 4.2         | 143    |
| 3      | A_PAH           | 0-20      | 189             | 3.3         | 127    |
| 4      | A_PAH           | 0-20      | 151             | 4.9         | 232    |
| 5      | A_PAH           | 0-20      | 119             | 3.1         | 185    |
|        | Solonets chernozem medium-sodium reclaimed (23 t/ha of phosphogypsum from the old dump) | | | | |
| 6      | A_PAH           | 0-20      | 324             | 3.7         | 80     |
| 7      | A_PAH           | 0-20      | 433             | 4.0         | 65     |
| 8      | A_PAH           | 0-20      | 345             | 3.7         | 75     |
| 9      | A_PAH           | 0-20      | 344             | 3.8         | 78     |
| 10     | A_PAH           | 0-20      | 376             | 3.9         | 74     |
|        | Solonets chernozem medium-sodium reclaimed (23 t/ha of phosphogypsum from fresh dump) | | | | |
| 11     | A_PAH           | 0-20      | 374             | 4.4         | 83     |
| 12     | A_PAH           | 0-20      | 260             | 4.3         | 119    |
| 13     | A_PAH           | 0-20      | 171             | 5.0         | 205    |
| 14     | A_PAH           | 0-20      | 370             | 4.8         | 92     |
| 15     | A_PAH           | 0-20      | 369             | 4.8         | 89     |
|        | Solonets chernozem medium-sodium reclaimed (46 t/ha phosphogypsum) | | | | |
| 16     | A_PAH           | 0-20      | 466             | 4.8         | 75     |
| 17     | A_PAH           | 0-20      | 355             | 4.3         | 87     |
| 18     | A_PAH           | 0-20      | 328             | 4.7         | 101    |
| 19     | A_PAH           | 0-20      | 551             | 4.9         | 63     |
| 20     | A_PAH           | 0-20      | 309             | 4.2         | 97     |
|        | Dark chestnut soil |   |                 |             |        |
| 21     | A_PAH           | 0-27      | 165             | 1.7         | 75     |
| 22     | C                | 200-215   | 240             | 5.5         | 165    |

With the introduction of a single dose of phosphogypsum (23 t/ha), the content of total strontium in the soil increased to 309-364, and a double dose - to 402 mg / kg, which is below the maximum permissible level.

In soils where the strontium content is below the maximum permissible level, the ratio between calcium and strontium in the soil before and after the application of the ameliorant becomes the determining factor for assessing the environmental hazard of the ameliorant. To date, there are no documents regulating it, which makes it difficult to make decisions on the environmental safety of applying phosphogypsum.

V.V. Kovalsky [3] found that with a decrease in the ratio between the gross forms of calcium and strontium in soils below 35-40, the first signs of the disease in humans can be observed. In cattle, developmental disorders are manifested when the ratio of calcium to strontium in soils is ≤ 10. In the Kursk chernozems, the Ca: Sr ratio is 200, on average in the soils of chernozem regions it is 111, and in non-chernozem regions - 50. Analyzing these data, I.N. Lyubimova et al. [6] are taken for satisfactory...
Ca: Sr ratios in soils > 60, and good > 100. The ratio in soils of gross calcium and strontium compounds below 50 is unacceptable.

In our samples, the ratio between calcium and strontium in the control averaged 161, and when phosphogypsum was added - 74-118, that is, it was at a good and satisfactory level.

The content of total strontium increases down the profile. Its maximum is confined to saline, gypsum and carbonate-bearing horizons. They are a kind of geochemical barrier for strontium. Total strontium 165 was found in the arable layer (0-27 cm) of the dark chestnut soil of the VolzhNIIGiM in the Engels district of the Saratov region, and 240 mg/kg in the carbonate parent rock (table 1).

The gross calcium content in the first case was 1.7, and in the second - 5.5%. The ratio between calcium and strontium in the arable layer was 75, and in the parent rock - 165, that is, in the dark chestnut soil of the Engels district of the Saratov region, the ratio between calcium and strontium is at a good and satisfactory level.

An integrating indicator in assessing the environmental consequences of the introduction of phosphogypsum is the ratio between calcium and strontium in agricultural products. Territories with a relatively satisfactory ecological situation, as mentioned above, should have more than 100 of it throughout the reclaimed area.

In the studies carried out on the salt licks of the syrt Trans-Volga region, the Caspian lowland and the Don plain, over 20 species of grain and forage field crops were studied [5]. Mustard, winter rye, winter wheat, millet, barley, sorghum, corn, Sudanese grass, sweet clover, wheatgrass, and alfalfa have the highest salt and salt tolerance, high productivity and profitability of production. We studied the ratio between calcium and strontium in the biomass of four crops growing on medium sodium chernozem solonetz - alfalfa, winter rye, barley and sorghum (table 2).

| Culture          | Sr, mg/kg | CaO, % | Ca : Sr |
|------------------|-----------|--------|---------|
| Control          |           |        |         |
| Winter rye       | 35        | 0.43   | 123     |
| Barley           | 30        | 0.41   | 137     |
| Sorghum          | 18        | 0.28   | 155     |
| Alfalfa          | 125       | 1.46   | 117     |
| Phosphogypsum, 23 t/ha | |        |         |
| Winter rye       | 48        | 0.55   | 112     |
| Barley           | 45        | 0.50   | 111     |
| Sorghum          | 35        | 0.41   | 117     |
| Alfalfa          | 155       | 1.60   | 103     |

The entry of strontium into plants is primarily determined by the content of its readily soluble compounds in the soil solution, the physiological characteristics of plants, and weather conditions. The relationship between these indicators is not always linear. The high content of calcium in soils reduces the absorption of strontium by plants, and the introduction of phosphogypsum leads to its increase.

The strontium concentration in plants varied from 18 to 125 mg/kg in the control area and from 35 to 155 mg/kg in the reclaimed area. In terms of strontium uptake, crops are ranked in the following decreasing order: alfalfa, winter rye, barley, sorghum. Phosphogypsum increased the strontium content in the biomass of alfalfa by 1.2 times, barley and winter rye by 1.4-1.5 times, and sorghum by 1.9 times. Despite the increase in the concentration of strontium in the biomass of plants in the variant with phosphogypsum, the ratio between calcium and strontium in all cases is more than 100, which indicates a satisfactory ecological situation. Thus, the introduction of phosphogypsum at ameliorative dose of 23 t/ha does not lead to contamination of soils and agricultural products with strontium.

There are three types of doses of ameliorant introduction - reclamation, agronomic and environmentally friendly. Reclamation is calculated on the displacement of exchangeable sodium or on
the improvement of the indicator, by which the degree of solonetzicity is estimated to the optimal level.

Agronomic is focused on maximum yield increase. Environmentally friendly is calculated by the element that is the first to reach the PDK level of pollutants for soil. Approximate ameliorative and agronomic doses of the introduction of gypsum-containing materials in the soils of the solonetz complexes of the Volga economic region are presented in table 3 [6].

To calculate the environmentally safe dose of phosphogypsum, use the following formula:

\[ D_e = \frac{(PDK - C_2)}{C_1} \times \frac{H \times d}{S_{fg} (100 - W)} \times 10^3 \]  

Where: \( D_e \) - ecologically safe dose of ameliorant, t/ha; \( C_1 \) - strontium content in the ameliorant, mg/kg; \( C_2 \) - strontium content in soil, mg/kg; \( H \) is the depth of the arable layer, cm; \( d \) - soil density, g/cm³; \( S_{fg} \) - gypsum content, %; \( W \) is the moisture content of phosphogypsum, %.

| No | Soil, class of solonetz complex | Humidification conditions | Reclamation Agronomic |
|----|--------------------------------|--------------------------|----------------------|
| 1  | Chestnut salt licks steppe and meadow-steppe medium sodium | Irrigated | 12 | 12 |
| 2  | Chestnut salt licks steppe and meadow-steppe medium sodium | Rainfed | 5-10 | 10 |
| 3  | Chestnut salt licks steppe and meadow-steppe medium sodium | Irrigated | - | 12 |
| 4  | Solonetz chernozem and chestnut steppe and meadow-steppe medium sodium | Rainfed | 10 | 10 |
| 5  | Solonets soils chernozem steppe low and medium sodium | Rainfed | 10 | 10 |
| 6  | Solonets soils chernozem meadow-steppe medium and multisodium | Rainfed | 6-8 | 8 |
| 7  | Solonets chernozem meadow-steppe and meadow medium- and multi-sodium | Rainfed | 10 | 10 |
| 8  | Solonetz chernozem and chestnut steppe and meadow-steppe low and medium sodium | Rainfed | 6-8 | 8 |
| 9  | Solonets chernozem meadow-steppe and meadow medium- and multi-sodium | Rainfed | 8-40 | 24 |
| 10 | Solonets soils steppe and meadow-steppe medium sodium | Irrigated | 12 | 12 |
We substitute the experimental data into the formula for the environmentally safe dose of strontium phosphogypsum and get:

\[ D_E = \frac{(600 - 173)}{14} \times \frac{20 \times 1.2}{92 (100 - 10)} \times 10^3 = 88.4 \text{ t/ha phosphogypsum} \] (2)

Calculations show that with the strontium content in phosphogypsum equal to 1.4%, only with a dose of ameliorant application of more than 88 t / ha, the strontium content in the soil will be exceeded equal to 600 mg / kg. It is also very important to carefully monitor the ratio between calcium and strontium in soils and plants. Control over it on background and reclaimed areas in the first 2 years after reclamation is mandatory.

It is possible to reduce the flow of pollutants from reclaimed soils into plants by using the underlying carbonate and gypsum-bearing horizons, the combined introduction of phosphogypsum with chalk, phosphorite flour or limestone, the use of glauconites and zeolites, which sorb strontium and other undesirable impurities.

4. Conclusion
Increased strontium concentrations in biological objects cause the development of bone tissue diseases in animals and humans. Therefore, it is extremely important in the reclamation of solonetz and solonetze soils to take into account the content of this element and its ratio with calcium in soil and plants.

When processing phosphate raw materials, most of the strontium goes into phosphogypsum. The average content of this element in phosphogypsum is 1.4%, and in some cases reaches 1.9-2.3%. The calcium to strontium ratio ranges from 12 to 18.

An average of 173 mg / kg of strontium was found in the arable layer of the chernozem-sodic solonetz. Reclamation doses of phosphogypsum (single and double) increase the content of this element in the soil by 1.8-2.3 times, bringing its concentration to 300-400 with the upper harmless limit of 600 mg / kg. The ratio of calcium to strontium in the topsoil of the solonetz is good in the control, and satisfactory with phosphogypsum.

In terms of strontium uptake, agricultural crops are ranked in the following decreasing order: alfalfa> winter rye, barley> sorghum. Phosphogypsum increases the strontium concentration in plants by 1.2-1.9 times. The ratio between calcium and strontium in plants varies from 103 to 155, which indicates a satisfactory ecological situation. Both tested doses of phosphogypsum (23 and 46 t / ha) are environmentally friendly. In the first two years after the reclamation, control over the strontium content and its ratio with calcium is mandatory.

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