

Agrochemical efficiency of slow release phosphate fertilizers derived on the base of phosphorite activation

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Abstract. Studies in which new phosphorus fertilizers containing additional organic substances are a tool for regulating soil fertility are described in this paper. The fertilizers were developed in Institute of General and Inorganic of Uzbek Academy Sciences. Phosphate fertilizers were obtained by decomposition of ordinary phosphorite powder with acid effluent that is a waste from the soap production of Urganch yog'-moy JSC in various ratios. According to the developers, ordinary phosphate powder (OPP), due to the treatment with acid effluent (AE), acquires new qualities as slowly soluble properties, which allows for a more rational use of nutrients, in particular phosphorus, increasing its efficiency and reducing wasteful losses. In addition, the introduction of organic substances into the composition of the AE enriches the phosphorus fertilizer with biologically active compounds, and gives it valuable growth-stimulating properties. New fertilizers are intended for use in irrigated agriculture, which have long lasting properties. It is assumed that derived fertilizers contribute to the improvement of the physical and chemical properties of the soil, optimize the vital activity of the cultivated crop without a negative increase in the activity of soil microorganisms.

1. Introduction

In the light of the development of the food industry, the issue of disposal of wastewater accumulated in the process of processing agricultural products such as fruits, vegetables, melons and oilseeds (palm, soybean, sunflower, cotton) is acute. During the processing of these crops in the technological cycle, effluents are formed that contain important nutritional components that can successfully ensure the normal growth and development of crops [1-3]. Cotton is the main oilseed crop in Uzbekistan; annually, the industry processes about 1.8 million tons of seeds to produce cottonseed oil. Usually, after the primary processing of raw cotton, cotton seeds are transferred to processing plants to obtain edible vegetable oil [4].

Naturally, during the refining of oil, a soap stock is formed, which, in turn, undergoes alkaline and sulfuric acid treatment to obtain crude fatty acids (oleic, palmitic, etc.). The resulting wastewater with a pH of 1.5-2.5 after neutralization with expensive reagents is not used, while it can be used as a source of organic humic-like substances [5], in particular, to increase crop yields. Earlier in [6], the process of obtaining phosphorus fertilizer was studied by neutralizing carbonate phosphorites of the Central Kyzyl Kum with acid effluents - waste products from the oil and fat industry. The resulting phosphorus fertilizers contain digestible forms of P₂O₅ (according to citric acid and Trilon B) 30.28-50.43 and 25.58-39.93%, respectively, as well as up to 4.5-8.0% of organic substances.

The purpose of this study is to determine the effect of new types of slow release phosphate fertilizers based on soap stock and phosphate rock on the yield of cotton crops, as well as the agrochemical properties of the soil.

2. Materials and methods

The objects of the described studies are phosphorus fertilizers obtained by decomposition of ordinary phosphorite powder with acid effluent that is a waste from the processing of cotton soapstock with alkali and sulfuric acid to obtain raw fatty acids.

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Ordinary phosphate powder (OPP) has a composition (wt.%): P₂O₅ - 17.54; CaO - 47.75; MgO - 1.79; CO₂ - 16.5; Fe₂O₃ - 0.73; Al₂O₃ - 0.95; SO₃ - 4.06; F - 1.7; SiO₂ - 1.24; insoluble residue - 4.03; CaO: P₂O₅ - 2.72. The composition of the acid effluent is shown in Table 1.

Table 1. Chemical composition of wastewater from soap production

Cations	mg/l	mg-eq/l	%-eq/l	Anions	mg/l	mg-eq/l	%-eq/l
H ⁺	100	100	87	Cl ⁻	38116	1075	50
Na ⁺	43158	1876.46	-	SO ₄ ²⁻	48145	1003.03	47
K ⁺	-	-	-	NO ₂ ⁻	20.01	-	-
NH ₄ ⁺	100	5.54	-	NO ₃ ⁻	840	13.55	-
Ca ²⁺	300	15	1	CO ₃ ⁻	-	-	-
Mg ²⁺	1824	150	7	HCO ₃ ⁻	3446	58.50	3
Fe ³⁺	0.3	0.01	-	Total		2148.08	100
Fe ²⁺	30	1.07	-				
Total		2148.08	100				

The technology for obtaining slow release fertilizers is described in [6]. To obtain slow release phosphate fertilizers with organic matter, phosphorite powder was decomposed by acid effluent at a mass ratio of AE: OPP: 100: 20 and 100: 40. Decomposition process was carried out at a temperature of 60°C for 30 min. After the completion of the process, the product was dried at a temperature of 80°C, with simultaneous granulation by the rounding method to prepare beads. It is assumed that due to the partial activation of various forms of P₂O₅ phosphate powder in an acidic environment and the introduction of humic-containing organic compounds, prolonged properties of fertilizers are achieved [7]. Slow release phosphate fertilizers are denoted according to the ratio of the initial components SRPF-20 and SRPF-40, respectively. In addition, the high content of organic substances (mainly organic acids) in the acidic effluent (2.1%) gives the activated phosphorite powder the properties of organomineral fertilizers.

The composition and properties of the studied slow-acting phosphorus fertilizers are given in Table 2.

Table 2. The composition of phosphorus organomineral fertilizers SRPF

Weight ratio of AE : OPP	H ₂ O, %	P ₂ O ₅ tot, %	P ₂ O ₅ avail. citric, %	P ₂ O ₅ avail. Trilone B, %	N tot, %	Organic %,	humic acid	Granule strength, mPa
	2.5				-	7.91		
100 : 20 (SRPF-20)	2.0	13.36	5.07	4.03	-	4.36	-	1.2
100 : 40 (SRPF-40)		15.03	4.57	3.86			-	1.5

2.1. Study area

The vegetation experiments were carried out in 2021 (one growing seasons) in Tashkent City, northeastern region of Uzbekistan (41°15'52", 69°12'58", 435 m above sea level). Climatic conditions: average July temperature +27°C, January -1°C, 384-409 mm of precipitation per year. The soil type of the experiment field is typical sierozem (Calcisol) [8], with an initial pH of 7.45, 12.88 g kg⁻¹ organic matter, 34.0 mg kg⁻¹ ammonium N, 18.4 mg kg⁻¹ nitrate N, 22.0 mg kg⁻¹ available phosphorus (P) and 203.0 mg kg⁻¹ available K in the 0-20 cm soil layer.

2.2. Experiment design

In the vegetation experiment, 4 options were investigated:

- 1) K1 N7 P5K3,5, where N is ammonium nitrate, P is ammophos, K is potassium chloride
- 2) K2 N7 P5K3,5, where N is urea, P is simple superphosphate, K is potassium chloride
- 3) SRPF-20 N7 P5K3,5, where N is ammonium nitrate, P is SRPF-20, K is potassium chloride
- 4) SRPF-40 N7 P5K3,5, where N is ammonium nitrate, P is SRPF-40, K is potassium chloride.

Nitrogen fertilizers were applied three times - in the phase of 2-4 true leaves (40%), in the phases of budding (40%) and flowering (30%); phosphorus and potash fertilizers twice - at sowing (70%) and in the flowering phase (30%). Soil moisture in the growing pots was maintained at 50-60% of full field capacity during the growing season.

New organomineral SRPFs were studied in a vegetative experiment on cotton (*Gossypium hirsutum*), Akdarya-6 variety. The average yield of raw cotton plants of this variety is 38.1 - 44.5 c/ha, the growing season is 117-128 days.

2.3. Soil sampling

Vegetation experiments were laid in Wagner vessels per 25 kg of soil in quadruple repetition. The complex of vegetation studies was carried out according to the classical generally accepted scheme in accordance with [9]. Soil samples for agrochemical studies were taken from the soil before sowing and according to the main phases of cotton development (2-4 true leaves, budding, flowering, ripening) from a depth of 0-20 cm.

2.4. Statistical analysis

Statistical analysis was performed using the Excel 2016 program (data analysis package). To determine significant differences between the options used standard deviation (standard deviation), Student's confidence interval (confidence St. interval) at a significance level of $P < 0.05$ and $P < 0.01$.

3. Results and Discussion

3.1. Soil Agrochemical characteristics depending on the use of slow release phosphate fertilizers

The content and composition of organic compounds in the soils of agrocenoses have a huge impact on almost all properties and functions of these soils. It is known that mineral fertilizers accelerate the mineralization of organic matter due to a sharp change in the C: N ratio, and therefore, special attention should be paid to the composition of fertilizers and their effect on the level of carbon in the soil [10]. The presence in the soil of a sufficient amount of various organic substances improves the structure of the soil, provides a favorable water-air regime, optimizes the composition of microbial communities, as well as the growth and development of plants. In this regard, the application of fertilizers with organic components can increase the potential of soils, their nutritional and environmental value [11].

It should be noted that the use of the studied prolonged fertilizers made it possible to increase the humus content by only 1.5-3.0% during one growing season. Although the change is not considered significant (at $P < 0.05$), regular application can have a positive effect on soil organic matter levels (Figure 1).

The share of mineral soil nitrogen accounts for no more than 1-3% of its total amount. The entry of oxidized or bound nitrogen into the soil in the form of ammonia occurs with precipitation, fertilizers, and enters in the form of various products of microbial fixation in the soil. At the same time, the mineralization of soil organic nitrogen-containing compounds proceeds under certain conditions [12, 13].

In the experiment, the level of ammonium forms of nitrogen as a whole varied within a narrow range - 1.46-3.61 mg N-NH₃, and only in the control variant in the budding phase the highest amount of ammonium ions was found - 5.89 mg N-NH₃ in 100 g soil. It is important that in all phases of development in the soil fertilized with SRPF-20 and SRPF-40, the level of ammonium ions was lower than K1 (by 6-75%) (Figure 2 A).



Fig. 1. Effect of SRPF on humus content in soil

Nitrates are the main pool of mineral nitrogen in the soil, and the main source of nitrogen for plant nutrition. The nitrate form of nitrogen is not adsorbed by the soil and is not chemically bound. Therefore, nitrates not used by plants

or microorganisms are carried away by irrigation or rainwater to the underlying soil horizons, then to groundwater or surface water, which can lead to dangerous pollution. Slow release fertilizers are one of the effective tools to prevent nitrate leaching from the root layer of the soil.

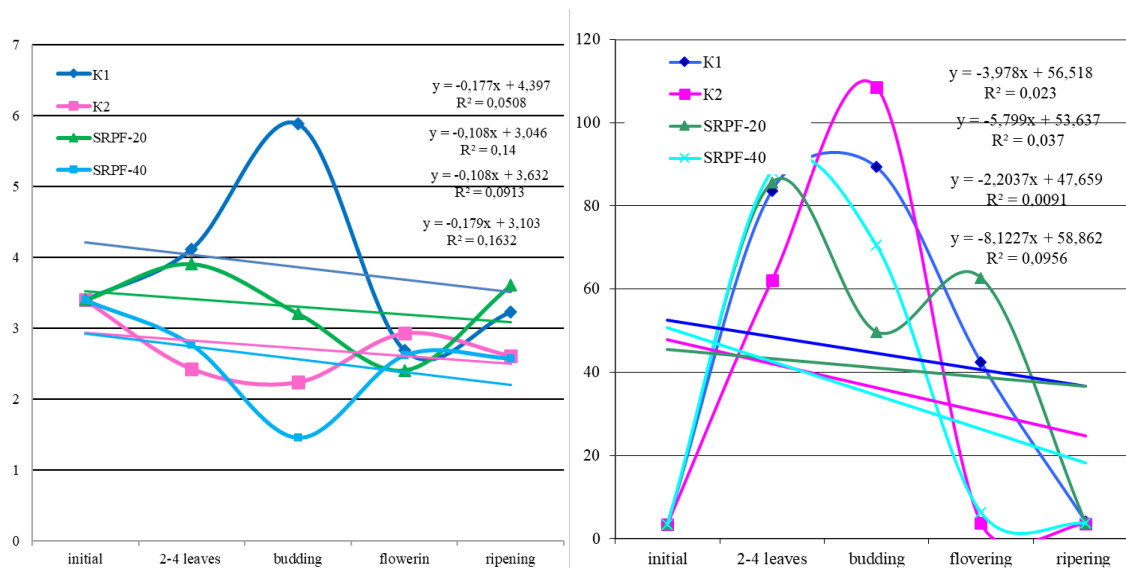


Fig. 2. Effect of SRPF on N-NH₃ (A-left) and N-NO₃ (B-right) content (mg/100 g soil)

The study of the dynamics of the level of nitrates showed very important results. The amount of nitrate nitrogen in the soil layer of 0-20 cm in the original soil was quite low - 3.57 mg NO₃ per 100 g of soil, while 10 days after the application of nitrogen fertilizers in the phase of 2-4 leaves, the content of NO₃ increased sharply in all variants. It should be noted that in variants K1, SRPF-20 and SRPF-40, where nitrogen was introduced in the form of ammonium nitrate, the level of nitrates reached a maximum in the phase of 2-4 leaves, while in the variant K2, the introduction of nitrogen in the form of urea (which dissolves with slower speed), the peak of the amount of nitrates was observed later - in the budding phase. It is important that by the maturation phase the plants have already used the main amount of nitrates, and their content decreases by 10-20 times to 3.78-4.14 mg NO₃/100 g of soil, returning to spring indicators (Figure 2B).

According to the total nitrates for the growing season, it can be concluded that SRPF-20 and SRPF-40, due to the presence of an organic component, reduce the content of nitrates in the soil by 8.0-22.9%, i.e. significant at P<0.05.

The use of slow-acting phosphate fertilizers is one way to increase the utilization rate of phosphate fertilizers and prevent soil fixation and P₂O₅ losses [14, 15]. In order to establish the prolonged properties of SRPF, a comparison was made of the content of phosphates in the soil. Thus, from the data presented in the figure, it can be seen that the level of P₂O₅ during the growing season is low and does not exceed 13 mg per 100 g of soil (Figure 3).

The content of mobile phosphates after the application of phosphate fertilizers in K1 and K2 increased by 1.5–2 times and gradually increased to a maximum (6.08–12.8 mg P₂O₅ per 100 g of soil) by the budding phase. Fertilizers SRPF showed a prolonged effect, since during all subsequent phases of plant development a uniform increase in phosphates was observed SRPF-20 - to the flowering phase up to 9.315 mg; SRPF-40 - to the ripening phase up to 10.074 mg / 100 g of soil.

Significantly, SRPFs not only affect soil nutrient levels, but due to their composition and slow acting properties, these fertilizers change the relationship between agrochemical characteristics. Therefore, in the variants with K1 and K2, there is a close correlation between the amount of nitrates and phosphates (r=0.76-0.70), while no such dependence was found when using SRPF. In addition, in variant K1, where rapidly soluble easily digestible ammonium nitrate and ammophos are introduced, there is a direct strong correlation between the content of ammonium and phosphates (r=0.63), ammonium and nitrates (r=0.72), on the contrary, in the variants with the introduction SRPF-20 and SRPF-40, these dependencies are reversed: (r=-0.70) and (r=-0.62), respectively. This is attributed by the fact that the release of nitrogen and phosphorus from SRPF fertilizers occurs in antiphase, i.e. not simultaneously, but with some lag in phosphorus.

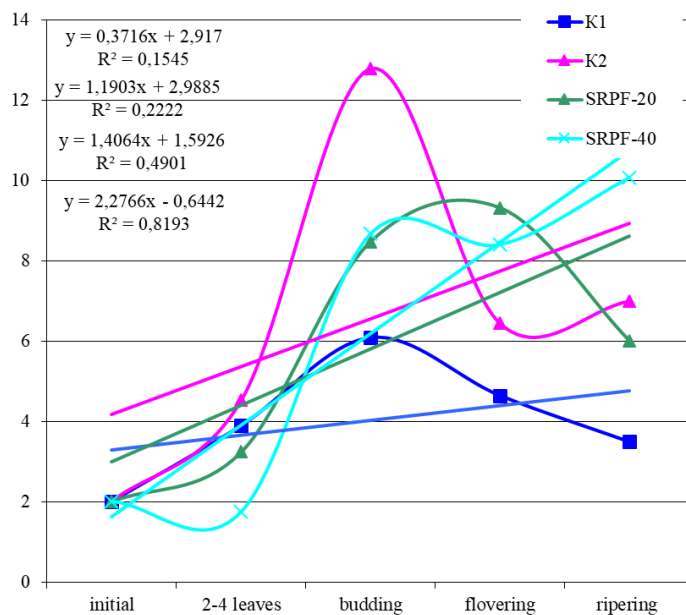


Fig. 3. Effect of SRPF on P2O5 content (mg/100 g soil)

However, it was these patterns that determined the dynamics of plant development and yield depending on the fertilizers used (Table 3).

Thus, the maximum amount of raw cotton was harvested on the variant with SRPF-20 - 107.75 g/plant, and up to 92.8% was the yield of the first harvest. On plants fertilized with SRPF-40, the yield reached 102.0 g/plant, with a first harvest yield of 89.2% of the total raw cotton. Although the SRPF boll count was inferior to the control, the weight of the cotton bolls was 7.6% and 19.5% higher. It should be noted that the number of unripe fruit elements (i.e., losses) in the variants with the use of SRPF was less than in the control variants (5.75 and 5.0 vs. 6.0 numbers) (Table 3).

Table 3. The effect of prolonged SRPF fertilizers on the yield of raw cotton

Options	Weight of raw cotton, g/per 1 plant				Number of boxes		Weight of one box		Unripe boxes	
	1 fee	2 fee	total	% to control	number	% to control	g	% to control	number	% to control
K1	89.25	11.75	101.0	100.0	24.0	100.0	4.209	100.0	6.0	100
K2	109.75	3.75	113.5	112.4	25.25	105.2	4.49	106.7	2.75	45.8
SRPF-20	100	7.75	107.75	106.7	23.75	99.0	4.53	107.6	5.75	95.8
SRPF-40	91	11.0	102.0	101.0	20.25	84.4	5.03	119.5	5.0	83.3
standart deviation	9.427	3.648	5.78		2.145		0.341		1.48	
confidence interval	9.239	3.575	5.66		2.102		0.335		1.45	

4. Conclusions

Vegetation experiments have shown that SRPF slow release phosphate fertilizers have positive effects on both soil agrochemical parameters and cotton yields.

The study of the agrochemical characteristics of the soil (the content of organic carbon - humus, ammonia and nitrate nitrogen, as well as phosphates) showed that phosphate fertilizers obtained by decomposition of ordinary phosphorite

flour with an acidic product - a waste of soap production, on a typical gray soil under cotton show prolonged properties.

A slight but steady increase in the amount of humus (1.5-3.0% compared with the index in the initial spring soil), a significant decrease in the ammonium form of nitrogen (by 17.5-40.8%) and nitrate nitrogen (by 8.05-22.9%) under the influence of SRPF. An increase in the content of mobile phosphates was also established due to its gradual and uniform release from SRPF fertilizers.

Optimal conditions for the plants development and yield were provided by the use of SRPF-20. An increase in the yield of raw cotton by 6.7% compared with the control was found, with an increase in the quality of the cotton fiber (lint) due to an increase of the size and weight of the bolls and earlier and more synchronous ripening of the crop.

References

1. M. Mainardis, D. Cecconet, A. Moretti, A. Callegari, D. Goi, S. Freguia, A.G. Capodaglio, Wastewater fertigation in agriculture: Issues and opportunities for improved water management and circular economy, *Environmental Pollution* **296**, 118755 (2022)
2. K.Y. Foo, B.H. Hameed, Insight into the applications of palm oil mill effluent: A renewable utilization of the industrial agricultural waste, *Renewable and Sustainable Energy Review* **14**, 1445-1452 (2010)
3. S.S. Ali, R. Al-Tohamy, E. Koutra, M.S. Moawad, M. Kornaros, A.M. Mustafa, J. Sun, Nanobiotechnological advancements in agriculture and food industry: Applications, nanotoxicity, and future perspectives, *Science of the Total Environment* **792**, 148359 (2021)
4. K. Velmourougane, D. Blaise, S. Savitha, V.N. Waghmare, Chapter 34 - Valorization of cotton wastes for agricultural and industrial applications: present status and future prospects. *Valorization of Agri-Food Wastes and By-Products*, Recent Trends, Innovations and Sustainability Challenges 665-692 (2021)
5. A.G. Sergejev, Guidelines for the technology of obtaining and processing vegetable oils and fats, Kolos, Leningrad (1975)
6. S. Shamuratov, U. Baltayev, U. Alimov, Sh. Namazov, S. Kurambaev, B. Ibadullaev, 2021 Utilization process research of the soap industry acid waste water with high carbonate phosphorite of central Kyzylkum, *E3S Web of Conferences* **264**, 04079 (2021)
7. S. Sithaphanit, V. Limpinuntana, B. Toomsan, S. Panchaban, R.W. Bell, Fertiliser strategies for improved nutrient use efficiency on sandy soils in high rainfall regimes," *Nutr Cycl Agroecosyst* **85**, 123-139 (2009)
8. World Reference Base, 2006. World Reference Base for Soil Resources (WRB) (2006) <http://www.isric.org/projects/world-reference-base-soil-resources-wrb>
9. M.P.J. Gautheryou, Handbook of Soil Analysis. Mineralogical, Organic and Inorganic Methods, Springer, Berlin (2006)
10. J.C. Cole, M.W. Smith, C.J. Penn, B.S. Cheary, K.J. Conaghan, Nitrogen, phosphorus, calcium, and magnesium applied individually or as a slow release or controlled release fertilizer increase growth and yield and affect macronutrient and micronutrient concentration and content of field-grown tomato plants, *Sci. Hort.* **211**, 420-430 (2016)
11. E. Bonifacio, G. Falsone, M. Petrillo, 2011 Humus forms, organic matter stocks and carbon fractions in forest soils of northwestern Italy, *Biol Fertil Soils* **47**, 555-566 (2011)
12. A. Kučera, L. Holik, E.M. Cerro, J. Petříček, Effect of gap size and forest type on mineral nitrogen forms under different soil properties, *Journal of Forestry Research* **31**, 375-386 (2020)
13. A. Shaviv, Advances in controlled-release fertilizers, *Adv. Agron.* **71**, 1-49 (2001)
14. D. Lawrenciá, S. Kiat Wong, D. Yi Sern Low, B. Hing Goh, J. Kheng Goh, U. Rungsardthong Ruktanonchai, A. Soottitantawat, L. Han Lee, S. Ying Tang, Controlled Release Fertilizers: A Review on Coating Materials and Mechanism of Release, *Plants* **238**, 1-25 (2021)
15. K. Gell, F.J.D. Ruijter, P. Kuntke, M.D. Graaff, A.L. Smit, Safety and effectiveness of struvite from black water and urine as a phosphorus fertilizer, *J. Agric. Sci.* **3**, 67-80 (2011)