Liquid Fertilizers with Organic Substances - Agrochemical Effects Obtained by Application

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The fertilization methods and technologies rapid development using extra-radicular fertilizers and liquid fertilizers with or without organic substances is due to both their controlled application possibilities depending on the vegetation phases, crop, agrochemical background, and nutrition deficiencies and efficiency increase of the indices regarding the fertilization costs -economical results The best agricultural practices application, compatible with the new climatic conditions, can actively contribute to environment preservation and protection at the same time with crops constancy and production capability securement. Fertilizers application with solid or liquid humic substances ensures all the needed compounds and minerals for creating and maintaining a fertile soil. At the same time their efficiency depends on multiple factors that include temperature, humidity, previous agricultural practices, soil physical and chemical characteristics, pesticides or other polluting products residues, microbial population present in the soil and the activity it develops. The humic compounds mediate pesticides and toxins degradation and contaminated soils biological reparation rests on humus help in microbial degradation. The paper presents the results obtained by radicular application of two experimental NPK type fertilizers with humic substances at the sunflower crop in vegetation pots. The fertilizers have been physically and chemically characterized and agrochemically tested as compared to an unfertilized control and two fertilized controls with a complex 15.15.15 NPK fertilizer in 120 and 180 kg/ha doses. The experimental fertilizers were applied in portions upon crops sowing and during vegetation in three 200, 300, respectively 400 liters fertilizer/ha and ensured significant gains as compared to the controls.The extracted humic substances and the fertilizers were physically and chemically characterized as well as through differential thermal gravimetric analysis and FT-IR spectrometry. The vegetal material and the sunflower seeds were analyzed regarding the nitrogen phosphorus, potassium, calcium, magnesium, zinc, copper, iron, and manganese contents.

Keywords: organic mineral fertilizers, organic fertilizers, humic substances

Fertilizers are products that contribute to plant nutrition and soil improvement through nutrient supply as well as through plant nutrition stimulation.

The fertilizers applied as diluted solutions in soil or on the plants have the advantage that they allow the quantization of nutrients and substances needed for plants optimum growth.

Foliar fertilization is a widely used method to supplement soil applications and to improve the yield and quality of crops. This fact is due to a rapid answer from the plant and it was noticed that approximately 30% of the nitrogen applied on the leaves was rapidly absorbed through them in studies with labeled substances (^{15}N) [A].

For most of the crops, deficiencies for nutrients often occur for a variety of reasons, some of them being unable to be controlled by the farmers.

Most of the foliar fertilizers are applied at the same time with the plants protection treatments which compensates part of the application costs.

Embedding natural organic substances in the composition with nutrition stimulating effects proved efficient for increasing nutrients radicular and foliar application performance.

Humic substances improve fruit quality, increase water stress tolerance, decrease disease incidence, enhance early growth and flowering [1-4].

Humic substances are recognized as the most chemically active compounds in soils, with cation and anion exchange capacities better than those of clays [5].

Applying liquid fertilizers with humic substances on/in the soil leads to its physical, chemical, and microbiological characteristics improvement and helps a better assimilation of the solid and/or liquid simple or complex fertilizers. Yields increases are obtained in the end [6 - 9].

The number of organic mineral fertilizers that contain vegetal organic substances is high and the types are very diverse due to the variety of sources from which they proceed [10-13]. The use of fertilizers that contain humic compounds proved efficient to a large range of crops on different soil types [1, 14-16, 43] and also in the case of amelioration technologies of the oil polluted soils, and pesticides degradation. The decontamination process relies on the humic substances help in the microbial degradation [17-20].

The range of fertilizers that contain vegetal humic substances developed much due to both the sources from which they can be obtained, the extraction (separation) manner from these sources and the fertilization technologies advances [21, 22].

Humic and fulvic acids present in the fertilizers stimulate the plants roots growth and development with 20% as compared to the untreated plants roots. They bind to the clay molecules and form stable organic-clay complexes which retain a higher water quantity and have a soil pH buffering role too [23-25].

The organic matter embedded in soil by application of fertilizers with humic substances also ensures the energetic substratum of soil micro flora activity and

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represents an important storage of chelate like compounds which have a high capability to bind different metallic ions (B, Cu, Ca, Fe, Mg, Mo, Zn) and to form organic metallic complexes with important role in building soil properties and in plant nutrition.

Experimental part

Material and methods

The humic and fulvic acids properties depend on sources and extraction methods and their behavior depends on these properties [26, 27]. Most of the extraction methods use aqueous sodium/potassium/ammonium hydroxide and sodium pyrophosphate as extracting solutions, but other chelating agents and organic solvents [28, 29].

Two NPK type liquid fertilizers with humic substances were experimentally obtained, both in laboratory stage and production pilot in order to carry out efficiency and effectiveness agrochemical tests [30, 31]. The humic substances were extracted from coal mass, lignite in potassium hydroxide alkaline solution and separated as potassium humate.

The humic substances extraction and separation processes and the fertilizers manufacturing technology took into account the humic and fulvic acids physical and chemical properties in alkaline, respectively acid, reaction mediums as well as their stability in the NPK type matrix [32-41].

The humic substances were physically and chemically characterized, by TA – thermal analysis and FTIR – Fourier Transform Infrared Spectroscopy. The equipment used were Diamond thermal weighing scale, Differential/ Thermogravimetric Analyzer from PerkinElmer Instruments, PerkinElmer SPECTRUM 100 FTIR spectrometer, and BRUKERVERTEX 70 [22,42].

The thermal analysis was carried out in heating linear dynamic conditions in the 20-1,000°C range, in a 150 mL/ min air flow, with 10 K/min heating rate, in aluminum crucibles, using á-alumina as reference and TG - thermal gravimetric, DTG - thermal gravimetric curve derivative, DTA - thermal derivative analysis, and DSC-scan calorimetric analysis curves registration.

FTIR analysis was carried out in the 4,000-600 cm^{-1} wavelengths range, with 10 scans for each spectrum acquisition, with a 4 cm^{-1} resolution and background correction for the CO_2/H_2O molecules. Spectra assessment was done with the Spectrum Search Plus specialized soft which assigned to the analyzed components the significance of aromatic compounds, alkylenes type non-saturated compounds, carboxylic and hydroxyl groups, which present infra-red absorption maximum peaks in the 1,640-1,585 cm^{-1}, 975-875 cm^{-1}, and 750-630 cm^{-1} wavelengths ranges.

The humic acids samples thermal analysis was carried out in aluminum crucibles, heated in air flux with a 10 K/ min rate, from room temperature (approximately 20°C) to 1,000°C, in order to intercept all the thermal effects of the samples that contain mostly organic matter and also inorganic matter. An aluminum crucible was used as control in which a small (equivalent) a-alumina quantity was placed. The thermal analyses curves of the humic substances samples (humic acids) are presented in figures 5-7. In each Figure the TG – thermal gravimetric analysis, DTG -thermal gravimetric curve derivative, DTA – thermal derivative analysis, and DSC – scan calorimetric analysis curves are drawn. The thermal analytical curves for the experimental samples were processed with the Pyris specialized program to assess the energetic processes developed in the 20-1,000°C temperature range.

The agrochemical experimentations took place in the INCDPAPM-ICPA Bucharest greenhouse. They were placed in Mitscherlich type vegetation pots in which 20 kg soil were introduced. The soil material that was used proceeds from the Comana area, Giurgiu County, and has the following physical and chemical properties: total nitrogen (Nt) - 0.16%, mobile phosphorus (P_{AL}) -110 mg/kg, mobile potassium (K_{AL}) - 315 mg/kg, organic carbon ($C_{organic}$) - 1.84%, humus – 3.18%; mobile microelements (extracted in ammonium acetate and EDTA solution at *p*H = 7): zinc (Zn) - 10 mg/kg soil, copper (Cu) - 1.7 mg/kg, iron (Fe) -40 mg/kg, manganese (Mn)- 6.6 mg/kg; total forms of microelements: zinc (Zn) – 105 mg/kg, copper (Cu) - 111 mg/kg, iron (Fe) - 2.5%, manganese (Mn) - 972 mg/kg, nickel (Ni) - 28.4 mg/kg, chromium (Cr) -21.6 mg/kg, cobalt (Co) - 10.6 mg/kg, lead (Pb) - 23 mg/kg, and cadmium (Cd) -0.6 mg/kg.

Soil humidity in the vegetation pots was ensured at a permanent 70% level of the field capacity. The tested experimental fertilizers were applied in 200, 300, and respectively 400 L/ha together with irrigation water. Half the dose was applied upon crop sowing and the difference in two stages during vegetation (at 20 respectively 35 days from emergence). According to the testing methodology a number of three replicates, three plants per pot each, was ensured for each experimental factors combination.

NK NEOMA Cruiser cross-breed (a semi-early cross-breed, recommended density 50,000-55,000 germinating grains/ha, medium height, grain type - Clearfield, high yield, good bearing for falling and breaking, high yield potential even in stress conditions, bearing for drought, good bearing for the main diseases: Sclerotinia, Phomopsis, Phoma) was sown for the sunflower agrochemical tests.

Table 1

No.	Experimental variant	Applied dose (kg/ha, respectively l/ha**)	Applied active substance (kg a.s. /ha*)
1	Unfertilized control	-	0
2	15.15.15 Control	120*	54
3	15.15.15 Control	180*	81
4	FERT	200**	54.4
5	FERT	300**	81.6
6	FERT	400**	108.8
7	FERT PLUS	200**	61.7
8	FERT PLUS	300**	92.5
9	FERT PLUS	400**	123.4

Note: * - kg applied fertilizer/ha; ** - liters applied fertilizers/ha.

Three controls were also sown: an unfertilized basic control and two controls to which 15.15.15 NPK type complex fertilizer was applied in 120 and respectively 180 kg/ha physical fertilizer doses (table 1). The agronomical testing design was aqs follows.

Results and discussions

Humic substances extraction and humic acids separation in order to characterize them was done using lignite from the Rovinari lignite excavation as coal mass with the characteristics: 60.4% organic matter, 24.9% humic substances, 34.4% ash, 20.7% SiO_2, and a 101.7 me/100 g coal cationic exchange capacity.

Humic acids extraction from the coal mass was done with a KOH alkaline solution with 1.0% K_2O concentration at 65-75°C temperature, under stirring for 6 h.

The thermogram of a humic acids sample is presented in figures 1a, 1b, and 2 (mass losses and thermal effects and their corresponding FTIR spectra).

In the first stage of the decomposition process (fig. 1), the TG curve area up to 163°C, samples drying phase is registered with a 45.63% mass loss. The humic substances samples drying action is accompanied by a thermo-negative process with a 666.5 J/g thermal effect.

In the 163-345.84°C interval the mass loss is 8.57%, and in the 345.8-630°C one - 35.13%. The oxidative degradation of the organic matter remained after essential substances elimination begins at 350°C and continues up to approximately 650°C. This is a complex stage, strongly thermopositive, in which two processes are identified. The transformation enthalpy is -5410.3 j/g, the generated heat maximum flux is 58.3 mW at 433.4°C. The small carbon quantities remained after the organic matter oxidative degradation (2-3%) is lost between 630 and 800°C. The sample remnant mass was 9.91%.

The FTIR spectra (fig. 2) presented the following characteristic band : the 3212 cm^{-1} band which can be assigned to the hydroxyl group belonging to the carboxylate, phenol, or alcohol group; the absorption band centered around the 1712/1738 cm^{-1} value belongs to the carboxyl group (a more intense band corresponds to a bigger number of carboxyl groups); the bands assigned to carboxylic acids, carboxylate ions, and carbonyl esters are between 1550 and 1790 cm^{-1}; the bands centered around the 1625-1615 cm^{-1} values can generally be assigned to the aromatic C-C bond or to the C-O bond characteristic for amide; the bands around the 1200 cm^{-1} value can be assigned to the C-O stretching of phenolic OH and/or aryl methyl ethers or to the combination of C-O stretching and O-H deformation. The stretching/deformation bands in the 1295-1130 cm^{-1} area correspond to the carboxyl group (COOH). The absorption band centered at la ~1033 cm^{-1-} corresponds to the -C-O stretching bond characteristic to poly-saccharides and aromatic esters.

SEM images were obtained with a HITACHI S2600N with an EDAX probe. SEM images (fig. 3) are very suggestive of the structure of humic substances.

The humic substances extracted from the coal mass (humic and fulvic acids salts) were used to obtain two NPK type experimental fertilizers with meso- and micro elements. The physical and chemical characteristics of

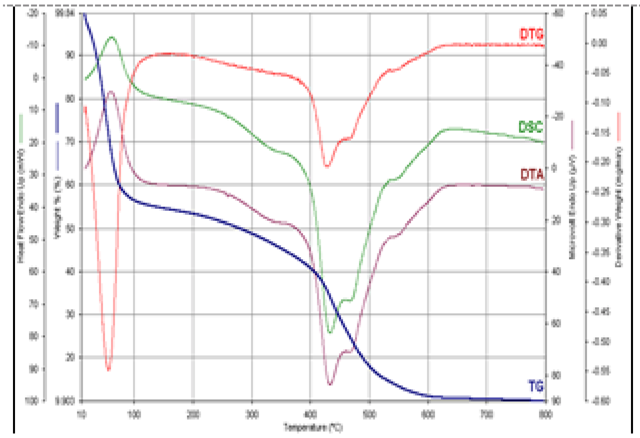

Fig. 1a. The thermogram of humic acids sample extracted from lignite.

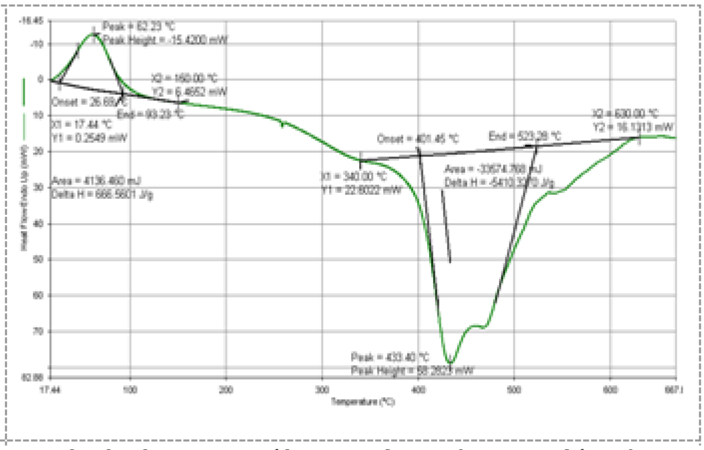

Fig. 1b. The thermogram of humic acids sample extracted from lignite, thermal effects

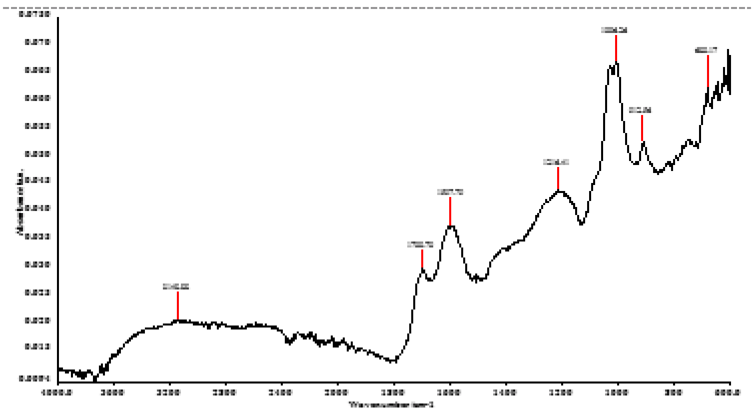

Fig. 2. FTIR spectrum registered for humic acids samples extracted from lignite.

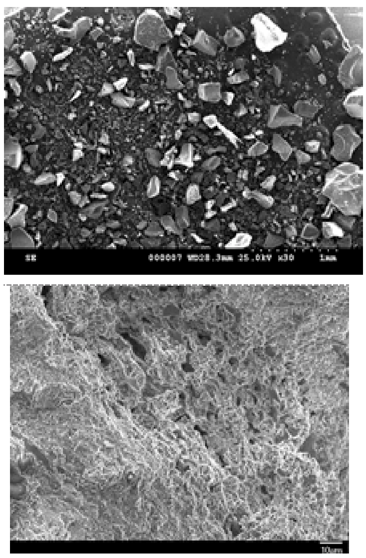

Fig. 3. SEM images obtained for the humic acids extracted from the coal mass

No.	Physical and chemical characteristics	M.U.	Experimental fertilizer	
			FERT	FERT PLUS
1	Nitrogen, N total	g/dm^3	154.1	172.4
2	Phosphorus, P_2O_5	g/dm^3	32.6	35.2
3	Potassium, K_2O	g/dm^3	37.5	41.1
4	Iron, Fe	g/dm^3	0.39	0.44
5	Copper, Cu	g/dm^3	0.16	0.22
6	Zinc, Zn	g/dm^3	0.11	0.21
7	Magnesium, Mg	g/dm^3	0.29	0.31
8	Manganese, Mn	g/dm^3	0.21	0.21
9	Boron, B	g/dm^3	0.31	0.32
10	Sulphur, SO_3	g/dm^3	18.6	25.6
11	Organic substances, out of which:	g/dm^3	27.6	32.4
	- humic compounds	g/dm^3	8.8	13.6
12	pH	pH units	6.58	6.72
13	Density, g/cm^3	g/cm^3	1.18	1.19

Table 2
PHYSICAL AND CHEMICAL CHARACTERISTICS OF THE EXPERIMENTALLY OBTAINED FERTILIZERS SAMPLES

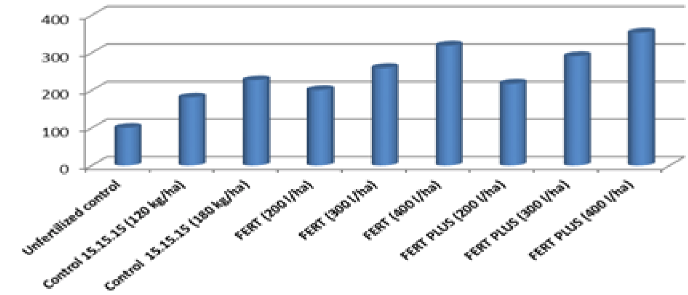

Fig. 4. The evolution of yield increases (%) as compared to the unfertilized control depending on the applied fertilization

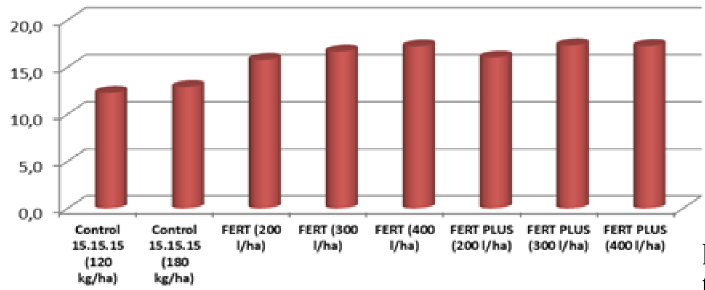

Fig. 5. The evolution of yield increases (kg/kg a.s.) depending on the applied fertilization.

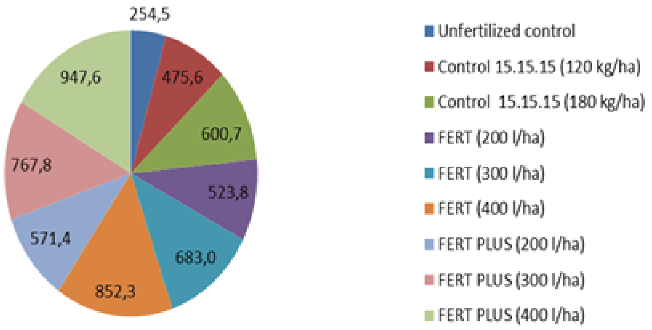

Fig. 6. The oil export (kg/ha) with the sunflower seeds yield.

the experimental fertilizers with humic substances used in the agrochemical tests are presented in table 2.

The results obtained in the agrochemical tests for the NK NEOMA Cruiser sunflower breed, respectively yield increases/kg applied active substance and the oil export are presented in figures 4-6.

The obtained yields were 1.8 and 2.8 times higher than the unfertilized control following basic fertilization with classic 15.15.15 NPK type fertilizers in 120 and 180 kg/ha doses. In the case of liquid fertilizers the obtained yields per hectare were 2 times higher as compared to the unfertilized control at the 200 L/ha dose and 3.2 times higher at the 400 L/ha dose.

The yields obtained when the FERT 200 L/ha dose was applied were comparable to those obtained with the 120 kg 15.15.15 NPK fertilizer/ha. At FERT 300 liters/ha dose the yields were with 14% higher than those obtained in the case of the 180 kg 15.15.15 NPK fertilizer/ha.

When the FERT 400 liters/ha dose was applied the yield was with 40% higher and for FERT PLUS – with 55% higher as compared to the application of 15.15.15 NPK in 180 kg/ha dose.

The yield increases obtained by application of one kg active substance/ha were 12-13 kg seeds/kg active substance for the classic 15.15.15 NPK type fertilizer. In the case of liquid fertilizers the yield increase was 15-16 kg seeds/kg active substance for the 200 liters/ha dose and 17 kg seeds/kg active substance for the 400 liters/ha dose, with better results for the FERT PLUS fertilizer.

The evolution of yield increases shows that there are no significant differences for the variants fertilized with 15.15.15 (180 kg/ha), FERT (200 l/ha) and FERT PLUS (200 l/ha), although the FERT Plus product yielded the most.

The oil export with the yield was 1.8-2.4 times higher in the case of 15.15.15 NPK fertilizer and 2-3.7 times higher wen liquid fertilizers were applied.

The liquid fertilizers performance as compared to the solid ones applied in 50-60 kg a.s./ha doses is with 15-20% higher, and in the case of 80-90 kg a.s./ha doses - with 20-28%.

The statistical analysis of the obtained data regarding the yield increase obtained by applying one kg active substance (figs. 7 and 8) showed that the applied liquid fertilizers presented distinctly significant and very significant differences as compared to the control fertilized

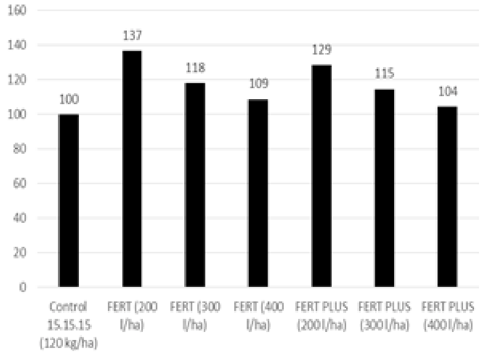

Fig. 7. The obtained yield increase (kg/kg s.a.) as compared to the control fertilized with 120 kg a.s./ha 15.15.15 fertilizer (DL 5% = 43 kg, DL 1% = 60 kg, and DL 0.1% = 85 kg).

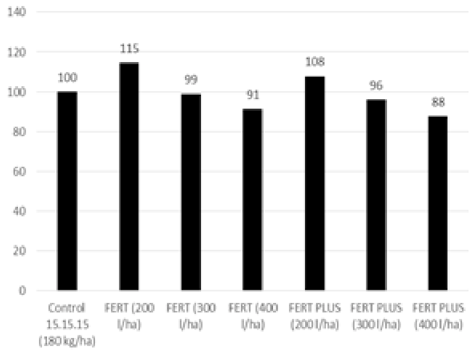

Fig 8. The obtained yield increase (kg/kg s.a.) as compared to the control fertilized with 180 kg a.s./ha 15.15.15 fertilizer (DL 5% = 2 kg, DL 1% = 2 kg and DL 0.1% = 3 kg).

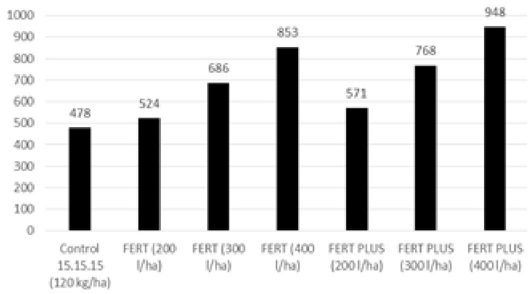

Fig. 9. The obtained oil export (kg/ha) with the yield as compared to the control fertilized with 120 kg a.s./ha 15.15.15 fertilizer (DL 5% = 43 kg, DL 1% = 60 kg and DL 0.1% = 85 kg).

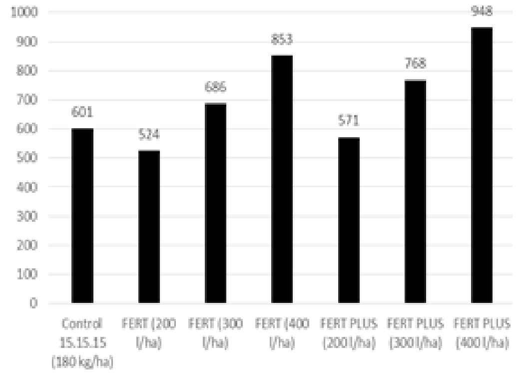

Fig. 10. The obtained oil export (kg/ha) with the yield as compared to the control fertilized with 180 kg a.s./ha 15.15.15 fertilizer (DL 5% = 44 kg, DL 1% = 62 kg and DL 0.1% = 88 kg).

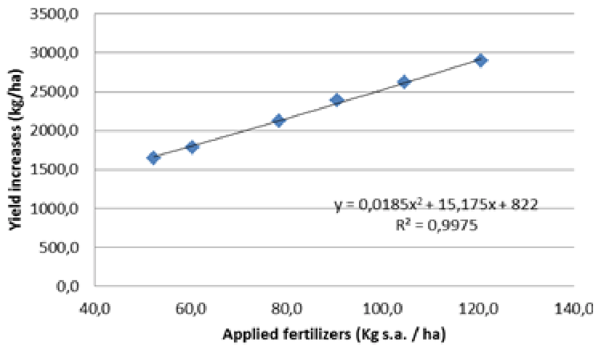

Fig. 11. The yield evolution (kg/ha) depending on the applied fertilization with liquid fertilizers (kg a.s./ha).

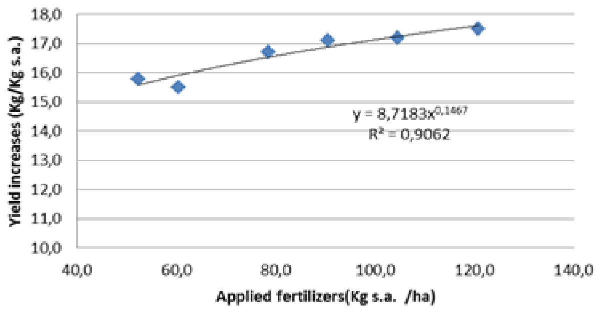

Fig. 12. The evolution of the yield increase (kg/ha/kg s.a.) depending on the applied fertilization with liquid fertilizers (kg s.a./ha).

with 120 kg a.s./ha for all the three applied doses. Very significant differences were only obtained for the application of the 200 L/ha doses of FERT and FERT PLUS fertilizers in the case of basic 180 kg a.s./ha fertilization.

The statistical analysis regarding the oil export with the yield (figs. 9 and 10) showed that the applied liquid fertilizers presented very significant differences for the 300 and 400 L/ha doses and significant ones for the 200 L/ha dose as compared to the control fertilized with 120 kg a.s./ha. Very significant differences were obtained for the application of 300 and 400 L/ha doses of FERT PLUS and 400 L/ha dose of FERT and a distinctly significant difference too for the latter's application in 300 L/ha dose in the case of basic fertilization with 180 kg a.s./ha.

An almost linear evolution of the sunflower seeds yield with the applied active substance as basic fertilization was ascertained in the given experimental conditions, respectively three stages fertilization with liquid fertilizers in 50-120 kg a.s./ha doses (fig. 11). The evolution of yield increases (kg seeds/ha/kg a.s.) depending on the applied active substance is presented in figure 12.

The sunflower plants respectively seeds chemical composition is presented in table 3 and 4 depending on the different applied fertilization variants.

The determinations were carried out in the Laboratory of physical and chemical analyses of the INCDPAPM – ICPA Bucharest.

No significant differences were ascertained as compared to the basic unfertilized control following sunflower plants chemical analysis both in the microelements (N, P, and K) and meso elements (Ca, Mg) cases.

The microelements contents of the analyzed plant samples didn't present significant differences between experimental variants depending on agrochemical background, liquid fertilizer, and the applied dose.

The macro elements nitrogen, phosphorus, potassium and the meso elements calcium and magnesium concentrations of the sunflower seeds laid within the normal values limits for the experiments carried out in vegetation pots. Significant differences were experimentally obtained as compared to the unfertilized

Table 3
CHEMICAL COMPOSITION OF THE SUNFLOWER PLANTS DEPENDING ON THE APPLIED FERTILIZATION VARIANT

Experimental Variant	Nitrogen	Phosphorus	Potassium	Cu	Zn	Fe	Mn	Mg	Ca
	%	%	%	ppm				%	
Unfertilized control	0.97	0.47	2.23	19.28	21.95	58.78	40.48	0.34	1.34
Control 15.15.15 (120 kg/ha)	1.03	0.56	2.48	19.55	21.48	63.60	40.05	0.32	1.33
Control 15.15.15 (180 kg/ha)	1.41	0.51	2.45	19.53	26.78	64.75	44.90	0.38	1.54
FERT (200 l/ha)	1.06	0.53	2.43	21.20	21.50	65.60	34.33	0.35	1.53
FERT (300 l/ha)	1.26	0.68	2.72	24.80	24.35	65.13	51.63	0.37	1.70
FERT (400 l/ha)	1.24	0.55	2.68	16.78	24.78	69.13	48.65	0.38	1.59
FERT PLUS (200 l/ha)	1.30	0.51	2.55	19.15	23.78	68.08	41.34	0.35	1.57
FERT PLUS (300 l/ha)	1.46	0.57	2.74	21.33	24.53	68.58	47.90	0.37	1.55
FERT PLUS (400 l/ha)	1.54	0.64	2.68	21.78	24.73	71.33	44.13	0.40	1.62

Table 4
THE CHEMICAL COMPOSITION OF THE SUNFLOWER SEEDS DEPENDING ON THE APPLIED FERTILIZATION VARIANT

Experimental Variant	Nitrogen	Phosphorus	Potassium	Cu	Zn	Fe	Mn	Ca	Mg
	%	%	%	ppm				ppm	%
Unfertilized control	1.61	1.20	0.78	18.31	37.79	69.33	5.90	147.50	0.13
Control 15.15.15 (120 kg/ha)	1.96	1.86	0.80	18.44	46.82	52.67	4.35	108.55	0.17
Control 15.15.15 (180 kg/ha)	1.98	1.93	0.83	21.49	50.11	41.96	4.37	109.17	0.17
FERT (200 l/ha)	1.95	1.93	0.80	22.59	49.40	38.57	4.68	117.08	0.17
FERT (300 l/ha)	2.21	1.90	0.75	21.84	50.73	90.18	5.07	126.67	0.17
FERT (400 l/ha)	2.08	1.99	0.82	20.18	48.14	46.31	4.86	121.46	0.18
FERT PLUS (200 l/ha)	1.98	1.96	0.85	19.37	52.25	48.13	4.69	117.09	0.17
FERT PLUS (300 l/ha)	1.91	1.93	0.78	18.31	37.79	69.33	5.90	147.50	0.13
FERT PLUS (400 l/ha)	1.84	1.85	0.76	20.50	39.92	80.81	6.12	152.92	0.13

control in the case of macro nutrients nitrogen and phosphorus. No significant differences of the potassium macro element and of the meso and micro elements concentrations were obtained as compared to the unfertilized control.

Conclusions

The fact results from the experimental data that applying liquid fertilizers with humic substances in several phases during plants vegetation is a viable solution for obtaining assured yield increases.

The FERT liquid fertilizer guaranteed statistically ensured very significant and significant yield increases at the 200 liters/ha dose as compared to the fertilized control with a 120 kg a.s./ha dose of 15.15.15 complex fertilizer while the FERT PLUS product yielded very significant increases for all the applied doses.

Very significant yield increases were only obtained in the case of liquid fertilizers application in 300 and 400 liters/ha doses as compared to the control fertilized with 180 kg a.s./ha.

The liquid fertilizers with humic substances applied in active substance doses equivalent to those of the solid fertilizers yielded efficiency with 15-28% higher in the given experimental conditions.

Using liquid fertilizers ensures a more efficient nutrients intake by plants, at the same time with the decrease of the classical fertilizers application.

The pollution risks due to soil leaching processes that occur in the case of solid fertilizers application are diminished by using liquid fertilizers.

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