Pestic. Phytomed. (Belgrade), 34(3-4), 2019, 145–156
DOI: https://doi.org/10.2298/PIF1904145N

UDC 632.95.02+631.81
Review paper

Some aspects of application of pesticides and fertilizers on nutritive value and other characteristics of crop plants

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SUMMARY

We surveyed different aspects of the application of agrochemicals (pesticides and foliar non-standard fertilizers) on the nutritive value and other non-yield characteristics of crop plants. The survey was based on results of our own trials and studies conducted by other researchers. Various parameters of plant and seedling growth, and yield, were analyzed, as well as the chemical composition, and energetic and thermodynamic parameters of plants in order to better assess the impact of these agrochemicals on crops. The application of various agrochemicals has been found to affect the germination of seeds produced by treated plants. The most significant and most diverse results have been obtained by analyzing the yield and yield components of many different crops (field crops, fruits, vegetables), as well as their chemical composition (mineral elements, different sugars, secondary metabolites, etc.) in terms of improving their nutritive quality. It was found that in maize seedlings it occurs by changing the content of various elements, as well as polyphenol profiles and thermodynamic parameters, and the effects did not only depend on the dosage of agrochemicals but also on maize genotype. We also found that agrochemicals affected the energetic and thermodynamic parameters of individual maize plants, as well as the parameters of plant growth and yield. It was noticed that these agrochemicals greatly affected the content of microelements, starch and crude proteins in maize and barley, sugar and polyphenol contents in various fruit trees and soybean. We noted that in certain agroecological situations these agrochemicals have led to spectacular magnification of yields of different crops, but there were also situations when they did not have any positive effect on crop yield, which is discussed also in the context of results of other researchers.

Keywords: pesticides; fertilizers; crop plants; yield; nutritional quality; plant stress

INTRODUCTION

Unlike conventional fertilizers, which are used as an agricultural practice to feed plants with certain elements, their treatment with non-standard nutrients aims primarily at intensifying the metabolism of plants either by applying specific metabolites (e.g. amino acids) and phytohormones (Nikolić et al. 2018) or plant extracts containing all these substances. Also, the use of plant regulators or other pesticide-active analogues of biologically active substances, mostly at sub-phytotoxic doses, also intensifies plant metabolism and thus has a beneficial effect on crop yield and quality (Dragicevic et al., 2013). This acceleration of plant metabolism occurs as a result of increased synthesis of protective substances, more intensive uptake of some essential nutrients or the presence of externally added signaling substances. This not only affects the yield of crops in quantitative terms, but more importantly their response to specific agroecological situations of abiotic, biotic and xenobiotic stress, as well as changes in some qualitative yield parameters in terms of increasing the nutritional value of consumerized plant parts. Thus, several effects are achieved which are not necessarily related only to crop mineral nutrition, but also to increased plant resistance to stressful situations, and also to possible biofortification of crops (Dragičević & Stojiljković, 2016) in a kind of organic food production. Unlike our previous article, which only applied to maize and fertilizer activity based on brassinosteroid phytohormones (Waisi et al., 2015b), here we provide a broader overview of crops and types of non-standard fertilizers. We also discuss relevant findings in the context of application of other agrochemicals, such as pesticides and plant growth and development regulators.

MATERIALS AND METHODS

Plant growth and yield parameters are described in methods given by Waisi et al. (2015b). Thermodynamic parameters were defined according to Sun (2002), and their calculation is described in more detail by Waisi (2016) and Waisi et al. (2017b). Quantification of total polyphenols, starch, sugars, crude proteins and oils contents is based on methods described by Waisi et al. (2015b), while a more detailed description of the methods for quantifying total polyphenols, proteins and polyphenolic fractions, and the antioxidant capacity of plant tissue is given by Đurović et al. (2019), and quantification of individual sugars is described by Waisi (2016). Element quantification was performed by the AAS method, as in Waisi et al. (2015b), which was described in more detail by Waisi et al. (2017b).

SURVEY OF RESULTS AND DISCUSSION

Ex-Yugoslav researchers had earlier noticed that the application of different pesticides affected nitrogen metabolism in seeds and seedlings of various cultivated plants (Štrbac, 1971; Janjić, 1975), and resultingly the germination of such seeds and seedling vigor, which has been repeatedly confirmed in later studies (e.g. Marinković et al., 1999). Also, it was noticed that some phytohormones and plant growth regulators can affect the phytotoxic process triggered by different herbicides (Nikolić et al., 2010a), indicating a possibility of their sophisticated application in terms of new formulations of so-called safeners. An overview of these aspects of the application of phytohormones as pesticides, plant growth regulators or fertilizers was explained by Nikolić et al. (2015).

In an earlier study (Nikolić & Waisi, 2012), we examined the results of micro-trials set up in two apple orchards (Obrenovac and Šid) located in northern parts of Serbia in 2011. The plots in those micro-trials were subjected to different treatments: 1) half and full doses of mancozeb and tebuconazole as two positive controls, 2) 24-EBL-based preparation combined with half the usual dose of mancozeb and tebuconazole; 3) non-standard fertilizes based on amino acids combined with half the usual dose of mancozeb and tebuconazole; and 4) plant extracts combined with half the usual dose of mancozeb and tebuconazole. We evaluated the usual parameter of fruit yield as a result of the influence of these different treatments, and determined the contents of reducing sugars in extracts of apple fruit pulp. In one trial (Obrenovac), the evaluated yield/ha of 24-EBL-treated apples was the same as in control plots, and pomological and fruit quality parameters of apples were comparable (Table 1). In another trial (Šid), the evaluated yield/ha of 24-EBL-treated apples was almost a quarter more than the apple yield from control plots (treated with half or full dose of fungicides) and the other treatment plots, also with comparable pomological and fruit quality parameters of apple fruits (Table 2).

Table 1. Pomological parameters and parameters of quality of apple fruit from Obrenovac orchard. Treatments: 1 - control with half doses of mancozeb and tebuconazole; 2 – 24-epibrassinolide-based fertilizer + half doses of mancozeb and tebuconazole; 3 – plant extract based fertilizer + half doses of mancozeb and tebuconazole; 4 – amino acid-based fertilizer + half doses of mancozeb and tebuconazole; 5 - amino acid-based fertilizer + half doses of mancozeb and tebuconazole; 6 - control with full doses of mancozeb and tebuconazole fungicides (from: Nikolić & Waisi, 2012)

Trial combinations	Mt (average fruit weight) ±σ (g)	n (average number of fruits per tree) ±σ	Evaluated yield/ ha (kg)	pH (±σ) of apple fruit pulp	Index of refraction (% of Brix ±σ) of apple fruit pulp
1	150.85±38.64	181.5±39.9	65 710.26	3.89±0.27	7.1±0.4
2	192.85±48.84	139.4±41.7	64 422.87	3.84±0.08	7.5±0.7
3	178.36±29.44	142.5±41.7	60 999.12	3.81±0.07	7.0±0.2
4	180.26±26.12	151.7±28.6	65 629.06	3.83±0.05	7.3±0.2
5	178.88±42.44	123.0±39.2	52 805.38	3.80±0.06	7.4±0.4
6	178.72±40.15	139.4±36.5	59 792.56	3.90±0.10	8.0±0.4

Table 2. Pomological parameters and parameters of quality of apple fruit from Šid orchard. Treatments: 1 - control with half doses of mancozeb and tebuconazole; 2 – 24-epibrassinolide-based fertilizer + half doses of mancozeb and tebuconazole; 3 – plant extract-based fertilizer + half doses of mancozeb and tebuconazole; 4 – amino acid-based fertilizer + half doses of mancozeb and tebuconazole; 5 - amino acid-based fertilizer + half doses of mancozeb and tebuconazole; 6 - control with full doses of mancozeb and tebuconazole fungicides (from: Nikolić & Waisi, 2012)

Trial combinations	Mt (average fruit weight) ±σ (g)	n (average number of fruits per tree) ±σ	Evaluated yield/ ha (kg)	pH (±σ) of apple fruit pulp	Index of refraction (% of Brix ±σ) of apple fruit pulp
1	208.37±29.94	152.9±50.0	53 078.38	3.88±0.03	7.0±0.0
2	238.91±20.90	207.9±27.9	82 729.20	3.92±0.02	7.1±0.2
3	225.64±25.54	174.6±17.6	65 634.50	3.89±0.01	6.7±0.6
4	217.19±29.71	163.7±29.0	59 232.97	3.88±0.02	6.7±0.6
5	236.52±24.74	135.1±16.6	53 235.12	3.89±0.03	6.0±0.2
6	214.66±27.32	130.4±29.5	46 634.11	3.89±0.01	6.3±0.2

We also assesed the efficacy of these procedures in protecting apple leaves and fruits from the notorious phytopatogenic fungus *Venturia inaequalis* (Stevanović et al., 2012). From the aspect of plant protection, our procedures were satisfactory with 78.71% and 77.69% efficacy of 24-EBL+half fungicide dose treatment of leaves and fruits (against 84.17% and 87.90% efficacy achieved by full fungicide dose) in Obrenovac. We got similar results in Šid, which is also satisfactory (data not shown). Our results are very similar to findings reported by other researchers (Khripach et al. 2000).

A similar trial was set up in an apple orchard near Belgrade with the application of different non-standard fertilizers (Waisi et al., 2014) and also with similar results as in the study by Nikolić and Waisi (2012). In experiments conducted near Smederevska Palanka (Nikolić et al., 2010b) we treated apple and tomato crops with several non-standard fertilizers based on phytohormones, aminoacids and plant extracts. The influence of these non-standard fertilizers on crop yield was variable, but we also detected a significant and very changeable effect of these fertilizers on seed germination following treatment of tomato plants.

We also examined the influence of non-standard fertilizers on yield and yield components of soybean and barley arable crops.

During the vegetation season 2012 we treated two soybean genotypes, one standard ("Nena"), and another with a low content of Kunitz-trypsin inhibitor protein ("Laura"), with non-standard fertilizers as a type of biofortification. This approach revealed a small impact by alterations in P_{phy} (content of phytic phosphorus), which is an important factor in restraining the availability of mineral nutrients (Table 3).

The first thing we noticed was that as the content of P_{phy} decreased (Table 3), Zn content in soybeans grains increased (Table 5). Moreover, the influence of β-carotene was significant for the availability of mineral nutrients (Table 4), but more importantly its increase was linked with parallel Fe increase, mainly in grain of higher weight as part of a better yielding potential (Table 5).

Table 3. The effects of non-standard foliar fertilizers on grain yield and contents of total phosphorus (P_{tot}) and phytic phosphorus (P_{phy}) in grain of two soybean cultivars (from: Dragičević et al., 2016b)

Treatment	Grain yield (t ha^{-1})			P_{tot} (g kg^{-1})			P_{phy} (g kg^{-1})		
	2011	2012	x̄	2011	2012	x̄	2011	2012	x̄
				LAURA					
Control	4.41	1.80	3.10	17.35	20.59	18.97	14.25	17.03	15.64
Agrostemin	4.39	1.82	3.10	17.20	19.70	18.45	13.78	15.80	14.79
Algaren B-Zn	4.03	2.49	3.26	17.21	19.10	18.16	14.06	15.75	14.91
Lithovit Forte	4.08	2.40	3.24	17.63	18.30	17.96	13.93	15.30	14.62
Epin Extra	4.50	1.94	3.22	16.60	18.96	17.78	13.62	15.45	14.53
Zircon	4.99	2.81	3.90	16.56	17.93	17.25	13.27	15.13	14.20
x̄	4.40	2.21	3.30	17.09	19.10	18.10	13.82	15.75	14.78
LSD 0.05	Year	Treat.	YxT	Year	Treat.	YxT	Year	Treat.	YxT
	0.78	1.43	0.83	0.72	1.26	0.18	0.53	1.15	0.14
				NENA					
Control	4.06	2.24	3.15	19.73	18.65	19.19	16.79	15.64	16.22
Agrostemin	3.76	2.16	2.96	19.96	19.46	19.71	15.01	15.86	15.43
Amalgerol premium	4.11	2.96	3.54	19.38	19.89	19.64	15.32	16.65	15.99
Eko-Fert	3.11	2.81	2.96	19.29	19.89	19.59	15.78	17.07	16.43
Zlatno inje	4.58	3.34	3.96	19.68	19.32	19.50	16.78	15.16	15.97
x̄	3.93	2.70	3.31	19.61	19.44	19.52	15.94	16.08	16.01
LSD 0.05	Year	Treat.	YxT	Year	Treat.	YxT	Year	Treat.	YxT
	0.82	1.01	0.79	0.40	0.39	0.10	1.01	1.04	0.90

Table 4. The effects of non-standard foliar fertilizers on inorganic phosphorus (P_i) and β-carotene contents in grain of two soybean cultivars (from: Dragičević et al., 2016b)

Treatment	P_i (g kg-1)			β-carotene (mg kg-1)		
	2011	2012	x̄	2011	2012	x̄
			LAURA			
Control	0.524	0.457	0.491	12.79	10.99	11.89
Agrostemin	0.497	0.327	0.412	12.37	13.32	12.84
Algaren B-Zn	0.500	0.475	0.488	12.93	11.99	12.46
Lithovit Forte	0.512	0.481	0.496	13.41	12.33	12.87
Epin Extra	0.462	0.474	0.468	11.02	11.44	11.23
Zircon	0.446	0.463	0.454	12.19	10.33	11.26
x̄	0.490	0.446	0.468	12.45	11.73	12.09
LSD 0.05	Year	Treat.	YxT	Year	Treat.	YxT
	0.045	0.044	0.006	0.92	0.76	0.22
			NENA			
Control	0.582	0.495	0.539	14.16	14.69	14.42
Agrostemin	0.761	0.406	0.583	13.75	10.94	12.35
Amalgerol premium	0.789	0.312	0.550	12.10	13.27	12.69
Eko-Fert	0.674	0.457	0.565	13.23	12.42	12.82
Zlatno inje	0.827	0.465	0.646	14.19	14.63	14.41
x̄	0.73	0.43	0.58	13.49	12.81	13.34
LSD 0.05	Year	Treat.	YxT	Year	Treat.	YxT
	0.083	0.190	0.021	1.20	0.84	0.15

It is important to underline that ratios between P_{phy} and β-carotene (as factors influencing the bioavabiality of minerals) and different mineral nutrients (Mg, Fe and Zn) could be altered to some degree by applying non-standard foliar fertilizers, but these relationships also depend on soybean variety. The applied 24-EBL-based preparation and the plant extract ("Zircon") were efficient in decreasing the mentioned ratio in "Nena" grain, while some plant extracts ("Zlatno inje" and "Zircon") were efficient for "Laura" (Table 6).

Table 5. The effects of non-standard foliar fertilizers on the content of Mg, Fe and Zn in grain of two soybean cultivars (from: Dragičević et al., 2016b)

Treatment	Mg ($mg\ kg^{-1}$)			Fe ($mg\ kg^{-1}$)			Zn ($mg\ kg^{-1}$)		
	2011	2012	x̄	2011	2012	x̄	2011	2012	x̄
				LAURA					
Control	2037	1969	2003	73.75	53.22	63.48	40.63	36.75	38.69
Agrostemin	2075	2172	2124	75.00	58.00	66.50	50.63	59.72	55.17
Algaren B-Zn	2110	2216	2163	78.75	60.09	69.42	44.69	56.59	50.64
Lithovit Forte	2099	2138	2118	72.50	55.16	63.83	42.81	54.81	48.81
Epin Extra	2139	2181	2160	83.75	57.13	70.44	49.69	45.03	47.36
Zircon	2195	2235	2215	80.63	66.13	73.38	45.00	50.81	47.91
x̄	2109	2152	2130	77.40	58.29	67.84	45.57	50.62	48.10
LSD 0.05	Year	Treat.	YxT	Year	Treat.	YxT	Year	Treat.	YxT
	75.9	44.5	21.2	4.36	11.31	1.39	7.60	6.83	5.78
				NENA					
Control	2137	2037	2087	56.28	56.41	56.34	31.22	37.44	34.33
Agrostemin	2184	2106	2145	65.88	59.97	62.92	37.63	35.63	36.63
Amalgerol premium	2150	2050	2100	62.38	57.69	60.03	36.69	32.50	34.59
Eko-Fert	2150	2222	2186	56.97	57.34	57.16	35.47	35.13	35.30
Zlatno inje	2203	2122	2162	66.13	64.34	65.23	40.50	33.16	36.83
x̄	2165	2107	2136	61.53	59.15	60.34	36.30	34.77	35.53
LSD 0.05	Year	Treat.	YxT	Year	Treat.	YxT	Year	Treat.	YxT
	57.7	57.0	33.1	3.91	2.25	1.36	4.01	4.32	4.08

Table 6. Molar ratios between phytate (P_{phy}) and inorganic (Pi) phosphorus, β-carotene, Mg, Fe and Zn in grain of two soybean cultivars (from: Dragičević et al., 2016b)

Treatment	Pphy/Pi		Phy/β-carotene		Phy/Mg		Phy/Fe		Phy/Zn	
	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
					LAURA					
Control	27.2	37.3	2124	2956	2.10	2.60	58.1	96.2	123.4	163.1
Agrostemin	27.7	48.3	2124	2262	2.00	2.19	55.2	81.9	95.8	93.1
Algaren B-Zn	28.1	33.2	2074	2504	2.00	2.14	53.7	78.8	110.7	97.9
Lithovit Forte	27.2	31.8	1981	2367	1.99	2.15	57.7	83.4	114.5	98.2
Epin Extra	29.5	32.6	2356	2575	1.91	2.13	48.9	81.3	96.4	120.7
Zircon	29.7	32.7	2075	2794	1.82	2.03	49.4	68.8	103.7	104.8
x̄*	28.2±3.9	36.0±17.6	2122±5.9	2576±10.1	1.97±4.9	2.21±9.0	53.8±7.4	81.7±10.8	107.4±10.1	113.0±23.2
					NENA					
Control	28.8	31.6	2260	2031	2.36	2.31	89.7	83.3	189.2	147.0
Agrostemin	23.4	37.4	2275	2621	2.21	2.31	83.3	89.5	156.6	171.0
Amalgerol premium	20.3	32.6	2254	1976	2.29	2.15	76.2	70.8	145.7	160.8
Eko-Fert	19.7	39.1	2080	2764	2.06	2.26	68.5	79.5	140.3	156.6
Zlatno inje	19.4	53.4	2415	2391	2.14	2.44	73.8	86.7	146.9	180.2
x̄	22.3±17.8	38.8±22.5	2257±5.3	2357±14.8	2.21±5.3	2.29±4.6	78.3±10.6	82.0±8.9	155.8±12.6	163.1±7.9

* x̄ ± Coefficient of variation (%)

Also, a correlation between 1000 grain weight (as a significant yield component) and the content of β-carotene and Zn in soybean grain was very significant (Dragičević et al., 2016b). In addition, we conducted a PCA statistical analysis of the relationships between P_{phy}, β-carotene and mineral elements (Table 7).

In the late winters of 2013 and 2014, we sowed hull-less barley (*Hordeum vulgare* L. *var. nudum*; cv. "Apolon"), and during the coming spring of both years we treated the crop with a 24-EBL-based preparation and other non-standard fertilizers (based mainly on plant extracts and other phytohormones). After summer harvest we assessed the yield (at 14% grain moisture content; kg ha^{-1}) and determined different chemical ingredients in barley grain using standard methods (Tables 8 and 9).

Table 7. Results of PCA for P_{phy}, β-carotene and mineral element contents in grain of two soybean cultivars (synthetic variables: PCA1 - principal component axis 1, PCA2 - principal component axis 2, and PCA3 - principal component axis 3) (from: Dragičević et al., 2016b)

	PCA1	PCA2	PCA3
Pphy	0.597	−0.353	−0.042
β-carotene	0.285	0.437	0.739
Mg	−0.186	−0.594	0.661
Fe	−0.565	0.389	0.124
Zn	−0.457	−0.426	−0.017
Explained variance	2.185	1.272	0.884
Proportion of total variance (%)	43.7	25.4	17.7

The results (Dragičević et al., 2016a) indicated that the year affected barley grain yield and its chemical

Table 8. Grain yield and 1000 grain weight of barley (cv. Apolon) influenced by different foliar fertilizers (from: Dragičević et al., 2016a).

Treatment	Grain yield (kg ha^{-1})			1000 grain weight(g)		
	2013	2014	Average	2013	2014	Average
Control	3231.7	922.3	2077.0	37.80	29.09	33.44
Epin extra	3113.0	1043.1	2078.0	39.30	36.64	37.97
Zircon	3752.0	623.7	2187.9	38.69	32.84	35.77
Chitosan	3856.3	1098.8	2477.6	39.14	31.55	35.34
Benzyladenine	3244.3	1107.5	2175.9	40.01	30.49	35.25
Siliplant	3194.3	933.3	2063.8	39.40	32.63	36.01
Propikonazole	3328.7	653.1	1990.9	40.67	33.78	37.23
Average	3388.6	911.7		39.29	32.43	
LSD 0.05*	Treatment	Year	T X Y	Treatment	Year	T X Y
	1462.0	532.5	569.4	4.03	1.95	1.05

*Least significant difference, P = 0.05 (n = 4)

Table 9. Effects of different foliar fertilizers on relations between phytic and inorganic P, phytate, *β*-carotene, Mg, Ca, Fe, Zn and Mn in barley (cv. "Apolon") grain (from: Dragičević et al., 2016a).

Treatment	Pphy/Pi	Phy/β-carot.	Phy/Mg	Phy/Ca	Phy/Fe	Phy/Zn	Phy/Mn
Control	5.10	5356.60	2.15	2.86	107.34	40.22	74.1
Epin extra	4.58	5242.48	2.11	2.68	100.90	27.52	60.0
Zircon	4.62	5411.22	2.14	3.11	103.15	37.21	71.0
Chitosan	4.60	5088.97	2.14	4.21	72.38	34.10	70.1
Benzyladenine	4.60	5349.25	2.03	2.36	62.91	31.81	69.1
Siliplant	4.47	5610.72	2.05	2.96	51.13	28.70	76.1
Propikonazole	4.74	5828.46	2.16	2.96	55.46	35.80	80.3
LSD 0.05*	0.8	2397.6	0.11	0.58	262.7	15.66	104.3

*Least significant difference, P = 0.05 (n = 4) composition, and the highest impact was found for Si under unfavourable conditions (data not shown). The applied treatments had the highest effectiveness on grain yield and increased grain quality, mainly through a reduction in P_{phy}/β-carotene ratio (Table 9) and increase in GSH content (data not shown), thus increasing potential bioavailability of the examined mineral elements. What is more, abiotic stress caused by high precipitation amounts (in 2014) could be mitigated by applying a fertilizer, i.e. by increasing potential bioavailability of P, Mg, Ca and Fe (Table 9). Generally, the 24-EBL preparation influenced the content of P_i, Zn and Fe, and the other fertilizers mainly affected potential availability of some other mineral elements and physiologically active ingredients (Ca, Mn, Si and GSH).

In previous field trials, carried out in one fruit (apple) and two field crops (soybean and barley), we showed that the preparation based on 24-EBL, considering other non-standard fertilizers, affected not so much the yield as the quality and chemical composition of crops (Nikolić & Waisi, 2012; Dragičević et al., 2016a, 2016b), acting protectively to the crop under stressful conditions (Stevanović et al., 2012).

Comparing these results with our previous studies conducted on maize treated with brassinosteroid phytohormones, i.e. reviewing the effects of brassinosteroids on germination and seedling growth (Waisi et al. 2015a, 2017a), and growth of whole plants and yield of maize in the field (Waisi et al., 2015b; Nikolić et al. 2018) by monitoring changes in chemical composition and energy and termodinamic parameters, we inferred that these are essentially related phenomena, which can be treated as specific forms of crop biofortification (Dragičević & Stojiljković, 2016), and thus as improvements in the nutritional quality of food obtained from plants so cultivated.

The mentioned concept of biofortification (Dragičević & Stojiljković, 2016) was further tested in a soybean crop to examine the impact of some non-standard fertilizers on the content of various polyphenolic fractions, as well as proteins, and their antioxidant capacity (Đurović et al ., 2019). It is known that various physico-chemical methods (heat and chemical treatment, centrifugation, exposure to electric and/or magnetic fields, etc.) are used in the processing of plant raw materials to produce food, which increases the availability of various nutrients previously existing in plant components (Đurović et al., 2018), which prompted us to combine the two approaches.

Our results (Figure 1) are in agreement with results of a previous study by Aludatt et al. (2013), in which the highest amount of phenolic acids in soybean seed was detected in free soluble form.

Aludatt et al. (2013) also confirmed that ferulic acid and *p*-coumaric acid were the predominant phenolic compounds in full-fat soybean and in defatted soybean meal, which is similar to the results of our study (Đurović et al., 2019). Kim et al. (2016) confirmed that *p*-coumaric and ferulic acids were strongly bound to cell components in soybean, and released after alkaline hydrolysis. This result demonstrated that some phenolic acids were synthesized as macromolecular bound components (i.e. polyphenol, tannin, and lignin) to support structural cell wall development. Chlorogenic, caffeic and *p*-coumaric acids are intermediates in lignin biosynthesis, while ferulic acid is also probably linked to polysaccharides, lignin, and suberin (Boerjan et al., 2003; Dixon & Paiva, 1995). The smallest amounts of phenolic acids are present in the bound fraction, which is also consistent with the findings of Aludatt et al. (2013).

Since antioxidants may act through different mechanisms, the antioxidant activity of soybean flour extracts was determined using different assays, DPPH, FRAP and BR (Briggs-Raucher potentiometric titration). All examined plant extract-based products expressed significant alterations in total phenol content (Figure 1) and antioxidant activity

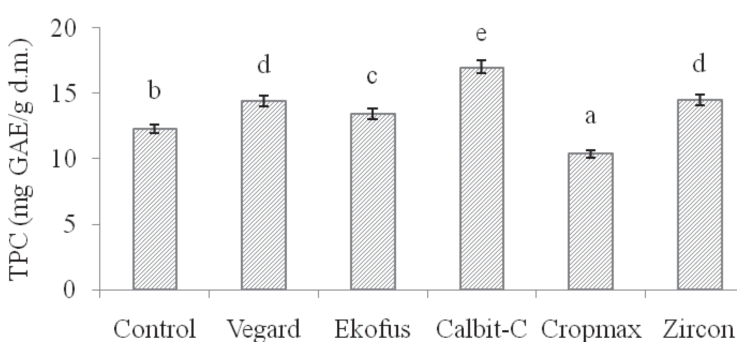

Figure 1. Total phenol content (TPC) in soybean seed influenced by treatment with different plant extract-based products, determined as mg GAE/g d.m. (from: Đurović et al., 2019)

of the soybean flour extracts. An exception was treatment with "Cropmax" amino acid fertilizer, which only led to a decrease in TPC (Figure 1) and antioxidant activity, determined by DPPH and FRAP methods (Figure 2).

All other treatments showed positive influence on the TPC, DPPH and FRAP (Figures 1 and 2), which is consistent with several other studies (Danilčenko et al., 2017; Verkleij, 2012) showing positive effects of biofertilizers (based on plant extracts) on yield, growth and antioxidant activity of different plant species.

The BR reaction method provides a "bigger antioxidant picture" and can also show synergistic effects (Milos & Makota, 2012). Therefore, the results obtained by the BR reaction method (Figure 3) demonstrate synergistic effects (phenols + proteins) on soybean treated with the "Cropmax" amino acid fertilizer, and show a much more pronounced effect than the fertilizers "Calbit-C" and "Zircon", based on plant extracts.

This indicates that it is not only the phenol content that participated in the inhibition of oscillatory regime as other species (such as proteins and some ions) also influenced the BR reaction, possibly building and/or stabilizing macromolecular structures of plant cells. In our study, the most positive influence on TPC, DPPH, FRAP data, and in the Briggs-Rauscher reaction method too, was exerted by "Calbit-C", which contains water-soluble Ca-lignosulphonate. This is consistent with the fact that Ca^{2+} in the form of functional Ca-pectate positively affects cell wall status (as well as many polyphenol compounds), which makes plants more resistant to different stressors. It also plays an important role in stabilizing the bond of phospholipids and cell membrane proteins, thus maintaining their functional stability (Murayama et al., 2016; Hepler, 2005).

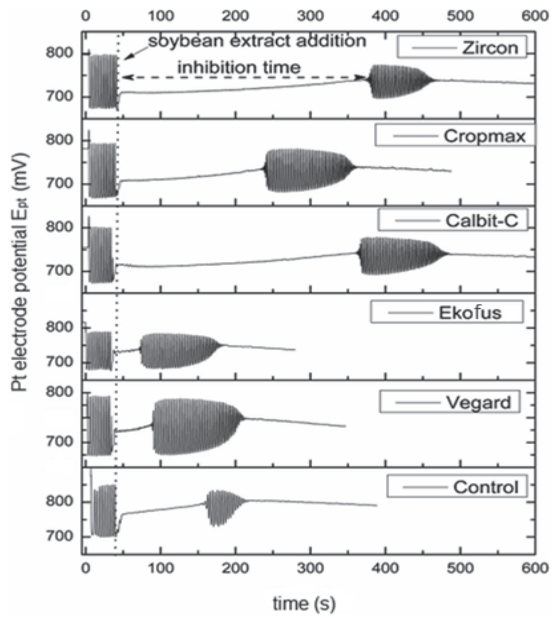

Figure 3. Briggs-Rauscher oscillograms obtained with particular soybean extract addition (100 µl) after 30 s from oscillatory reaction beginning. The initial concentrations of reactants for BR reaction were $[CH_2(COOH)_2]_0$ = 0.0789 mol/dm^3, $[MnSO_4]_0$ = 0.00752 mol/dm^3, $[HClO_4]_0$ = 0.0300 mol/dm^3, $[KIO_3]_0$ = 0.0752 mol/dm^3 and $[H_2O_2]_0$ = 1.2690 mol/dm^3. (from: Đurović et al., 2019)

PCA analysis is a very useful tool to reduce a large number of variables to a small number of composite variables (main components). It explains the variability of data in a most concise manner. It reveals hidden connections and interdependence of data.

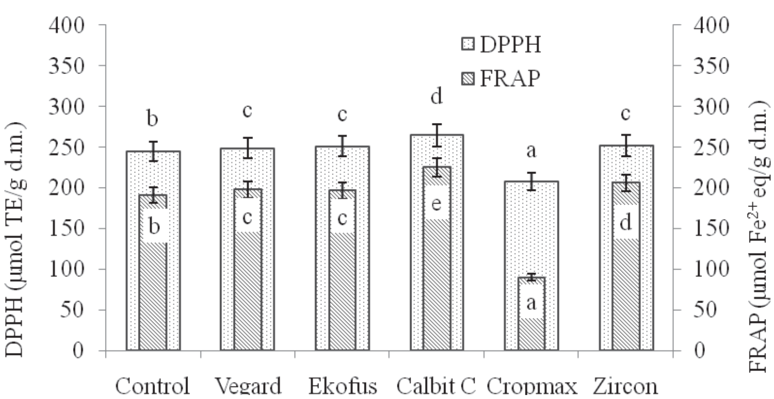

Figure 2. Antioxidant activities determined by DPPH and FRAP assays in soybean seed influenced by treatment with different plant extract-based products (from: Đurović et al., 2019)

The results (Figure 4) of this study indicate that the "Cropmax" amino acid fertilizer induced the h ighest variability in caffeic acid concentration, and somewhat less in the concentrations of gallic and chlorogenic acids.

The "Calbit-C" and "Zircon" plant extract fertilizers were responsible mainly for variations in concentrations of *trans*-cinnamic, gallic and chlorogenic acids. The other treatments (particularly "Ekofus" plant extract fertilizer and control) provoked no variation in the investigated phenolic acids. It means that the application of plant extract-based products affects not only yield, but the chemical composition of grain too. Accordingly, phenolic composition and concentration can be altered in a specific way (Taie et al., 2008; Konopka et al., 2012).

Another important group of biologically active compounds in soybean seed are proteins. In this study, we have shown that using different types of natural products based on plant extracts can affect protein (and oil) contents in soybean seed, and the best effect was achieved with the „Cropmax" amino acid fertilizer (Figure 5).

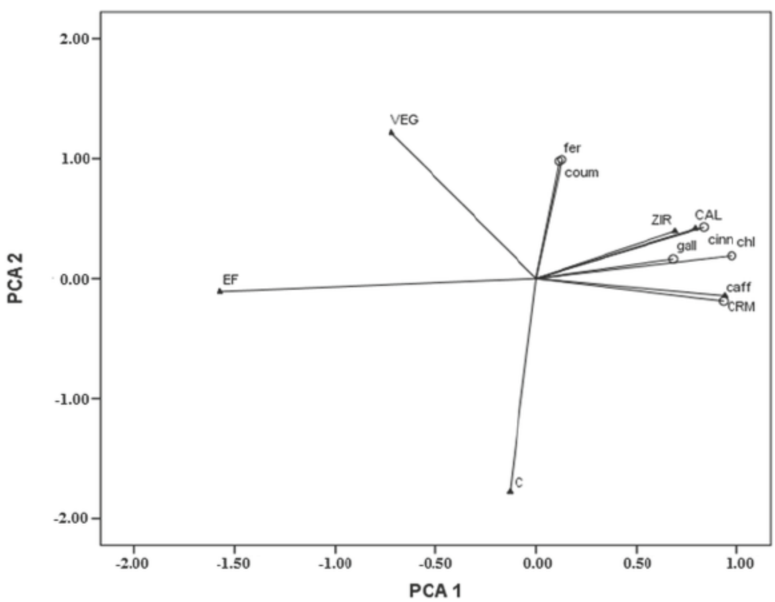

Figure 4. Principal Component Analysis (PCA) for gallic acid (gall), chlorogenic acid (chl), caffeic acid (caff), *p*-coumaric acid (coum), ferulic acid (fer) and trans-cinnamic acid (cinn), in soybean seed influenced by treatment with different plant extract-based products (control - C; Vegard - VEG; Ekofus- EF; Calbit-C - CAL; Cropmax - CRM; Zircon - ZIR). (from: Đurović et al., 2019)

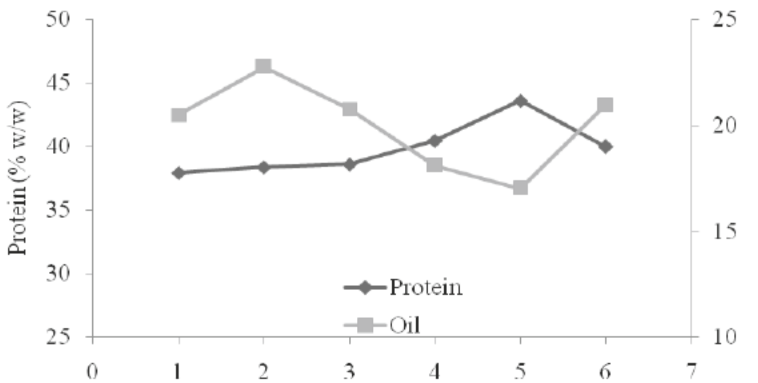

Figure 5. Protein and oil contents in soybean seed influenced by treatment with different plant extract-based products (1-control, 2-Vegard, 3-Ekofus, 4-Calbit-C, 5-Cropmaxand 6-Zircon), expressed as % (w/w) (LSD for proteins is 0.702; LSD for oil is 0.701). (from: Đurović et al., 2019)

This was expectable since "Cropmax" contains about 2% amino acids, which have proved to have positive effect on nitrogen metabolism and increase the content of raw proteins in plant material (Liu & Lee, 2012; Dromantiene et al. 2013). The synergistic effect of proteins and polyphenols on the antioxidant capacity of soybean meal was also observed using the Briggs-Raucher method (Figure 3).

The results presented, and compared to our previous reports and works by other researchers, show that treatments of crops with different agrochemicals (pesticides and non-standard fertilizers) affect not only the yield of crops or their resistance to various abiotic and biotic stresses, but very importantly they also affect the chemical composition of seeds and/or fruits of cultivated plants used in the food industry, which creates possibilities for targeted improvements in the nutritional quality of food through so-called biofortification programs.

ACKNOWLEDGMENT

This review was funded by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Grants No. TR 31018, TR 31043 and TR 37021).

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Neki aspekti uticaja pesticida i đubriva na nutritivnu vrednost i druge karakteristike gajenih biljaka

REZIME

Analizirali smo različite aspekte primene agrohemikalija (pesticida i folijarnih nestandardnih đubriva) na hranjivu vrednost i ostale karakteristike useva, pored prinosa. Istraživanje je zasnovano na rezultatima našeg i rezultatima ispitivanja drugih istraživača. Analizirani su različiti parametri rasta biljaka i sadnica i njihov prinos, kao i hemijski sastav, a takođe i energetski i termodinamički parametri biljaka, kako bi se bolje procenio uticaj ispitivanih agrohemikalija na useve. Pre svega, utvrđeno je da primena različitih agrohemikalija utiče na klijanje semena koje proizvode tretirane biljke. Najznačajniji i najraznolikiji rezultati dobijeni su analizom prinosa i komponenata prinosa mnogih različitih kultura (useva, voća, povrća), kao i njihovog hemijskog sastava (mineralnih elemenata, različitih šećera, sekundarnih metabolita, itd.) u smislu poboljšanja nutritivnog kvaliteta. Takođe je utvrđeno da u biljkama kukuruza dolazi do promene sadržaja različitih elemenata, zatim polifenolnih profila, kao i termodinamičkih parametara, pri čemu taj efekat ne zavisi samo od doziranja agrohemikalija, već i od genotipa kukuruza. Takođe smo otkrili da agrohemikalije utiču na energetske i termodinamičke parametre pojedinih biljaka kukuruza, kao i na parametre rasta i prinosa biljke. Primećeno je da ove agrohemikalije izuzetno utiču na sadržaj mikroelemenata, skroba i sirovih proteina u kukuruzu i ječmu, šećera i polifenola u raznim voćkama, kao i u soji, pri čemu napominjemo da su u nekim agroekološkim situacijama ove agrohemikalije dovele do spektakularnih uvećanja prinosa različitih kultura, ali bilo je i situacija kada nisu imale pozitivnog efekta na prinos, o čemu će biti reči, takođe u kontekstu rezultata drugih istraživača.

Ključne reči: pesticidi; đubriva; usevi; prinos; nutritivna vrednost; stres biljke