



Research on the Efficiency of Complex Fertilizer Produced from the New Serpentine-Based Ingredient

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ABSTRACT

Using serpentine, which is widespread in Armenia, we developed two new fertilizers. First fertilizer, is composed of phosphorus, calcium, magnesium, and sulfur, as well as amorphous silicon dioxide, and fertilizer 2, which contains a small amount of phosphorus (in the form of a mixture in the mineral), calcium, magnesium, sulfur, and amorphous silicon dioxide. Fertilizers were soluble in water and a 1 % ammonium carbonate solution. Laboratory studies have shown that fertilizers positively affect spring barley seed germination percentage, germination rate, growth, yield, and grain NPK content. The yield of spring barley increased by 28.4-33.1 % under the influence of fertilizers, which is equivalent to the efficiency of double superphosphate. However, serpentine, the most common in Armenia, can be used to obtain recommended fertilizers in a much cheaper and safer manner.

Introduction

The agricultural lands of the republic are known to be low in fertility. As a result, cultivated lands in RA have a low nitrogen supply of 100 %, a low phosphorus supply of 71-72 %, and a low potassium supply of 30-31 %. It has been proven by field experiments and by recording the harvest of many production crops that fertilizers are needed to increase crop production (Babayan, et al., 1990; Yeritsyan, et al., 2017; Ghazaryan, et al., 2022; Yagodina, 1989).

A majority of nitrogen fertilizers are imported from the Russian Federation, the Islamic Republic of Iran, the Republic of Georgia, and European countries, as mineral fertilizers have not been produced in RA since the 1990s. However, phosphorus is also important for RA, partly because potassium fertilizers are needed. There is also an importation of nitrogen-phosphorus-potassium complex fertilizers which are exclusively used in greenhouses and drip-irrigated gardens in the republic. In the republic, organic and biological fertilizers are produced in small

quantities, but they cannot completely replace mineral fertilizers. Due to the high prices of fertilizers, the majority of farmers in the republic cannot afford to purchase phosphorus and potassium fertilizers. Several studies have shown that fertilizers should also contain substances that indirectly contribute to plant growth as well as nutrients (Matychenkov and Lapushkin, 2023; Galstyan, et al., 2019). This creates an opportunity to periodically reduce the amounts of nitrogen, phosphorus, and potassium fertilizers applied in the given area. It has been proven that these are mainly silicon-containing fertilizers (Bagarnikova, 2011; Silicon fertilizers, 2014; Rabinovich, 2020) also improve the physical and chemical properties of the soil (The mineral serpentine helps restore contaminated soils, 2022; Myazin, 1997; The use of serpentine in agriculture in the book Soil conditions and plant growth, 1955; Shveikina, et al., 1999; Farsian, et al., 2020).

It is important to note that one of the indirect benefits of such fertilizers is the reduction in water consumption during harvest (Silicon Fertilizers, 2014; Kulikova, et al., 2007). This makes it possible to obtain an economically justified harvest from grain and fodder crops in the arid agricultural areas of the Republic of Armenia. In addition to mitigating the development of plant diseases (such as blackleg and black leg), these fertilizers also reduce pest development (such as the Colorado potato beetle, and tick) thus reducing pesticide use (Aleshin, et al., 1986; Ammosova, et al., 1990; Matychenkov, et al., 2016 and 2022; Pashkevich, et al., 2008).

Taking into account the above, the Institute of General and Inorganic Chemistry Named After Academician Manvelyan State Non-Profit Organization and the Scientific Center of Soil Science, Agrochemistry and Reclamation named after H. Petrosyan of the ANAU, have been working in recent years to develop a technology to obtain complex fertilizers of a new composition based on serpentines, which are widespread in the Republic of Armenia, including containing phosphorus, calcium, magnesium, sulfur, amorphous silicon dioxide and containing calcium, magnesium, sulfur, amorphous silicon dioxide. It should be noted that the technologies for obtaining these waste materials are extremely simple, environmentally safe, and less expensive.

Materials and methods

An important scientific novelty is to observe the results of serpentine-based fertilizers obtained by the research group in laboratory and vegetation experiments: “fertilizer

1” (phosphorus, calcium, magnesium, sulfur, amorphous silicon dioxide) and “fertilizer 2” (calcium, magnesium, sulfur, amorphous silicon dioxide) agrochemical properties: solubility in distilled water and a 1 % solution of ammonium carbonate, including successively affecting the same weight with the specified solutions.

The effects of these fertilizers on spring barley seed germination, germination rate, and shoot and embryonic root growth were determined in laboratory and vegetation studies as follows:

- Germination percentage and germination rate of spring barley seeds in a field.
- Concerning the weight and growth of plants' above-ground mass and root system.
- The main nutrients in the ground-mass and root system during rooting.
- Grain yield and chemical composition.
- Content and absorption capacity of mobile nutrients (NPK) in the soil.

Double superphosphate was used as a standard fertilizer containing phosphorus.

The following scheme was used to determine seed germination and germination energy in laboratory conditions (Victorov, 1969):

1. Without fertilizer (water, checker)
2. Serpentine+ H_3PO_4 (soaking of seeds)
3. Serpentine+ H_2SO_4 (soaking of seeds)
4. Double superphosphate (seed soaking, standard)

On the 19th kilometer of the Yerevan-Hrazdan road, near the arable land on the left side of the road, where autumn wheat was sown, four repetitions of dark brown soil were used for vegetation experiments. The vegetation vessel can hold 6 kg of soil. Plants and soil were analyzed chemically using the methods accepted in RA (Mineev, 2001). Experiments were conducted according to the following scheme.

1. Without fertilizer (check)
2. $N_{0.1}K_{0.1}$ (background)
3. Background + $P_{0.2}$ fertilizer 1
4. Background + $P_{0.2}$ fertilizer 2
5. Background + $P_{0.2}$ double superphosphate (standard)

Where, 0.1 means 0.1 g of active substance for 1 kg of soil, 0.2 means 0.2 g of active substance for 1 kg of soil.

During the vegetation period, observations and counts were made. We measured seed germination, germination

energy, plant height at tuber and maturity stages, above-ground mass, and root mass weight of 10 plants. Nitrogen, phosphorus, and potassium were determined in the above-ground mass and roots of the plants. In this process, the weight was burned in sulfuric acid, then nitrogen content was determined by distillation, phosphorus by colorimetry, and potassium by flame photometry (Mineev, 2001). Using the dispersion analysis method (Khachatryan, 2002), harvest data were mathematically processed.

The soil was characterized by humus content using Turin, mechanical composition using Kaczynski, pH using a pH meter, and carbonates using a calcimeter. A complexometric method was used to determine the amount of soluble calcium and magnesium in water. The amount of nitrogen available to plants was determined by Tyurin-Kononova, phosphorus by Machigin, and potassium by Machigin solution (Mineev, 2001).

Results and discussions

Knowing the agrochemical characteristics of the soil in advance is crucial to planning the fertilization of crops effectively. Based on this information, fertilizers can be applied scientifically. In this case, it is important to design the experiment scheme correctly, particularly when determining the effectiveness of new composition fertilizers. To reduce costs, such studies typically begin with laboratory and vegetative experiments, which allow daily control of the growth and development of plants.

As for the soil used for the vegetation experiments, it had a powdery structure, hardened when dried, and had a loamy mechanical composition. This is because crop rotation is not carried out in this area, and organic fertilizers are not applied. At the same time, such a situation is currently characteristic of a significant part of the cultivated land areas of the republic (Babayan, et al., 1990; Soil Atlas of the Republic of Armenia, 1990).

According to the agrochemical analysis of the soil selected

for vegetation experiments (Table 1), the humus content was 2.59 %, the reaction was weakly basic, and calcium was 1.38 times greater in the aqueous solution than magnesium. The experiment scheme was developed based on these data.

An important property of fertilizers is their solubility in water and in solvents used to determine soil mobile nutrients (phosphorus, potassium). The results of the studies carried out in laboratory conditions (Table 2) revealed that when the fertilizers with the mentioned solvents were first treated with distilled water, 3.86 % of fertilizer 1, passed into a solution with the following composition mg/% phosphorus (1400), potassium (8.64), calcium (560), magnesium (1520), sodium (25.7).

Meanwhile, 23.41 % solution passed from fertilizer 2, where phosphorus (in the form of a mixture in the mineral) was only 250 mg, potassium was 8.64 mg, calcium was 800 mg, magnesium was 10880 mg, and sodium was 25.76 mg in 100g of fertilizer. It should be added that the main substance dissolved in fertilizer 2 was amorphous silicon dioxide, which was well-soluble in acid.

The same weight of fertilizer treated with distilled water for a second time leaches more phosphorus from fertilizer 1. In contrast, the amount of soluble substances in fertilizer 2 decreased dramatically because phosphorus was lacking in fertilizer 2. There was also a decrease in calcium and magnesium dissolved in the water.

When fertilizers were treated with ammonium carbonate solution for the first time, the amount of phosphorus came out the same as when it was treated with water, and the amount of other nutrients did not change significantly. The amount of phosphorus decreased significantly after the second treatment, while the other nutrients remained virtually unchanged.

Accordingly, 1 % aqueous and ammonium carbonate solutions passed the majority of phosphorus from the recommended fertilizers. In addition to being essential and irreplaceable nutrients, these nutrients were also used by plants.

Table 1. Agrochemical characteristics of soil taken for vegetation experiments*

Soil type, sampling depth, cm	Humus, %	Mechanical composition, physical clay, %	pH	Carbonate content, %	Dissolved in water mg/eq in 100 g soil		The content of nutrients available to plants in (mg), in 100 g soil		
					Ca	Mg	N	P ₂ O ₅	K ₂ O
Dark brown 0-30 sm	2.56	47.4	8.1	3.5	1.8	1.3	3.7	1.45	47.61

*Composed by the authors.

Table 2. Solubility of serpentine-based fertilizers in distilled water and 1% ammonium carbonate solution*

Options	pH	Substances dissolved in water, %	mg in 100 g of fertilizer				
			P_2O_5	K_2O	Ca	Mg	Na
Solubility in water at 1st exposure							
Serpentine+ H_3PO_4 (Fertilizer 1)	7.9	3.86	1400	8.64	560	1520	25.76
Serpentine + H_2SO_4 (Fertilizer 2)	4.5	23.41	250	8.64	800	1088	25.76
Solubility in water at 2nd exposure							
Serpentine+ H_3PO_4 (Fertilizer 1)	7.9	5.15	1714	8.61	1280	1440	12.27
Serpentine + H_2SO_4 (Fertilizer 2)	7.0	2.30	5	8.63	680	840	9.20
Solubility in $(NH_4)_2CO_3$ at 1st exposure							
Serpentine+ H_3PO_4 (Fertilizer 1)	-	-	1400	8.64	800	720	25.74
Serpentine + H_2SO_4 (Fertilizer 2)	-	-	250	8.60720	560	712	25.72
Solubility in $(NH_4)_2CO_3$ at 2nd exposure							
Serpentine+ H_3PO_4 (Fertilizer 1)	-	-	96	8.51	560	710	24.53
Serpentine + H_2SO_4 (Fertilizer 2)	-	-	76	8.53	480	705	8.00

Table 3. Effects of Serpentine-Based Fertilizers on Laboratory and Field Germination percentage, Germination Rate, and Seedling Growth of Spring Barley Seeds*

Options	Under laboratory conditions					Under vegetative conditions	
	Germination, %	Germination rate, %	The weight of the embryonic roots of 10 seedlings, g	Root weight, g	Number of roots per seed	Germination, %	Germination rate, %
1	91.6	76.4	0.28	0.061	6.1	86.5	71.3
2	95.4	84.3	0.33	0.079	6.4	90.9	81.2
3	95.9	85.8	0.35	0.084	6.8	92.9	83.0
4	91.7	76.7	0.30	0.065	6.1	86.9	71.7

Options: 1. No fertilizer (water/control), 2. Serpentine+ H_3PO_4 (seed soaking), 3. Serpentine+ H_3PO_4 (seed soaking), 4. Double superphosphate (seed soaking).

*Composed by the authors.

It was completely favorable for crops to grow in aqueous solutions of fertilizers, except crops growing in soils with an acid reaction (Table 2).

It was found that soaking spring barley seeds in a 0.1 % solution of fertilizer before sowing increased germination percentage, and germination rate, primarily due to the indirect effect of fertilizers, including the significant amount of

amorphous silicon dioxide present in fertilizers, and promoted increased seed germination and germination energy (Table 3).

The results were in line with the findings of (Ammosova, et al., 1990; Vlasenko, 2019; Application of serpentine in agriculture, 1955; Slukovskaya, 1922). Thus, under the influence of the studied fertilizers (versions 2, 3), seed germination increased by 4.1-4.7 %, and the rate

of germination increased by 10.3-12.3 % compared to the control. In vegetation experiments, germination parameters changed similarly under the influence of these fertilizers (Table 3).

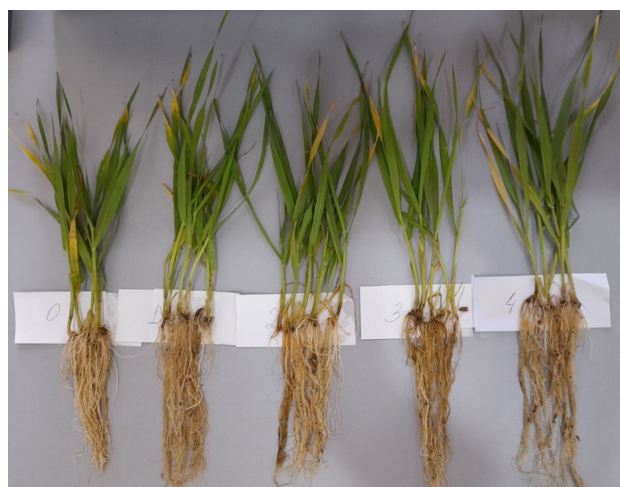
Meanwhile, in laboratory conditions, germination parameters under double superphosphate had almost no change. In both laboratory and vegetative experiments, the recommended fertilizers increase the number of sprouts and embryonic roots. Table (3) shows that serpentine plus H_2SO_4 has a slightly higher effect.

In vegetative experiments, fertilizer effects on spring barley growth are also preserved in later stages of plant development, such as stemming (Pic., Table 4).

According to the tester, at this stage of plant growth, under the influence of fertilizers of the new composition (options 2, 3), plants increased by 10.2-16.0 % in mass, root mass weight increased by 12.3-13.6 %, stem height increased by 14-16.7 %, and leaf number increased by 3.8-5.1 %. Superphosphate also has a positive effect, but it is partially inferior to recommended fertilizers. A fertilizer effect on the above-ground mass and root system content of NPK was also observed at the above-mentioned stage of plant growth and development (Table 5).

According to the table, the content of the specified nutrients in the plant's dry mass depends on the fertilization option.

Thus, nitrogen, phosphorus, and potassium content in the groundmass and root system of the plant increased when the recommended fertilizers were applied. Even though



Picture. The effect of serpentine-based fertilizers on spring barley sprout growth.

these fertilizers do not contain nitrogen, they are still effective. It is because they contain amorphous silicon dioxide, which helps the soil absorb NPK more effectively (Bagarnikova, et al., 2011; Report, 2020).

When phosphorus-containing fertilizers were applied (options 2, 4), the phosphorus content in the plant's above-ground mass increased dramatically, indicating that the plants had access to it. The root system of the plant showed a similar pattern. NPK amounts in the roots increased due to the recommended fertilizers.

Table 4. The effect of serpentine-based fertilizers on spring barley sprout growth*

N	Options	Seedling dry weight, in 10 seedlings, g	Compared to the checker, %	Root dry weight, g	Compared to the checker, %	Seedling length, cm	Compared to the checker, %	The number of leaves per seedling
1	No Fertilization (Checker)	2.25	-	0.81	-	15.0	-	7.8
2	Serpentine+ H_3PO_4 (Fertilizer 1)	2.48	10.2	0.91	12.3	17.1	14.0	8.1
3	Serpentine + H_2SO_4 (Fertilizer 1)	2.61	16.0	0.92	13.6	17.5	16.7	8.2
4	$Ca(H_2PO_4)_2 \cdot H_2O$ (standard)	2.41	7.1	0.87	7.4	17.1	14.0	8.1

*Composed by the authors.

Table 5. Effect of fertilizers applied to the base of serpentines on the above-ground mass and root system of spring barley at the 7-8 leaf stage (dry mass) *

N	Options	Above ground biomass, %			Root mass, %		
		N	P ₂ O ₅	K ₂ O	N	P ₂ O ₅	K ₂ O
1	No Fertilization (Checker)	2.45	0.18	0.68	2.06	0.14	0.51
2	Serpentine +H ₃ PO ₄	2.61	0.30	0.77	2.18	0.26	0.58
3	Serpentine +H ₂ SO ₄	2.58	0.21	0.79	2.21	0.19	0.59
4	Ca(H ₂ PO ₄) ₂ H ₂ O (standard)	2.49	0.28	0.67	2.07	0.27	0.50

Table 6. Effect of serpentine-based fertilizer on yield of spring barley under vegetative conditions*

Options	Plant height, sm	Number of grains per spike	Grain yield, g/pot	Yield increase		Content per grain, %		
				g/pot	%	N	P ₂ O ₅	K ₂ O
1	39.1	15.4	6.62	-	-	1.79	0.57	0.51
2	42.4	17.8	7.15	0.53	8.0	2.10	0.48	0.67
3	44.3	19.3	8.50	1.88	28.4	2.36	0.86	0.69
4	44.5	20.3	8.81	2.19	33.1	2.39	0.85	0.68
5	43.4	19.4	8.69	2.07	31.3	2.31	0.78	0.65
LSD _{0.95}		0.49		Sx%	1.38			

Options: Options 1. No fertilizer (control), 2. N₂K₂ (background), 3. Background+P₂ serpentine+ H₃PO₄, 4. Background+P₂ serpentine+ H₃PO₄, 5. Background+P₂ double superphosphate.

*Composed by the authors.

A fertilizer's effectiveness in enhancing crop growth yield and crop quality indicators must be determined before it can be recommended for production. Thus far, only vegetative experiments have been conducted on proposed fertilizers.

Using the recommended fertilizers (table 6), the results showed that both the yield of spring barley and its content of essential nutrients increased, as evidenced by the results in the version without fertilizer and the version receiving double superphosphate fertilizer.

Conclusion

Results of the experiments indicate that serpentine-based complex fertilizers gradually dissolve in water, so

they have a long-lasting effect. Fertilizers also contain amorphous silicon dioxide, which gives them indirect benefits, including improving the germination of seeds in the lab and the field, increasing mobile nutrients in the soil, and increasing yields. To fully discover the effectiveness of fertilizers and to invest in production, field, and production experiments in different soil zones of RA, in wet and dry conditions, will be required to evaluate the effectiveness of fertilizers obtained by researchers in comparison with superphosphates.

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Declarations of interest

The authors declare no conflict of interest concerning the research, authorship, and/or publication of this article.

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