Agroecological efficiency of periodic use of neutralized phosphogypsum in rice crops

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Abstract. The purpose of the experiment was to study the influence of periodic using of neutralized phosphogypsum on the fertility of meadow chernozem soils of Krasnodar Territory, achieving of the appropriate level of rice agroecosystem productivity, and the quality of rice grain. The timing of the effective use of phosphogypsum as a phosphorus fertilizer was revealed during the experiment. It was proved that the same level of mobile phosphorus content in rice soils can be achieved by using either phosphogypsum or standard phosphorus-containing fertilizers. Given the fact that nitrogen and potassium fertilizers are already used, using of phosphogypsum provides an opportunity of getting a 6,34 tons/hectare yield of rice (the same result was achieved using N120P80K60 fertilizer). 3 years after re-fertilizing the soil with phosphogypsum we can notice that effectiveness of phosphogypsum in optimization of rice mineral nutrition program contributes to cost savings of 4155 RUB/hectare in comparison with traditional fertilizing system.

1 Introduction

The country's sustainable development strategy in the agroecological sphere should be based on the saving and restoration of natural agroecosystems, stabilization and improvement of environmental quality, and implementation of recycling of industrial waste (including phosphogypsum). Using of phosphogypsum is associated with the problem of rational use of natural resources. At the same time, a lot of critical tasks can be solved, such as fuller use of raw materials, improvement of ecological situation in the region, economically and agronomically effective increase in soil fertility.

The use of phosphogypsum is effective in various soil and climatic zones as the main fertilizer for the soil and the top-dressing for cereals, vegetables, technical crops and other crops. The use of phosphogypsum in rice cultivation can significantly improve the physicochemical properties of soils and their water-air and nutrition regimen. It can also increase the calcium content in the soil absorption complex [1,2].

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The country's agricultural sector needs for phosphogypsum to eliminate excessive alkalinity and salinity of soils is 2.5-3.2 million tons. Natural gypsum is used in small quantities for this purpose (not more than 4%) [3,4]. The increase in the content of sodium ions in soil leads to disruption of the soil structure, also a crust which is impervious to water appears on the surface of the soil. Phosphogypsum effects on the soil more effectively than natural gypsum, because it dissolves better in soil solute [5,6,7]. When it is used, calcium ions in soil absorbing complex displace sodium ions, soil alkalinity is decreasing, and soil water-permeability is restoring [8].

In neutralized phosphogypsum produced by LLC EuroChem-BMF the percentage of the main substance ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is 92%, calcium content indicator is more than 37%, sulfur content indicator is 21% and phosphorus content is 1.5-2.1%. Phosphogypsum should be used for fertilizing the soil once in a few years. This fertilizer gives an opportunity to get a significant yield increase due to improving soil structure and increasing the indicator of phosphorus, sulfur and calcium content [9].

However, phosphogypsum has a number of disadvantages, and the main one is the presence of heavy metals in its composition as unwanted impurities. Thereby, an important task of agriculture is the development of evidence-based standards and methods of using phosphogypsum for environmentally friendly crop production. That's why there are obvious relevance and need for research on the agroecological assessment of the effect of re-fertilizing the soil with phosphogypsum in the conditions of rice cultivation on the agrochemical and physicochemical parameters of soil fertility, yield and quality of rice grain [10].

2 Materials and Methods

The object of study are meadow chernozem soils of the Krasnodar Territory which were mainly formed on heavy alluvial deposits [11,12]. The soil is moderately provided with mobile forms of nitrogen, humus content in the arable layer of the soil is 3.26%, phosphorus content is 54.8 mg/kg, exchange potassium content is 328.5 mg/kg, exchange calcium content is 34.6 mEq/100g, pH w. 6.6 [13]. The experience scheme in 2011 with a single use of phosphogypsum included 6 options: 1. Control values (without any fertilizers); 2. N120K60; 3. N120P90K60; 4. Phosphogypsum, 3 tons/hectare; 5. N120K60+ phosphogypsum, 3 tons/hectare; 6. N120P90K60+ phosphogypsum, 3 tons/hectare. Each experiment was repeated 4 times. Phosphogypsum was used before rice sowing superficially with further deepening into the soil to a depth of 10-15 cm. Nitrogen fertilizers were used fractionally: 60% of fertilizers were used as a main fertilizer and 40% of it were used as a top-dressing in the tillering phase. The seeding rate is 5-7 million of seeds per 1 hectare with deepening into the soil to a depth of 1.5 cm when shortened rice flooding is chosen, or with deepening to a depth of 0.5-1.0 cm if it is planned to get rice seedlings from under the water.

3 Results and discussion

The use of phosphogypsum positively affected the growth of rice: after 4 years of research experimentator noticed an increase in plant height by an average of 3.0-5.8 cm (from control value which equals to 89.7 cm, to 95.5 cm after using 3 tons of phosphogypsum per hectare of rice plantations). The number of plant roots has also increased on 11.0-14.0 roots/plant, the indicator of bushiness and the number of spikelets of rice are also increased on 162-206 spikelets/10 plants. The highest values of indicators were noted during the experiment with using of phosphogypsum in a dose of 3.0 tons/hectare (in particular, the

weight of 1000 grains increased by 1.4 g to 31.4 g which led to an increase in rice grain yield).

The use of phosphogypsum separately and in combination with nitrogen and potassium fertilizers led to obtaining a sustainable increase in grain yield (over an average of 4 years, the yield indicator was equal to 4.2-7.0 centners/hectare due to using mineral fertilizers). The increase was 10.2-53.5% if we compare results of experiments with control values (table 1). The use of phosphogypsum allowed to get an additional yield (4.2 centners/hectare), the optimal variant was “N120K60+ phosphogypsum, 3 tons/hectare”. The use of phosphorus fertilizers simultaneously with phosphogypsum did not have noticeable effectiveness. However, if phosphogypsum was not used, the effect of phosphorus fertilizers was quite clear and perceptible.

Table 1. The dependence of the rice crop on the conditions of phosphogypsum usage.

Experiment options	Yield. centners/hectare	Increase		Grain quality indicators. %			
		% to control values	Depending on the ph.gypsum. centners/hectare	Protein content	Fracture	Yield of rice	
						Whole grain	Crushed grain
Control values (without any fertilizers)	41.3	-	-	7.1	28	75.3	24.7
N ₁₂₀ K ₆₀	56.4	36.5	-	7.4	24	76.0	24.0
N ₁₂₀ P ₉₀ K ₆₀	58.4	41.4	-	7.5	20	79.0	21.0
Phosphogypsum. 3 tons/hectare	45.5	10.2	4.2	7.1	25	75.8	24.2
N ₁₂₀ K ₆₀ + phosphogypsum. 3 tons/hectare	63.4	53.5	7.0	7.2	25	76.8	23.2
N ₁₂₀ P ₉₀ K ₆₀ + phosphogypsum. 3 tons/hectare	63.4	53.5	5.0	7.3	26	79.9	20.1
HCP ₀₅	1.6			0.15	2.0	2.0	

The use of phosphogypsum in combination with mineral fertilizers provided a significant increase in the amount of proteins from 7.1 to 7.3%. When using mineral fertilizers, the percentage of grain cracking decreased from 28 to 20% (when using phosphogypsum without any other fertilizers or in combination with mineral fertilizers - to 25%). The total yield of rice in the mentioned experiment variants varied from 70.8 to 71.5%. But different combinations of fertilizers affected a lot on the number of whole and cracked rice grains: the control value is equal to 75.3% of rice with the whole grain, the use of full complex of fertilizers and different combinations of mineral fertilizers and phosphogypsum led to increasing of this value to 79.0 and 79.9% respectively (which means that the percentage of cracked grains was 21.0-20.1%).

Results of the research demonstrate that the content of heavy metals did not go beyond the natural range of values, the increase in concentration of heavy metals after using phosphogypsum (3 tons per hectare) was not confirmed during the experiment. It means that the use of phosphogypsum fits into environmental regulations. The content and proportions of mobile forms of heavy metals after using of phosphogypsum did not exceed the maximum permissible concentrations. Therefore, phosphogypsum was not a threat to plants.

Rice grain analysis results also did not reveal a significant increase in heavy metals, grain quality met requirements of sanitary standards and regulations 2.3.3.1078-01

established in Russian Federation. The ratio of calcium to strontium in phosphogypsum is 75-85 which indicates its environmental safety. The strontium content in the soil ranged from 0.2 to 0.4 mg/kg. The ratio of Ca/Sr in soils which took part in experiment is 157-149:1, and the significant difference between experimental indicator and the control value (without any fertilizers) was not found. Therefore, the contamination of the soil with strontium due to using phosphogypsum is unlikely [14].

The experiment in assessing the agroecological effectiveness of re-fertilizing soil with phosphogypsum in conditions of rice crop rotation was conducted in 2016 when the single using of phosphogypsum was tested during the other field experiment. It helped to simulate the stages of rice crop rotation. Following variants of fertilizing were tested during the experiment: 1. Without any fertilizers; 2. N120P80K60; 3. N120K60 + phosphogypsum, 4 tons per hectare (the 1st year); 4. N120K60+ phosphogypsum aftereffect (2nd year); 5. N120K60+ phosphogypsum aftereffect (3rd year). Rice sowing method - spreading. Regime of irrigation - shortened flooding.

Plant growth analysis in mentioned experiments (including the tests with phosphogypsum aftereffect) demonstrated that re-fertilizing the soil with phosphogypsum has a positive effect as well. The height of plants is 23.2-28.1% greater if we compare to control values in the tillering phase, 12.6-25.1% greater in seed germination phase and 14.9-26.1% greater in full ripeness phase (table 2). The absence of significant differences in plant height at the phase of seed germination means that re-fertilizing the soil with phosphogypsum isn't toxic, and that plant nutrition is balanced because we don't see the excessive stretching of the plant stem (and it means that the risk of plants dying reduces).

Table 2. Rice plant height, cm.

Variations	Plant vegetation phase		
	Tillering	Sweeping	Full maturity
Without any fertilizers	30.2	84.6	85.5
N ₁₂₀ P ₈₀ K ₆₀	38.5	105.8	107.8
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (1st year)	38.7	103.4	105.1
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (2nd year)	37.8	98.6	99.9
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (3rd year)	37.5	97.3	98.8
HCP ₀₅	2.1	5.2	5.6

Fertilizing the soil in doses of N120P80K60 provides nutrition supply in an amount that allows plants to form the biomass, which is 37.1% more at the tillering phase, 28.3% more at the seed germination phase and 18.8% more at the full ripeness phase in comparison with biomass to be formed by rice that has not received any fertilizers. The result of experiment in which the effect of N120K60 and the aftereffect of phosphogypsum was taken into account (at the 1st and the 2nd year) is the same. As for the 3rd year of phosphogypsum aftereffect, experimentator noticed the decrease of accumulating biomass by rice (we should remember that mineral fertilizers were not used during the 3rd year as well) (table 3).

Table 3. Dry weight of rice plants, g.

Variations	Plant vegetation phase		
	Tillering	Sweeping	Full maturity
Without any fertilizers	0.35	2.51	3.67
N ₁₂₀ P ₈₀ K ₆₀	0.48	3.22	4.36
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (1st year)	0.48	3.21	4.35

N ₁₂₀ K ₆₀ ⁺ phosphogypsum aftereffect (2nd year)	0.47	3.17	4.32
N ₁₂₀ K ₆₀ ⁺ phosphogypsum aftereffect (3rd year)	0.46	3.14	4.25
HCP ₀₅	0.04	0.04	0.03

The results of analysis of the plant mass by the content of nitrogen, phosphorus and potassium in all variants of experiment showed us that the amount of mentioned chemical elements when using phosphogypsum was significantly bigger than that of plants in the control variant. This indicates the same level of mineral nutrition of agrocenosis, both when using N120P80K60 and when using N120K60 + phosphogypsum. 3 years after re-fertilizing the soil with phosphogypsum (4 tons per hectare) the positive effect of phosphogypsum as phosphorus fertilizer was maintained, although the fading effect of fertilizing was already noticeable at this time. The downward trend is noted in relation to these indicators, but the difference between previous and newly obtained values is doubtful (table 4).

Table 4. Dynamics of nitrogen, phosphorus and potassium content in rice plants, % of dry mass.

Variations	Seedlings			Tillering			Sweeping			Full maturity					
										Leaves + stems			Grains		
	N	P	K	N	P	K	N	P	K	N	P	K	N	P	K
Without any fertilizers	2.11	0.61	2.85	1.29	0.46	2.61	0.81	0.33	2.11	0.63	0.25	1.82	1.21	0.50	0.32
N ₁₂₀ P ₈₀ K ₆₀	2.74	0.79	2.97	2.01	0.58	2.73	1.11	0.36	2.42	0.71	0.29	1.89	1.26	0.65	0.35
N ₁₂₀ K ₆₀ ⁺ phosphogypsum aftereffect (1st year)	2.72	0.81	2.98	2.00	0.61	2.75	1.12	0.36	2.39	0.69	0.29	1.88	1.28	0.67	0.35
N ₁₂₀ K ₆₀ ⁺ phosphogypsum aftereffect (2nd year)	2.72	0.77	2.98	1.99	0.57	2.76	1.12	0.34	2.38	0.68	0.28	1.89	1.28	0.66	0.36
N ₁₂₀ K ₆₀ ⁺ phosphogypsum aftereffect (3rd year)	2.71	0.77	2.93	1.89	0.55	2.69	1.09	0.34	2.31	0.67	0.27	1.89	1.27	0.65	0.34
HCP ₀₅	0.03	0.04	0.06	0.03	0.03	0.05	0.04	0.04	0.05	0.05	0.03	0.05	0.03	0.02	0.03

The annual use of fertilizers in doses of N120P80K60 let to an increase in yield by 39.4%. If the N120K60 was used during the phosphogypsum aftereffect at the 1st year after fertilizing, the yield increasing was 37.2%. At the 2nd year of phosphogypsum aftereffect when N120K60 was also used the increase value was 33.1%, at the 3rd year the value was 32.3%. At the 1st year of phosphogypsum aftereffect (when phosphorus fertilizers weren't used) the rice yield was less by 1.4% than when experimentator used also N120P80K60. The difference (1.4%) isn't significant. 2 years after re-fertilizing the soil with phosphogypsum the effect of using phosphogypsum as a phosphorus fertilizer slightly decreased. However, a noticeable decrease (5.0%) in yield was noted only after 3 years of phosphogypsum aftereffect (table 5).

Table 5. Rice crop.

Variations	Yield. tons/hectare	Increase	
		tons/hectare	%
Without any fertilizers	4.62	—	—
N ₁₂₀ P ₈₀ K ₆₀	6.43	1.81	39.2
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (1st year)	6.34	1.72	37.2
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (2nd year)	6.15	1.53	33.1
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (3rd year)	6.11	1.49	32.3
HCP ₀₅	0.30		

The analysis of the crop structure demonstrated that the decrease in yield has place due to a decrease in individual productivity of plants (table 6).

Table 6. Biometric indicators of plants, and yield structure.

Variations	Number of...		Height of plants. cm	Empty grains. %	Weight. g	
	productive stems. stems/m ²	grains in the main whisk. grains.			Grains in 1 whisk	1000 grains
Without any fertilizers	235	71.5	85.0	18.2	1.95	27.4
N ₁₂₀ P ₈₀ K ₆₀	243	92.4	108.2	15.5	2.91	32.4
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (1st year)	240	91.4	105.8	15.0	2.82	32.5
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (2nd year)	239	85.7	98.5	15.7	2.61	32.4
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (3rd year)	240	84.2	96.7	15.7	2.42	31.8
HCP ₀₅	15	7.2	6.1		0.11	1.1

Differences in plant nutrition system did not affect the grain quality during the first 3 years after re-fertilizing soils with phosphogypsum (table 7). The use of phosphogypsum in combination with nitrogen and potassium fertilizers acts as a complete plant nutrition which is not worse than complex mineral fertilizer if we pay attention to how it affects on plants.

Table 7. Quality of rice grains, %.

Variations	Grain membrane indicator	Glassiness of grain indicator	Grain fracture indicator	Germination
Without any fertilizers	17.8	92.4	10.2	70.2
N ₁₂₀ P ₈₀ K ₆₀	17.0	95.0	10.5	72.5
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (1st year)	17.7	95.5	9.9	71.5
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (2nd year)	17.5	95.0	10.1	72.7
N ₁₂₀ K ₆₀ + phosphogypsum aftereffect (3rd year)	17.8	94.2	10.2	70.8

The results of the field experiment showed that the content of heavy metals in the rice soil did not go beyond the natural range of values when re-fertilizing with neutralized phosphogypsum was used (just as when the single use of phosphogypsum had place). The significant increase in the concentration of heavy metals in soil after using 4.0 tons/hectare of phosphogypsum was not confirmed by any experimental results (table 8). The content of mobile forms of toxicants after re-fertilizing soils with phosphogypsum also doesn't exceed the maximum permissible concentrations. Therefore, the risk of environmental pollution and of an excessive accumulation of toxicants in plants is minimal.

Table 8. The influence of phosphogypsum on the content of heavy metals in meadow chernozem soils.

Experiment options	The content of heavy metals in the soil. mg/kg							
	Zn	Cd	Pb	Hg	Cu	Co	Ni	Mn
Gross content. mg/kg								
Control values (without any fertilizers)	58.0±2.7	0.19±0.05	6.9±0.2	0.07±0.008	21.0±2.6	10.1±2.4	36.0±2.3	490±21.0
Phosphogypsum. 3 tons/hectare	58.0±2.4	0.17±0.07	5.9±0.3	0.08±0.012	23.0±1.8	11.3±3.0	35.0±3.3	485±30.0
N ₁₂₀ P ₉₀ K ₆₀ + phosphogypsum. 3 tons/hectare	60.7±4.1	0.19±0.09	6.6±0.2	0.09±0.015	23.4±2.1	12.4±1.9	38.0±1.9	494±28.9
HCP ₀₅	11.5	0.04	1.51	0.033	3.5	1.5	4.1	44.3
MPC*	100	3.0	32.0	2.1	55.0	50	85.0	1500
The content of mobile forms of heavy metals. mg/kg								
Control values (without any fertilizers)	1.59	0.06	0.7	0.0031	1.45	0.26	2.66	42.0
Phosphogypsum. 3 tons/hectare	1.67	0.05	1.1	0.0040	0.99	0.20	2.19	36.5
N ₁₂₀ P ₉₀ K ₆₀ +	1.59	0.07	0.9	0.0035	1.29	0.30	2.74	39.8

phosphogypsu m. 3 tons/hectare								
HCP ₀₅	0.91	0.03	0.5	0.002	0.24	0.37	0.92	6.76
MPC*	23.0	1.0	6.0	0.1	3.0	5.0	4.0	400

Where: * MPC - Maximum permissible concentration.

Rice grain analysis results also did not reveal a significant increase in heavy metals, grain quality met requirements of sanitary standards and regulations 2.3.3.1078-01 established in Russian Federation (table 9). The ratio of calcium to strontium in grains after re-fertilizing soil with phosphogypsum is 178. And the significant difference between experimental indicator and the control value (without any fertilizers) was not found. Therefore, the contamination of the soil with strontium due to using phosphogypsum (4.0 tons/hectare) is unlikely.

Table 9. The content of chemical elements in rice grains, mg/kg.

Experiment options	The content indicator. mg/kg								
	Ni	Mn	Cu	Zn	Pb	Cd	Co	Ca	Sr
Control values (without any fertilizers)	0.07	19.9	4.8	28.9	0.35	0.036	0.07	565	3.1
N ₁₂₀ P ₉₀ K ₆₀	0.08	21.0	4.9	27.9	0.40	0.030	0.08	575	3.2
Phosphogypsum. 3 tons/hectare	0.07	20.9	5.0	29.0	0.36	0.032	0.09	592	3.3
N ₁₂₀ P ₉₀ K ₆₀ + phosphogypsum. 3 tons/hectare	0.09	22.0	5.0	29.2	0.38	0.038	0.07	589	3.3
HCP ₀₅ . mg/kg	0.05	3.2	0.61	2.3	0.2	0.017	0.04	59.0	0.54

The results of analysis of economic indicators of rice production (experimental values were taken for calculations) showed us that fertilizing rice soils by N120P80K60 led to the following financial expenses: 79,066 RUB/hectare, including 9,965 RUB spent for buying mineral fertilizers (ammonium phosphate - 150 kg/hectare, fine fraction; potassium chloride - 100 kg/hectare; carbamide - 220 kg/hectare). The prime cost of 1 ton of rice grains is 11,559 RUB. Production profitability is 35.6%. The use of N120K60 in combination of phosphogypsum reduces the cost of mineral nutrition of rice agrocenosis by 4,155 RUB/hectare. As a result, the cost of 1 ton of rice grains is reducing by 445 RUB at the 1st year of phosphogypsum aftereffect, by 105 RUB at the 2nd year of phosphogypsum aftereffect and by 34 RUB at the 3rd year of phosphogypsum aftereffect. Profitability of rice production equals to 35.6% if the complex mineral fertilizer is used, but this value increases to 41.0%, 36.9% and 36.0% at the 1st, the 2nd and the 3rd year respectively if we decide to use phosphogypsum.

Not only the direct action of phosphogypsum (the effect of such fertilizing was proved by results of previous field experiments) allows production owners to increase the agroeconomical effectiveness of using mineral fertilizers, to make enough supplies of plant nutrition and to save some amount of fertilizers and money [15]. The aftereffect of phosphogypsum allows to do the same during 3 years after fertilizing the soil. If we talk about rice cultivation with using complex mineral fertilizers, there will be 7.07 kg of rice grains for every kilogram of active substance. In conditions of phosphogypsum aftereffect the payback ratio per 1 kg of active substance equals to 10.75 kg of grains at the 1st year, 9.56 kg at the 2nd year and 9.31 kg at the 3rd year (as we can see, the indicator increases by 3.68 kg, 2.49 kg and 2.24 kg respectively).

4 Conclusion

The one of the promising ways to implement the following concept: “phosphate raw-stuff → phosphogypsum → chemical reclamant and/or complex calcium phosphate sulfur fertilizer → soil → plant → yield and quality of product” can solve the important ecological-economic and national economic task of organization of non-waste production with high efficiency of the use of raw materials and achieving high nutrient efficiency.

The use of standard phosphorus-containing fertilizers and phosphogypsum as phosphorus fertilizer in the rice fertilizer system equally affects the nutritional regime of soils, the growth of rice plants, the formation of productivity and grain quality. The positive effect of phosphogypsum becomes apparent within 3-4 years after fertilizing the soil.

The effectiveness of phosphogypsum in the aftereffect aimed at the optimization of mineral nutrition program of rice agroecosystem contributes to cost reduction by 4155 RUB/hectare in comparison with the traditional fertilizer system. It also decreases the prime cost of 1 ton of rice grain by 445 RUB at the 1st year of phosphogypsum aftereffect, by 105 RUB at the 2nd year and by 35 RUB at the 3rd year. And the profitability of rice production increases by 5.5%, 1.3% and 0.4% at the first, the second and the third year of phosphogypsum aftereffect respectively.

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