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Effect of Thermo-Tribochemical Activated Natural Phosphates on Productivity and Nutrient Uptake of *T. aestivum* L.

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Abstract

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In a vegetation pot experiment (Luvic Faeozem) the effect of thermo-tribochemically activated (TTCA) natural phosphorites (Tunisian and Morocco) and dicalcium phosphates - industrial and waste (DCP_i and DCP_w) on yield and uptake of nutrients in three *T. aestivum* L. varieties (Aglika, Kristal and Svilena) was investigated. These were introduced in soil independently and in combination with fertilizer additive [$(NH_4)_2SO_4$ + KCl + dolomite].

Clear genotype specificity was established in the productivity of its elements, as well as in nitrogen, phosphorus and potassium uptake. Variety Svilena responded positively to the independent introduction of DCP (industrial and waste), and the effect of the introduction of Morocco phosphorites was equal to the effect of triple super phosphate. Tunisian and DCP (industrial and waste) proved most unsuitable for variety Aglika. Regardless of the lower absolute yield values of variety Aglika, the positive response to the introduction of P-sources was highest. Variety Kristal was less responsive in comparison to Svilena and Aglika. Grain yield from this variety was highest after fertilization with DCP (industrial and waste) in combination with fertilizer additive.

The independent effect and the interaction of the factors “fertilizer source” and “variety” was highest in GHI and absolute grain weight. The mean productivity of the varieties increased with 9.2 % as a result from the combining of TTCA P-sources with fertilizer additive in comparison to their independent application. The effect of this combination was most evident in variety Svilena. Activated waste DCP as a phosphate source was equal or slightly conceding to triple super phosphate.

This phosphate source contributed to the increased uptake of nitrogen and potassium in the total shoot mass formed with 15 % for both elements, as compared to the independent use of TTCA P-sources. The activation of waste DCP from the production of gypsum lead to the uptake of greater phosphorus and potassium amounts in wheat in comparison to fertilization with triple super phosphate.

Key words: thermo-tribochemically activation, natural phosphorites, dicalcium phosphates (industrial and waste), genotypes, nutrient uptake

Introduction

Processing of natural phosphates into phosphate fertilizers involves phosphorus transformation from less to more readily available forms for the plants. The methods used in classical fertilizer industry are expensive, technologically complicated and ecologically inexpedient. The ongoing exhaustion of the rich natural phosphates deposits and their replacement with poor ones imposes the necessity of searching for new more rational solutions, one of which can be tribochemical activation of natural phosphates (Kostadinova and Dombalov, 2003[a,b]). Their mechanical processing not only increases dispersion but also induces a number of physical and chemical processes resulting in modification of the lattice structure. According to some authors, the expenses for activation are many times lower than that for acid decomposition. Furthermore, the tribochemical methods allow the use of both rich and poor phosphate raw materials.

Depending on the conditions of tribochemical activation, natural phosphates may become a suitable form for direct use in agriculture (Kostadinova and Dombalov, 2005). They do not concede, by their properties, to the different kinds of classical phosphorus fertilizers (Dombalov, 2003; Yaneva, 2005; Kostadinova, 2006). The possibility to combine mechanic activation with chemical methods for processing of phosphate raw materials is of special interest.

The aim of this work was to investigate the effect of thermo-tribochemical activated (TTCA) natural phosphate sources of various origin (rock phosphorites), triple superphosphate and of dicalcium phosphates (industrial and waste products) on yield and nutrient uptake of wheat.

Material and Methods

Related to the aim of the investigation, a vegetation experiment was carried out at Dobroudja Agricultural Institute in Green House. Soil from the control variant and all other variants of a stationary field trial was used (Luvic Phaeozem-FAO) which had not been fertilized since 1967 (<1 mg P_2O_5/100 g soil). This allowed the maximum expression of the possibilities of each tested phosphorus source. The vegetation trial was performed in plastic pots, containing 400 g soil in five replications. The tested variants are presented in Table 1.

The tested variants differed themselves depending on concentration and forms of phosphorus and presence of nitrogen (Table 2).

The aim of the fertilizer additive, applicated to the tested phosphate sources was to optimize the nutrition of wheat and to achieve the proportion between N:P:K:Mg = 2:1:0.2:0.2 (Table 3).

The industrial dicalcium phosphates (DCP-i) were produced by Agrobiohim Ltd. - Stara Zagora, and the waste dipotassium phosphates were waste products of GIPS Ltd. - Koshava, Vidin district.

The rate of P-materials was in accordance with the physical characteristics of slightly leached chernozems (volume weight) and with the low available phos-

Table 1
Description of tested fertilizer sources and variants of the experiment

№	Types of P-containing materials
1	Tunisian phosphorite + fertiliser additive [$(NH_4)_2SO_4$ + KCl + dolomite] - (TP + FA)
2	Marocco phosphorite + fertiliser additive [$(NH_4)_2SO_4$ + KCl + dolomite] - (MPh+ FA)
3	TSP (Triple superfosphate) + fertiliser additive [$(NH_4)_2SO_4$ + KCl + dolomite] - (TSP + FA)
4	Dicalcium phosphate - industrial + fertiliser additive [$(NH_4)_2SO_4$ + KCl + dolomite] - (DCP-i + FA)
5	Dicalcium phosphate - waste + fertiliser additive [$(NH_4)_2SO_4$ + KCl + dolomite] - (DCP-w + FA)
6	Tunisian phosphorite – (TP) - (independently)
7	Marocco phosphorite – (MP) - (independently)
8	TSP - (independently)
9	DCP-i - (independently)
10	DCP-w - (independently)
11	$(NH_4)_2SO_4$ - (independently)
12	Absolute control - initial soil

phorus content in soil. For the purposes of the vegetation experimentl, the rate was recalculated on the basis of the field norm of 15 kg P_2O_5/da. The fertilizers were applied insoluble, being mixed with the entire soil volume. This type of application is correct to a maximum degree and comparable to fertilization under production conditions.

The following *T. aestivum* varieties were included in the testing: Svilena, Kristal and Aglika (developed at Dobroudja Agricultural Institute - General Toshevo). The selection of varieties was based on previous investigations done at Dobroudja Agricultural Institute. A main criterion of selection was the amount of phosphorus uptake in the crop without mineral fertilization.

Results and Discussion

The mathematical analysis of the results obtained confirmed the discussed differences in the effect of the tested fertilization variants on the productivity of varieties (Table 4). The same was confirmed at a medium level of significance - “b”. The role of both variety and type of phosphorus sources was expressed to a maxi-

Table 2

Nitrogen and phosphorus content and forms in the tested fertilizer sources

Var.№	Types of P-containing materials	Total - P_2O_5, %	Citric soluble P_2O_5, %	Water soluble P_2O_5, %	Total N, %
1	TP + FA	7	3.1	0	14.7
2	MP+ FA	7	1.9	0	14.8
3	TSP + FA	8.6	7.9	6.9	16.4
4	DCP-i + FA	7.3	7.2	0	15.7
5	DCP-w + FA	6.8	5.2	0	14.4
6	TP	27	12	0	0
7	MP	30	8	0	0
8	TSP	50	46	40	0
9	DCP-i	35	32	30	0
10	DCP-w	25	19	0	0
11	$(NH_4)_2SO_4$	0	0	0	21

Table 3

Ratio of nutrients in the tested fertilizer sources

Var. No	Ratio of nutrients				Types of P-containing materials	Conditions
	N	P_2O_5	K_2O	MgO		
1	2	1	0.2	0.2	TФ + AS + KCl + doldmite	TTCA*
2	2	1	0.2	0.2	MФ + AS + KCl + doldmite	TTCA*
3	2	1	0.2	0.2	TSP + AS + KCl + doldmite	TTCA*
4	2	1	0.2	0.2	DCP-i + AS + KCl + doldmite	TTCA*
5	2	1	0.2	0.2	DCP-w + AS + KCl + doldmite	TTCA*
6	-	1	-	-	TP	TTCA*
7	-	1	-	-	MP	TTCA*
8	-	1	-	-	TSP	TTCA*
9	-	1	-	-	DCP-i	TTCA*
10	-	1	-	-	DCP-w	TTCA*
11	1	-	-	-	AS	TTCA*

Note: *All tested fertilizer sources were tribochemically activated. The samples were treated mechanically in a triboreactor - Vortex installation with spinning magnetic field (VISMF) under the following conditions:

- weight ratio - material : grinding particles = 1:25
- magnetic field spinning frequency 2800-3000 r/min.
- duration - 10 min
- intensity - 100 % VISMF load (V=220 V; B=0.168, synchronic frequency of bipolar magnetic field spinning - 3 000 r/min.

Table 4
Dispersion analysis

Index	MS_A	MS_B	MS_{AxB}	Error
Yield g/pot	0.37^b	0.03	1.36^c	0.13
Grain/spike g	0.04	0	2.06^c	0.33
GHI	58.33^c	27.98^c	17.83^c	0.18
1000 grain weight	62.49^c	133.18^c	34.91^c	0.09
df	11	2	22	140

Factor A - fertilizer source

Factor B - variety

mum degree in the indices "harvest index" and "1000 grain weight". The interaction of the two factors was also significant at the highest statistical level for all investigated indices.

Averaged for the tested varieties, highest grain yield was registered in the variant with independent application of nitrogen, variety Svilena exceeding Kristal and Aglika. The tested P-sources lead to the occurrence of highly expressed specificity in the response of the varieties - from negative to a very strong positive effect on their productivity. In varieties Svilena and Aglika a negative reaction to the type of P-source was not observed. Averaged for these variants, variety Svilena formed higher absolute yields than variety Aglika. In the latter variety, however, the mean increase according to the check variant was higher (138.7 %) in comparison to variety Svilena (123.9 %). Productivity of variety Svilena was strongly and positively affected by the variants with TP, MP and TSP with fertilizer additive. It is interesting to note that DCP-i and DCP-w when applied independently produced the same effect on grain yield as when introduced in combination with fertilizer additive. The efficiency of Tunisian phosphorites was lowest (with 3.9 %), and the efficiency of Morocco phosphorites was equal to that of triple super phosphate.

Highest increase of grain yield from variety Aglika was established after using triple super phosphate (with 54.2 %), and the increase from the application of MP, TP, DCP-w and DCP-i, with and without fertilizer additive, was also significant - from 17.2 % to 49.7 %. Among the tested varieties, this was the only one which responded highly positively to TTCA Morocco and Tunisian phosphorites, without combination and with additive.The increase according to the control was 48.4 % and 21.7 %.

Variety Kristal had very week responsiveness to the tested fertilizer sources. Tunisian phosphorites caused sharp decrease of its productivity. Highest increase of its productivity was registered after using the two types of DCP in combination with the additive - a mean of 21 % according to the check variant.

The results obtained for grain yield showed that the productivity of varieties Kristal and Aglika, averaged for the P-containing sources, was 86.2 % and 94.2 % from that of variety Svilena. After using independent nitrogen fertilization, the grain yield from variety Kristal was 96.9 %, and from variety Aglika - 83.3 % from the yield of Svilena.

After independent application, the fertilizer sources can be ranked in the following descending order according to their effect on grain yield (% from control variant):

$(NH_4)_2SO_4$ > TSP > DCP-w- ≥ MP > DCP-i > TP

133.03 > 122.91 > 116.55 ≥ 115.47 > 113.93 > 108.38

Especially important are the results from their combining with the fertilizer additive (AS + KCl + dolomite). Three of the tested fertilization material was in practice equal by their effect on grain yield. Their ranking according to efficiency on yield expressed in % can be done in the following descending order:

TSP = DCP-w = MP > DCP-i > TP

128.55 = 128.25 = 128.23 > 124.56 > 121.29

Grain weight per spike, one of the structure-formative parameters of yield, demonstrated a wide range of variation depending on the type of fertilizer variant and the variety. It varied from 0.530 g (Kristal - TP) to 0.802 g (Svilena - AS). In the control variant variety Svilena showed higher grain weight per spike, and averaged for the variants with introduction of P, varieties Svilena and Aglika significantly exceeded variety Kristal. Once again highest increase according to the control was registered in variety Aglika (from 116.3 % to 151.5 %), regardless of the lower absolute values in comparison to variety Svilena. Averaged for the three varieties TTCA of TSP + fertilizer additive lead to the highest grain weight per spike increase (with 28.3 %). The values of this index increased with from 15 to 20 % when using TP and MP in combination with additive. Variety Kristal formed the highest grain weight per spike in the variants with DCP-w and DCP-i with fertilizer additives, and when using triple super phosphate independently.

Only in variety Aglika an 8.8 % increase of the mean value of 1000 grain weight according to the control variant was registered. This variety formed the largest grain after independent nitrogen fertilization (with 29.2 %) and TSP with and without fertilizer additive (f. a.) - with 22.7 and 24.6 % in comparison to the control variant, respectively. The mean size of the grains from varieties Svilena and Kristal was 97.4 % and 97.7 % from that of their control variants. In both varieties the grain was largest in the variants with introduction of DCP-w - with 14.2 % and 16.0 %.

The share of grain in the total shoot mass formed (GHI) was comparatively less affected by the fertilizer sources. In variety Aglika they lead to decrease of values with an average of 5.4 % from the control variant. Averaged for variety Kristal, deviations from the control variant were not registered, and GHI of this variety was lowest at TSP + f. a. (84.2 %) and highest at DCP - i + f. a. (109. 2%). In variety Svilena the fertilizer sources lead to the same and slightly increased GHI values. The mean increase was with 2.3 %, being highest after independent nitrogen fertilization (with 7.8 %) and MP + f. a. (with 7.0 %).

The effect on grain yield from the combination of P-sources with fertilizer additive of ammonia sulfate + potassium chloride + dolomite was an average of 9.2 % from their independent introduction. In comparison to independent fertilization, the effect was lowest at TSP (6.5 %), and highest at MP (12.5 %). The positive effect of the additional fertilizer correction of the initial TTCA P-sources was most evident in variety Svilena (with 15.9 %). The increase in varieties Aglika and Kristal was 8.2 % and 3.3 %, respectively.

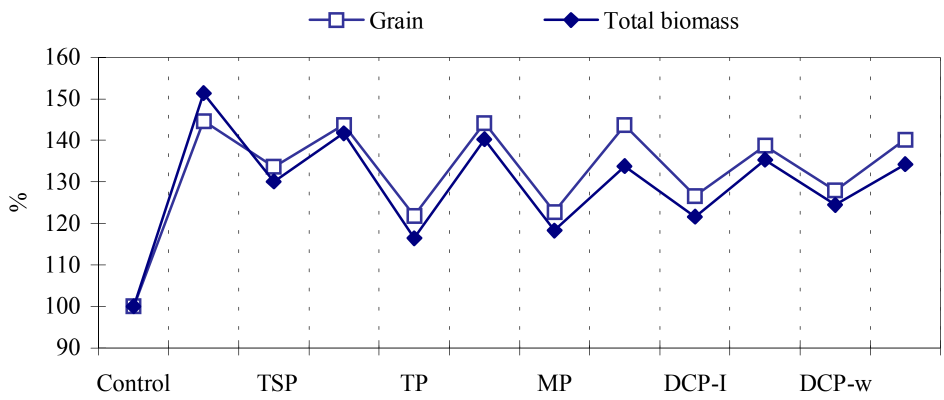

Fig. 1. Grain and total biomass N uptake in wheat varieties Svilena, Kristal and Aglika (averaged data) - in % of control variants

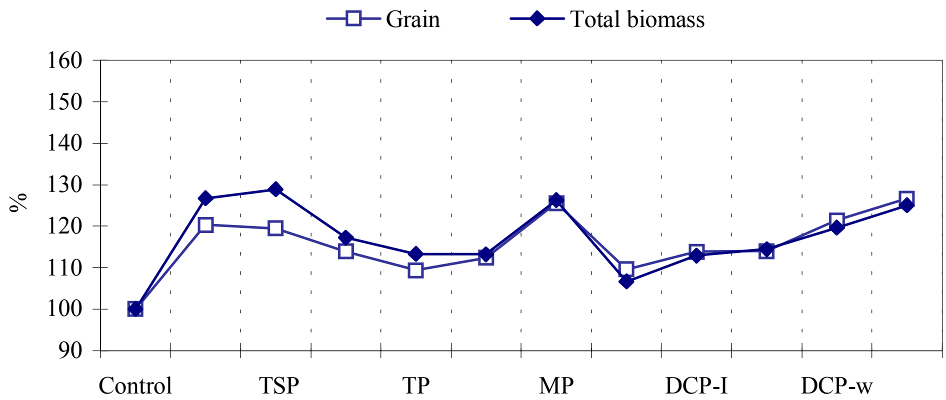

Fig. 2. Grain and total biomass P uptake in wheat varieties Svilena, Kristal and Aglika (average data) - in % of control variants

The tested fertilization variants had a strong effect on the chemical composition of the individual plant parts. All this lead to uptake of different amounts of the main macro elements in them, and as a whole in the total biomass. This, on its part, lead to changes in the harvest index values of nitrogen, phosphorus and potassium. Detailed investigation on the effect of P-sources on these indices can be found in the diploma paper of Irina Valcheva (2003). Figure 1 shows the effect of the studied fertilization variants on the nitrogen uptake in grain and total biomass averaged for the three varieties.

It is evident that ammonia sulfate had the highest positive effect on nitrogen uptake in grain, which is quite logical since this is a nitrogen fertilizer. Among the tested varieties containing phosphorus at various concentrations and degree of availability to plants, TSP and DCP-w also had a strong effect on nitrogen uptake and its accumulation in grain. The effect of the other P-sources was lower.

It is an extremely interesting fact that

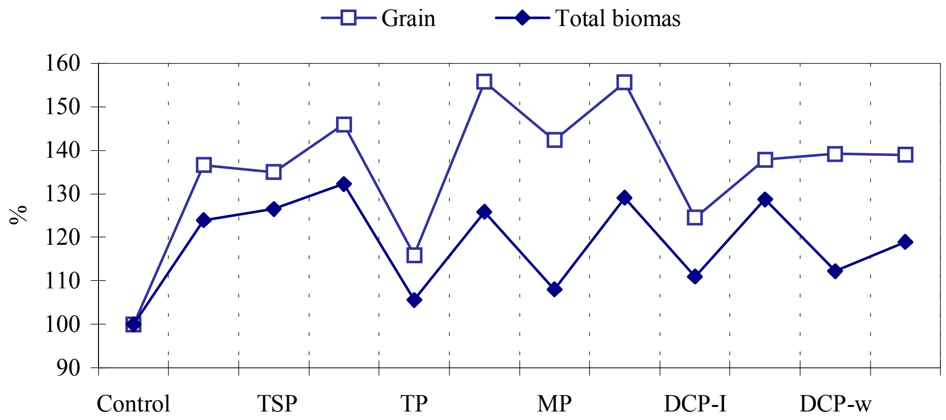

Fig. 3. Grain and total biomass K uptake in wheat varieties Svilena, Kristal and Aglika (average data) - in % of control variants

DCP-w and ammonia sulfate had a higher positive effect on the amounts of phosphorus uptake in comparison to the triple super phosphate, a classical fertilizer for our agriculture. What is more, MP after TTCA was equal to it (Figure 2).

MP, TSP and DCP-w had the most significant contribution for accumulation of more potassium in grain.

Figure 2 gives the effect of the tested fertilization variants on the amount of nitrogen, phosphorus and potassium uptake in the total shoot biomass formed, as well as their efficiency according to the control variant. Basically, the mentioned tendencies for the amount of nutrition elements uptake with grain yield remained the same. This is fully valid for the uptake of nutrients with the total shoot biomass formed. Maximum amounts of nitrogen and phosphorus, averaged for the tested varieties, were registered in the variants with independent introduction of ammonia sulfate. Triple super phosphate was the most efficient fertilizer among all tested phosphate sources.

With regard to phosphorus uptake in shoot biomass, the independent use of each of the tested phosphate sources had a higher effect than their combination with fertilizer additive. DCP-w was an exception in this respect; the amounts of phosphorus uptake in this case were practically equal to the variant with fertilizer additive.

With regard to nitrogen uptake, the independent introduction of DCP-i and DCP-w exceeded both phosphorites. Their combination with fertilizer additive lead to a significant increase of nitrogen uptake. This was most evident in Tunisian phosphorites, followed by Morocco phosphorites. In DCP- industrial and waste the efficiency of the fertilizer additive was lower.

The amounts of potassium uptake in shoot biomass in the variant with independent application of TSP exceeded the amounts from the variant with ammonia sulfate (Figure 3).

In all other variants of independent introduction of phosphate sources the potassium uptake was lower than in the variants with ammonia sulfate and triple super phosphate; however, they significantly exceeded the control variant. Similar to nitrogen, the combination with the fertilizer additive lead to a significant increase of potassium uptake in shoot biomass. This increase was most evident in the tested phosphorites and least expressed in triple super phosphate.

Morocco phosphorites had low efficiency with regard to nitrogen accumulated in grain; they, however, had a leading role with regard to the amounts of phosphorus and potassium accumulated in grain. Their advantage to triple super phosphate was well expressed.

When applied independently, the fertilizers lead to accumulation of more nutrients in grain, averaged for the tested varieties. They can be arranged in the following order, according to their efficiency in comparison to the control variant:

Independent application

Nitrogen:AS>TSP>DCP-w>DCP-i>MP>TP(144.63→121.84%)

Phosphorus:MP>AS>DCP-w>TSP>DCP-i>TP(125.61→109.35%)

Potassium:MP>DCP-w>AS>TSP>DCP-i>TP(142.36→115.89%)

The combined use of the fertilizer sources with fertilizer additive (AS+ KCl+dolomite) changed both the size of effect and the ordering of varieties.

Combined application

Nitrogen: AS>TP>TSP≥MP>DCP-w>DCP-i (144,63 → 138.75%)

Phosphorus: DCP-w>AS≥DCP-i>TSP≥TP>MP (126.66 → 109.60%)

Potassium: TP=MP>TSP>AS>DCP-w≥DCP-i (155.71 → 137.83%)

The obt ained results showed that the effect of the fertilizer additive according to the independent application was well expressed for the uptake of potassium and nitrogen in grain, averaged for the tested varieties. It is evident that by the fertilizer additive the Tunisian phosphorites, triple super phosphate and Morocco phosphorites become in practice equal in efficiency to the independent action of ammonia sulfate. The positive effect of potassium was 15.42 % more in comparison to its independent application, and of nitrogen - 15.53 %, averaged for the tested P-sources. Concerning the phosphorus uptake in grain, the fertilizer additive had no effect, averaged for the tested P-sources (-2.6 %). The additive had a negative effect on Morocco phosphorites and triple super phosphate. DCP-waste had the highest positive effect on the phosphorus uptake in grain.

The calculated mean effect from the independent use and combined application with a fertilizer additive of the tested P-sources arranged the fertilization variants as follows:

Mean effect:

Nitrogen: AS > TSP>DCP-w >MP = TP> DCP-i

(144.63 → 132.68%)

Phosphorus: DCP-w > AS > MP = TSP> DCP-i > TP

(124.02 → 110.87%)

Potassium: MP > TSP ≥ DCP-w > AS ≥ TP > DCP-i

(148.98 →131.18%)

The idea for direct usage of natural or waste phosphates in agriculture is not new in science.

Scientists from different fields concerned with their end use have been constantly searching for ways to increase phosphorus uptake from such natural sources. Phosphorus fertilizer production is expensive. On the other hand, the coefficient of use of phosphorus from triple super phosphate is rather low. It is affected by a number of factors (moisture, temperature, soil type, crop, variety, etc.) and under the most favorable conditions hardly exceeds 30 % during the year of fertilizer application. The method developed for TTCA and the results obtained from the experiment carried out allow us to be optimistic. Research work should be put on a much larger basis to be able to consider a number of aspects such as:

- a complete ecological and melioration effect, especially in soils with high acidity;
- fertilization rates used according to the peculiarity of soil type;
- range of post-effect, because these are slow-effect fertilizers in essence;
- very good knowledge on the response of crops and varieties to the respective types of natural phosphate sources.

This experiment, a main one in a student's diploma paper, showed that there are serious grounds to use in practice natural and waste phosphates processed by TTCA. It also leads to a wider range of research work on these problems at DAI - General Toshevo.

Conclusions

Clear genotype specificity in productivity and some of its elements was established, as well as in nitrogen, phosphorus and potassium uptake of wheat depending on the type of phosphate sources tested. Grain yield was positively affected by their use. Variety Svilena reacted positively to independent introduction of DCP- waste and industrial and the effect from the application of Morocco phosphorites was equal to that of triple super phosphate. A high positive effect was established on variety Aglika from their use in comparison to the control variant, although the absolute yield values were lower. Tunisian phosphorites and DCP - waste and industrial were the least suitable to apply to variety Aglika. Variety Kristal was less responsive, as compared to Svilena and Aglika. Grain yield from this variety was highest after using DCP - waste and industrial in combination with fertilizer additive.

The independent action and interaction of the factors "fertilizer source" and "variety" was strongest in GHI and absolute grain weight. The mean productivity of the varieties increased with 9.2 % as a result from the combination of TTCA P-sources with (NH_4) SO_4+KCl + dolomite, in comparison to their independent application. The effect from this combination was most evident in variety Svilena. As a phosphate source the activated waste DCP-s were equal or slightly conceded to triple super phosphate. This combination contributed for the increased nitrogen and potassium uptake in the total shoot biomass formed with a mean of 15 % for the two nutrients, in comparison to the independent use of TTCA P-sources. The activation of waste DCP from the production of gypsum lead to the higher uptake of phosphorus and potassium in wheat, as compared to the use of triple super phosphate.

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