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Examining the Influence of Sludge from Municipal Wastewater Treatment Plants Processed by Euphore Installations on the Quantity and Quality of Rapeseed and Soybean Production

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Abstract: Sludge management is a complex issue due to the environmental standards. It is required that the wastewater treatment activity be in close connection with the controlled recovery and storage of sludge. Thus, by using sludge in agriculture, nutrients essential for plant development can be recycled and some soil properties can be improved. The purpose of this paper was to present some results on the influence of municipal sludge treated and processed in a Euphore plant on the quantity and quality of rapeseed and soybean production. This technology allows for the recovery of the constituents of phosphorus, nitrogen, potassium, sulfur, magnesium, calcium, manganese, zinc, and copper. Our experimental data revealed that the obtained yield of Pioneer PT225 rapeseed hybrid was 5200 kg/ha in the variant treated with the Euphore process compared to that of the control variant at only 2356 kg/ha. For the Condor variety soybean crop, the highest average number of pods obtained per plant was 195.3 compared 88 pods per plant in the control variant. Thus, the sludge obtained from urban wastewater treatment plants processed using the Euphore method is a good source of macro and micronutrients in agriculture, without having a negative impact on the environment.

Keywords: sewage sludge; Euphore technology; rapeseed; soybean

1. Introduction

An important challenge in wastewater management is the use of sewage sludge, which can be an important source of nutrients for agriculture, being rich in N, P, K, organic matter, and other elements that can stimulate plant development [1–3].

Thus, the use of sludge in agriculture has become an alternative for the use of waste for economic and practical reasons [4–6].

In the European Union, the ecological capitalization of sewage sludge has been at the center of attention of producers with the implementation of EEC (European Economic Community)-(Directive 91/271, on urban wastewater treatment [7,8]. Thus, at the level of European states, the amount of sludge used in agriculture has increased in the last 15 years from 3,000,000 tonnes dry substance/year to 6,100,000 tonnes dry substance/year in 2020 [9–11].

In Romania, the amount of sewage sludge has increased in the last eight years from about 80,000 tonnes dry substance/year to about 416,000 tonnes dry substance/year in 2020 [12].

Two areas of major importance are the method for treating the sludge in such a way as to comply with the European Union Directives and how to apply it as a fertilizer in order to obtain healthy crops, preserve the fertility of the soil, and ensure environmental protection [13,14].

The progressive implementation of the Urban Wastewater Treatment Directive 91/271/EEC in all member states is increasing the quantities of sewage sludge requiring disposal. Sludge can

be concentrated in heavy metals [15–21], poorly biodegradable trace organic compounds, and potentially pathogenic organisms (viruses, bacteria, etc.) that are present in wastewater [22–25], therefore, the capitalization of sludge must be in accordance with the Sewage Sludge Directive 86/278/EEC [26] that seeks to encourage the use of sewage sludge in agriculture and to regulate its use in such a way as to prevent harmful effects on soil, vegetation, animals, and man.

When applying the sludge, the climatic and soil conditions in the areas near their processing stations must also be taken into account [26–30].

Through research-development activity and the implementation of top technology regarding the renewable energy resources, in Germany, the capitalization of the sewage sludge experienced a considerable increase from 9% to 53.2% (an increase of 491%), from the total sludge produced, with a humidity of 60% [31,32].

One of the most advanced German technologies for sludge treatment is the Euphore method, which aims in particular at reducing pollutants and recovering valuable components from sludge and reintroducing them into the economic cycle. It eliminates most of the technological disadvantages of the existing competing technologies, which are usually a combination of incineration and subsequent thermochemical treatment.

Due to the significant energy content of sludge, along with that of phosphorus in particular, thermo-chemical recovery processes now have much more efficient results than purely thermal or chemical processes and allow for an almost complete recycling of nutrients [33].

The Euphore-type sewage sludge treatment plant (Figure 1) together with its reactor (Figure 2) offers the possibility to use both natural gas and cogeneration or biogas waste gas.
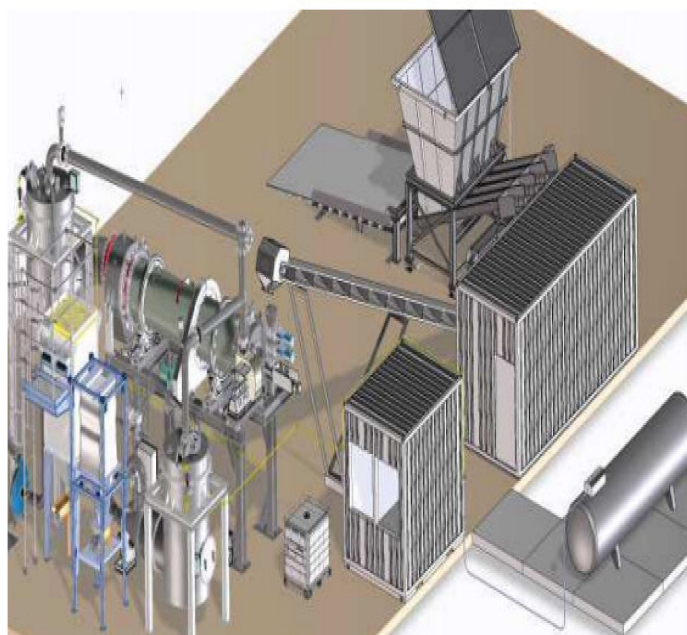
Figure 1. Euphore-type thermochemical treatment plant.

Drying uses the pure waste gas stream of a cogeneration plant and is therefore an energy source that would otherwise be lost to the atmosphere. A pure waste gas stream contains 50% of the thermal energy of a cogeneration plant. With the help of hot waste gases of 550–600 °C, drying is achieved at an evaporation capacity of 600 W per liter of water, thus achieving an unprecedented efficiency. The sewage sludge is transported through a controlled and fully automated process through the drying chambers. Depending on the user, the degree of drying can be set and can vary between 80 and 95% dry substance. The entire exhaust air passes through an integrated fine filtration system, which almost completely retains dust, ash, and other solid components. To remove olfactory pollution (odors), the air is treated in a biofilter. The fine dust resulting from the filtration chamber

falls into a screw conveyor and is transported to the discharge chamber, where it is mixed with the dried sludge and then hermetically transported in an intermediate container. By applying the hot gas, a complete sanitization of the sludge is carried out, destroying pathogens such as viruses, bacteria, endotoxins, fungi, protozoa, and worms, in addition to evaporating the water. By using waste gas, the sewage sludge can be treated and dried without emissions. The waste gas drying system transforms a tonne of wastewater full of noxious substances into 250 kg of sanitized biomass, from which nutrients can be recovered. The installation can also be provided with a pelletizer, specially designed so as not to emit dust and other emissions, which produces a dry and pelletized sludge, ideal for further recovery both as agricultural fertilizer and for gasification or combustion.

All processes are easy to view and monitor using Wireless ARC (Active Radio Control) technology.

Figure 2. Reactor for Euphore-type treatment.

2. Materials and Methods

The main purpose of this paper was to present the influence of sludge from municipal treatment plants processed by Euphore-type installations on rapeseed and soybean crops, whilst respecting protection rules imposed by the EU and encouraging farmers to use products resulting from innovative sludge treatment techniques. Representative soil profiles were developed at the studied location.

The experimental field was located in Fălticeni on a Luvic stagnic Phaeozems or Faeoziom clinogleic soil type, as defined in the Romanian Soil Taxonomy System [34]. In the field, we collected soil samples to conduct laboratory analyses [35]. Where the samples were collected, images related to the aspect of the soil profile were taken with a digital camera.

Luvic stagnic Phaeozems (Figure 3) has a loamy-clay texture and medium-to-good fertility with a moderate humus content (3.1%) and relatively high total nitrogen, and medium levels of mobile phosphorus and potassium. The soil is slightly acidic (pH = 6.3).

Chemical and mineralogical characterizations of the sludge were performed in a laboratory based on SEM/EDX analysis. The chemical analysis of the sludge was based on the following methods: determination of the pH by the method SR EN 12176/2000, humidity U (%)—SR EN 12880, total organic carbon—SR EN 12880, nitrogen—STAS 12200/85, phosphorus—

STAS 12205/84, potassium—STAS 12678/88, cadmium STAS—128 76/90, chromium—STAS 13117/92, copper—SR 13179/93, Ni—STAS 13094/92, Pb—SR 13225/94, and Zinc—SR 13181/93.
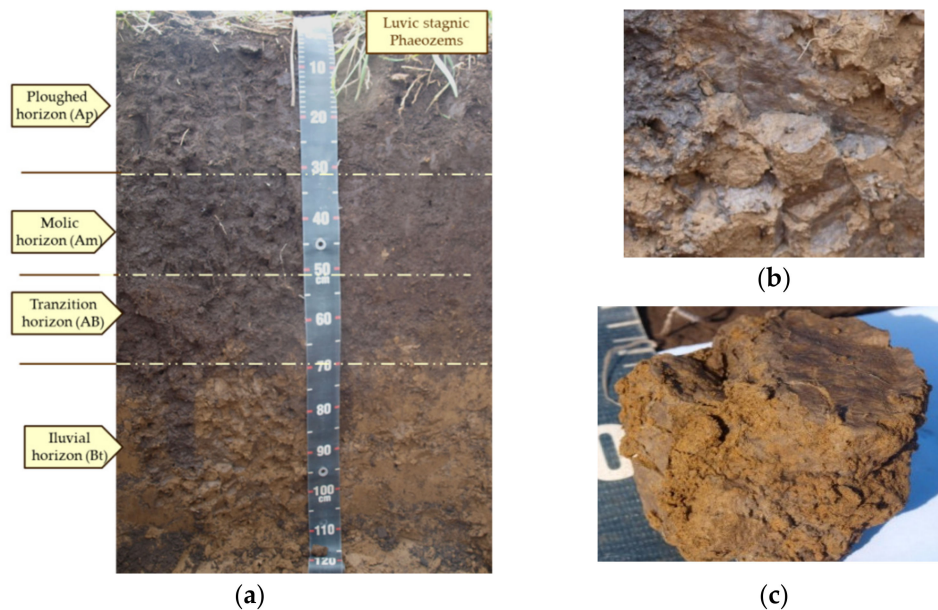

Figure 3. Profile of stagnic Phaeozems (**a**), complex clay-humic cutans on the faces of the structural aggregates (**b**), and fragment of prismatic aggregate with rediximorphic colors (**c**).

The types of sludge that were studied had the following characteristics: specific density, r_s = 1.65–1.85 g/cm^3; density, r = 1.05–1.12 g/cm^3; upper limit of plasticity, w_L = 100–333%; lower limit of plasticity, w_P = 42–218%; linear contraction, 11%, free swelling, 1.21–1.285%; pore index, e = 1.25–5.15; compression index, C_c = 0.38–1.68; secondary consolidation coefficient, C_s = 0.04–0.25; permeability coefficient, k = 10^{-7}–10^{-11} m/s; volume compressibility coefficient, m_n = 2 m^2/MN; consolidation coefficient, c_n = 0.039–1.1 m^2/year; optimal Proctor compaction humidity, w_{oc} = 39–53%; maximum dry weight, gd_{max} = 8.2 kN/m^3; internal friction angle, f = 37–45.5°; cohesion, c = 14.25–46.35 kPa; and undrained shear strength, s_u (Vane test) = 138–155 kPa. All these characteristics contribute to the soil structure.

The treatment of soil samples that were collected for the tests was in accordance with the standard SR ISO 11464/1998: soil quality, samples pre-treatment for physical-chemical tests. Therefore, samples were dried in the stove and were hashed with an electric soil mill. The heavy metals used were Cd, Cu, Zn, and Pb. Heavy metals determination was made in accordance with the standard SR ISO11047/1999S: soil quality, through atomic absorption spectrometry.

Metals extraction was completed with concentrated sulphuric acid and oxygenate water 50%, with a mineralisator type Digestal HACH (Standard SR ISO 11047/1999: Soil quality).

Table 1 shows the compositions of the main elements for naturally dried sludge compared to those of Euphore sludge. It can be seen that Euphore-type sludge, through its specific phosphorus recovery technology, contains about 2.55 times more phosphate, with 1.1% more N, and 2.5% more K compared to that of naturally dried sludge. Phosphates are readily available to plants and can be combined with other fertilizing ingredients.

The experiments performed were multifactorial of the A × B × C type. The placement of the experiments was done according to the "subdivided plots method" in three repetitions. Experimental factors took into account soil fertilization with various application doses (between 5–35 t/ha): 1—unfertilized soil, i.e., control sample soil (V1); 2—organic fertilization with urban sludge treated by innovative Euphore-type installations (V2); and 3—organic fertilization with dry urban sludge from the Fălticeni treatment

plant (V3).The crops studied were autumn rapeseed and soybeans. The biological material consisted of plant samples (parts, organs, products) from these crops during their vegetation period.

Table 1. Sludge composition.

Chemical Indicators	Sludge Used in Agriculture CMA, D. 86/278/EEC, mg/kg Dry Substance (CMA = Maximum Allowable Concentration)	Naturally Dried Sludge/ Value kg Dry Substance	Dried Sludge Euphore Installation/Value kg Dry Substance
Humidity	-	38%	6%
pH	-	6.92	7.93
Nitrogen	-	2.4%	3.5%
Phosphate	-	9.4%	24%
Potassium	-	2.5%	5.2%
Cadmium	20–40 mg	3.8 ppm	3.6 ppm
Copper	1000–1750 mg	166.35 ppm	165.57 ppm
Nickel	300–400 mg	5.6 ppm	5.2 ppm
Lead	750–1200 mg	20.15 ppm	19.58 ppm
Zinc	2500–4000 mg	1362 ppm	1355 ppm
Chromium	500 mg	92.65 ppm	91.75 ppm

The experimental area was divided into rectangular plots with areas of 10 square meters. In the research performed, soybean/rapeseed were selected for each variant, $N_p = 28$ plots were allocated, and for the average crop productions and rapeseed oil content $N_{obs} = 1$ observations were made. The means of the differences between the analyzed and control variants (mean of experience) were determined and interpreted using the Duncan's new multiple range test (MRT) and the limit difference test (DL) [36].

ISO 659:2009 specifies a reference method for the determination of the hexane extract (or light petroleum extract), called the "oil content", of oilseeds used as industrial raw materials [37].The oil content of rapeseed, according to ISO 659:2009, was measured directly by grinding the seed and extracting the oil using a 2055 Soxtec Manual Extraction Unit (Soxtec Avanti, Foss).This method is the reference method for oil content and is recommended by the Federation of Oils, Seeds and Fats Associations Ltd. (FOSFA) International in its list of official methods of analysis [38].

3. Results and Discussion

For the soybean crops, the Condor variety was chosen. Soybeans were sown with about 50–55 seeds per square meter on 1 April 2020, at a depth of about 3 cm. The sowing was done in strips of three rows with a distance of 45 cm between them. The distance between the strips was 60 cm. Irrigation was completed by sprinkling, with a watering rate of about 750 m^3/ha.

In Table 2 we can observe the soybean crop production in the nine experimental variants. On average, production obtained for the soil treated with Euphore-type sludge was about 30.6% higher than that of the control soil and about 12% compared to that of the soil treated with dry raw sludge.

To determine which of the nine variants, T1, T2, . . . , T9, were significant and which were insignificant, the algorithm related to Duncan's new multiple range test (MRT) was applied. Then, applying the test based on the limit difference, DL, a classification of the variants was made from the point of view of their representativeness. The Table 3 shows the values for the average soybean crop production, in descending order.

Table 2. Soybean average crop production in the nine experimental variants.

Dosage of Applied Sludge (t/ha)	Control Soil Untreated with Sludge Production kg/ha	Soil Treated with Euphore Type Sludge Production kg/ha	Soil Treated with Dry Raw Sludge on Treatment Plant Platform Production kg/ha
15		T2 = 3265	T6 = 2994
25		T3 = 3443	T7 = 3072
30	T1 = 2880	T4 = 3555	T8 = 3146
35		T5 = 3761	T9 = 3226

Table 3. Values for the average soybean crop production, in descending order.

Rank, r	1	2	3	4	5	6	7	8	9	Mean
Variant	T5	T4	T3	T2	T9	T8	T7	T6	T1	-
Average soybean production, S_r,(kg/ha)	3761	3555	3443	3265	3226	3146	3072	2994	2880	$\overline{S} = 3260$
Standard error, σ_r, (cm)	23.84	27.03	28.51	29.43	31.14	24.79	25.44	26.05	26.71	$\overline{\sigma} = 26.9946$

On the last line of Table 3, the values for standard error, σ_r, related to the determination of the values for average soybean crop production, were also centralized. In the following, the multiple range test (MRT) uses only the average value $\overline{\sigma} = 0.464$. In the statistical analysis related to the MRT, the following quantities are used as basic data:

- probability of transgression, α;
- degrees of freedom for the observations, p;
- degrees of freedom, γ for estimating the standard error.

At the same time the MRT also uses the following statistical functions:

- $\gamma\,(p, v, \alpha)$ = the quantile of the studentized range distribution;
- $R\,(p, v, \alpha)$ = the shortest significant range (the actual critical value of the test).

For the probability of transgression, $\alpha = 5\% = 0.05$ was considered.

The degrees of freedom, p, takes all the values from the set $\{2, 3, \ldots, NV\}$, where NV represents the number of variants; in the present paper NV = 9.

The degrees of freedom, v were determined with the following equation:

$$v = N_p \cdot N_{obs} - 1 \tag{1}$$

where: N_p is the number of plots assigned to a variant, and N_{obs} is the number of observations made on each plot.

In the research performed, for each variant, N_p = 28 plots were allocated (with an area of 10 m^2) and N_{obs} = 1 observations were made; thus, for each variant, the degrees of freedom presents the value:

$$v = 28 \cdot 1 - 1 = 27$$

The standardized critical values for $\gamma\,(p, v, \alpha)$ were obtain from the table corresponding to the value, $\alpha = 0.05$ [39].

The values thus determined are summarized in Table 4, second row, where, because $v = 27 = $ const. and $\alpha = 0.05 = $ const., the notation was used: $\gamma_p = \gamma(p)$.

Table 4. Standardized critical values for functions $\gamma_p = \gamma(p)$ and $R_p = R_{(p)}$.

Degrees of Freedom for Observations, p	2	3	4	5	6	7	8	9
Standardized critical value, γ_p	2.9	3.05	3.15	3.21	3.26	3.3	3.33	3.36
Shortest critical range, R_p	63.18	66.38	68.45	69.91	71.01	71.87	72.54	73.1

The shortest critical range is computed as:

$$R(p, v, \alpha) = \overline{\sigma} \cdot \gamma(p, v, \alpha) \tag{2}$$

The values for the shortest critical range are summarized in Table 4, third row, where the notation $R_p = R(p)$ was used.

An algorithm for performing the MRT test is as follows:

1. For each m_i sample mean (H_i), from largest to smallest, the differences are calculated:

$$\left(\Delta_{i,j}\right)_k = \left(m_i - m_j\right)_k = \left(S_i - S_j\right)_k \tag{3}$$

with:

$$k = 1, 2, \ldots N_\Delta$$

where:

i, ($i = 1, 2, \ldots, N_V$) is designated as the *Superior Rank of variants*, and
j, ($j = N_V, N_{V\text{-}1}, \ldots, 2$) is designated as the *Inferior Rank of variants*.

2. The values for shortest significant range, $\left(R_p\right)_k$ were taken from Table 4, where $p = j - \mu$, with $\mu = 0, 1, \ldots\ldots, N_v - 2$, $p \geq 2$.

3. The values for the Ranks of variants, i and j, as well as for the difference $\left(\Delta_{i,j}\right)_k$ with the values $\left(R_p\right)_k$ are compared: $\left(\Delta_{i,j}\right)_k < \left(R_p\right)_k$ or $\left(\Delta_{i,j}\right)_k - \left(R_p\right)_k \leq 0$.

   - 3.1. If $\left(\Delta_{i,j}\right)_k > \left(R_p\right)_k$ or $\left(\Delta_{i,j}\right)_k - \left(R_p\right)_k > 0$ the variants used in the difference $\left(\Delta_{i,j}\right)_k$ are significant.
   - 3.2. If $\left(\Delta_{i,j}\right)_k < \left(R_p\right)_k$ or $\left(\Delta_{i,j}\right)_k - \left(R_p\right)_k \leq 0$ the variants used in the difference $\left(\Delta_{i,j}\right)_k$ are insignificant.

The values for the ranks of variants, i and j, as well as for the index p are shown in Table 5.

Table 5. The values for the ranks of variants, i and j, as well as for the index p.

Difference between Pairs of Variants, k	1	2	3	4	5	6	7	8	9
Superior Rank of variants, i	1	1	1	1	1	1	1	1	2
Inferior Rank of variants, j	9	8	7	6	5	4	3	2	9
Index p for shortest significant range, R_p	9	8	7	6	5	4	3	2	8
Difference between pairs of variants, k	10	11	12	13	14	15	16	17	18
Superior Rank of variants, i	2	2	2	2	2	2	3	3	3
Inferior Rank of variants, j	8	7	6	5	4	3	9	8	7
Index p for shortest significant range, R_p	7	6	5	4	3	2	7	6	5
Difference between pairs of variants, k	19	20	21	22	23	24	25	26	27
Superior Rank of variants, i	3	3	3	4	4	4	4	4	5
Inferior Rank of variants, j	6	5	4	9	8	7	6	5	9
Index p for shortest significant range, R_p	4	3	2	6	5	4	3	2	5
Difference between pairs of variants, k	28	29	30	31	32	33	34	35	36
Superior Rank of variants, i	5	5	5	6	6	6	7	7	8
Inferior Rank of variants, j	8	7	6	9	8	7	9	8	9
Index p for shortest significant range, R_p	4	3	2	4	3	2	3	2	2

In Table 6, because the observed differences $\left(\Delta_{i,j}\right)_k$ are equal or smaller than the corresponding shortest significant range $\left(R_p\right)_k$ or differences $\left(\Delta_{i,j}\right)_k - \left(R_p\right)_k$ are negative, then we conclude that the pair of means in question is insignificantly different.

Thus, the conclusions of the Duncan test are as follows:

- of the $p = 9$ treatment variants, 5 variants are insignificant, and 4 are significant
- insignificant treatment options are T2, T6, T7, T8, and T9
- significant treatment options are T1, T3, T4, and T5.

Table 6. Values for the sizes and $\left(\Delta_{i,j}\right)_{k'}$, $(R_p)_k$ and $\left(\Delta_{i,j}\right)_k - (R_p)_k$ corresponding to case 3.2.

Difference between Pairs of Variants, *k*	26	33	35
Values for difference between pairs of variants, $\left(\Delta_{i,j}\right)_k$	39.0	74.0	78.0
Values for shortest critical range, $(R_p)_k$	78.379	78.379	78.379
Value of the difference, $\left(\Delta_{i,j}\right)_k - (R_p)_k$	−39.379	−4.379	−0.379
Variant for superior rank	T2	T8	T7
Variant for inferior rank	T9	T7	T6

From Annex no.3 [40] for degrees of freedom $v = 27$ the normal deviations were obtained by linear interpolation, with the probabilities of transgression $P_\% \in \{5\%, 1\%, 0.1\%\}$, as $t_{5\%} = 2.05$, $t_{1\%} = 2.77$ and $t_{0.1\%} = 3.69$.

Then, we calculated, with the same probabilities $p\%$, the limit difference, DL, using the equation:

$$DL = t \cdot \sigma_d \tag{4}$$

where: $\sigma_d = 260.1$ is the standard deviation related to average crop production, S_r.

Thus, the following values for DL resulted: $D_{L5\%} = 533.20$, $DL_{1\%} = 720.47$, and $DL_{0.1\%} = 959.76$.

In Table 7, the differences between the crop productions corresponding to each variant (except for the control variant) and the production corresponding to the control variant (with the Rank r = N_v = 9) are summarized:

$$\Delta S_r = S_r - S_{Nv} \tag{5}$$

Table 7. Centralization of the data necessary for the classification of variants by the limit difference (DL) test.

Rank, *r*	1	2	3	4	5	6	7	8
Difference of production, $\Delta S_r = S_r - S_{Nv}$	881	675	563	385	346	266	192	114
$sign(\Delta S_r - DL5\%)$	+	+	+	-	-	-	-	-
$sign(\Delta S_r - DL1\%)$	+	-	-	-	-	-	-	-
$sign(\Delta S_r - DL0.1\%)$	-	-	-	-	-	-	-	-
Significance	T5:DS	T4: S	T3: S	T2:NS	T9:NS	T8:NS	T7:NS	T6:NS

For this purpose, the sign afferent to the respective differences was determined $sign(\Delta S_r - DL5\%)$, a sign that establishes the meaning assigned to each variant:

(NS—insignificant; S—significant; DS—distinctly significant; FS—very significant).

The results thus obtained with the DL limit difference test are compatible and complementary with those of the Duncan test, but it cannot take into account the T1 variant.

In Figure 4 we can observe in the nine experimental variants that the highest number of pods per plant is for those on the soil treated with the Euphore-type sludge, where we had an average number of 137 pods per plant, compared to that of the soil treated with dry raw sludge with approximately 120.5 pods per plant, and that of the control soil with only 95 pods per plant.

In Table 8, the centralization of the data necessary for the classification of variants by DL test for the average number of beans/plants is presented.
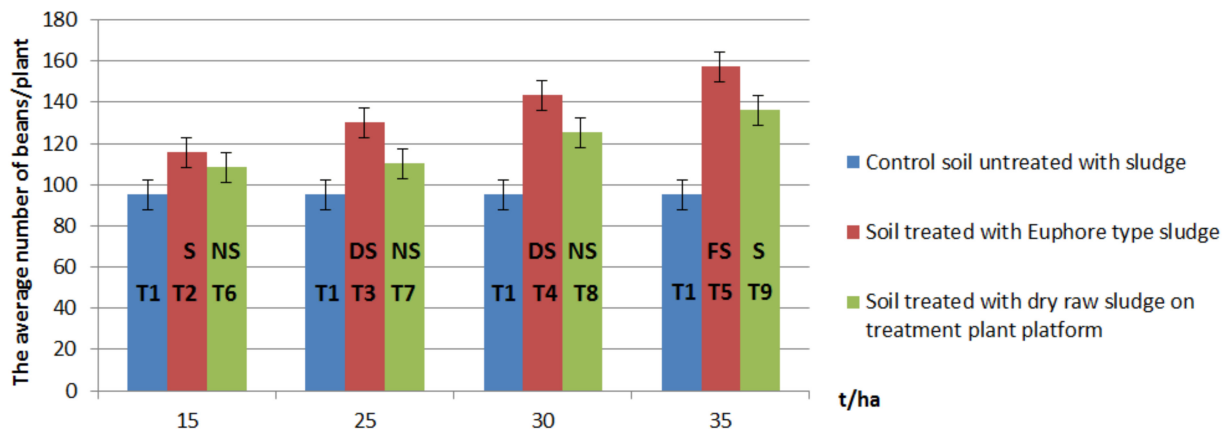
Figure 4. The average number of beans/plant for the soybean crops in the nine experimental variants. Error bar with standard error of deviation (%).

Table 8. Centralization of the data necessary for the classification of variants by the DL test for the average number of beans/plants.

Rank, r	1	2	3	4	5	6	7	8
Difference of number, $\Delta S_r = S_r - S_{Nv}$	28.8	20.6	16.7	16	13.2	12	10.6	8
$sign(\Delta S_r - DL5\%)$	+	+	+	+	+	-	-	-
$sign(\Delta S_r - DL1\%)$	+	+	+	-	-	-	-	-
$sign(\Delta S_r - DL0.1\%)$	+	-	-	-	-	-	-	-
Significance	T5: FS	T4:DS	T3:DS	T2: S	T9:S	T8:NS	T7:NS	T6:NS

Where: DL5% = 13.0862, DL1%= 17.3276, DL0.1%= 22.391, T1: Control variant.

Chemical analysis performed on the soybean plants (stems, roots) and grains highlighted the following aspects (Table 9):

- the roots of the soybean plant contained heavy metals below the maximum permissible values, except for Pb that exceeded the value by 0.45 mg/kg dry substance; the highest concentrations of Pb (15.45 mg/kg dry substance), Cd (0.19 mg/kg dry substance.), Ni (12.74 mg/kg dry substance.), Cu (8.8 mg/kg dry substance.), and Zn (29.4 mg/kg dry substance.) were obtained for the dose of 35 t/ha, for the variant of soil treated with dry raw sludge.

- the stems of the soybean plant contained heavy metals below the maximum allowable values; the highest concentrations of Pb (13.98 mg/kg dry substance), Cd (0.17 mg/kg dry substance.), Ni (8.15 mg/kg dry substance), Cu (7.64 mg/kg dry substance), and Zn (23.45 mg/kg dry substance) were obtained for the dose of 35 t/ha, for the variant of soil treated with dry raw sludge.

- soybeans had a heavy metal content below the maximum admissible values; the highest concentrations of Pb (11.34 mg/kg dry substance), Cd (0.17 mg/kg dry substance), Ni (6.71 mg/kg dry substance), Cu (8.08 mg/kg dry substance), and Zn (24.96 mg/kg dry substance) were obtained for the dose of 35 t/ha, for the variant of soil treated with dry raw sludge.

- the concentration of Ni, Cu, and Zn in stems, roots, and beans were well below the level of toxicity in all organs of the soybean plant regardless of the applied dose. Rapeseed crops consume a lot of phosphorus. That is why it is recommended to fertilize the soil before sowing and plowing. The Pioneer PT225 Rapeseed Hybrid was chosen because it is resistant and it has good production.

Table 9. The influence of different doses of sludge on the content of heavy metals in soybean stems, roots, and pods.

Dosage of Applied Sludge (t/ha)	Control Soil Untreated with Sludge		Soil Treated with Euphore-Type Sludge		Soil Treated with Dry Raw Sludge from Treatment Plant Platform	
	Metal	Quantity mg/kg Dry Substance	Metal	Quantity mg/kg Dry Substance	Metal	Quantity mg/kg Dry Substance
CMA Pb = 3–15 mg/kg dry substance, CMA Cd =1 mg/kg dry substance, CMA Ni = 30 mg/kg dry substance, CMA Cu = 15–20 mg/kg dry substance, CMA Zn = 150 mg/kg dry substance						
Soybean Root						
15 t/ha	Pb	11.89	Pb	12.3	Pb	12.8
	Cd	0.11	Cd	0.12	Cd	0.13
	Ni	8.5	Ni	9.2	Ni	9.6
	Cu	6.25	Cu	6.84	Cu	7.13
	Zn	22.3	Zn	22.75	Zn	23.6
25 t/ha	Pb	12.45	Pb	13.77	Pb	14. 02
	Cd	0.12	Cd	0.13	Cd	0.14
	Ni	9.7	Ni	10.4	Ni	10.78
	Cu	7.11	Cu	7.65	Cu	7.98
	Zn	23.15	Zn	25.75	Zn	26.06
30 t/ha	Pb	13.6	Pb	14.1	Pb	14.59
	Cd	0.16	Cd	0.17	Cd	0.21
	Ni	10.78	Ni	11.89	Ni	12.16
	Cu	7.86	Cu	8.27	Cu	8.98
	Zn	25.7	Zn	26.29	Zn	27.02
35 t/ha	Pb	14.4	Pb	14.7	Pb	15.45
	Cd	0.17	Cd	0.18	Cd	0.19
	Ni	12.4	Ni	12.66	Ni	12.74
	Cu	8.4	Cu	8.67	Cu	8.8
	Zn	26.8	Zn	28.7	Zn	29.4
Soybean Stem						
15 t/ha	Pb	10.65	Pb	10.87	Pb	11.23
	Cd	0.9	Cd	0.10	Cd	0.11
	Ni	4.3	Ni	4.76	Ni	5.12
	Cu	5.35	Cu	5.64	Cu	6.15
	Zn	20.1	Zn	20.64	Zn	21.2

Table 9. *Cont.*

Dosage of Applied Sludge (t/ha)	Control Soil Untreated with Sludge		Soil Treated with Euphore-Type Sludge		Soil Treated with Dry Raw Sludge from Treatment Plant Platform	
	Metal	Quantity mg/kg Dry Substance	Metal	Quantity mg/kg Dry Substance	Metal	Quantity mg/kg Dry Substance
25 t/ha	Pb	11.8	Pb	11.95	Pb	12.12
	Cd	0.10	Cd	0.11	Cd	0.12
	Ni	5.6	Ni	6.16	Ni	6.54
	Cu	5.85	Cu	6.41	Cu	6.85
	Zn	21.2	Zn	22.34	Zn	23.12
30 t/ha	Pb	12.9	Pb	13.26	Pb	13.68
	Cd	0.12	Cd	0.13	Cd	0.14
	Ni	6.73	Ni	7.25	Ni	7.56
	Cu	6.37	Cu	6.89	Cu	7.12
	Zn	21.85	Zn	22.58	Zn	22.97
35 t/ha	Pb	13.6	Pb	13.79	Pb	13.98
	Cd	0.15	Cd	0.16	Cd	0.17
	Ni	7.66	Ni	7.92	Ni	8.15
	Cu	6.75	Cu	7.32	Cu	7.64
	Zn	22.32	Zn	23.13	Zn	23.45
Soybean Beans						
15 t/ha	Pb	9.3	Pb	9.7	Pb	9.9
	Cd	0.09	Cd	0.10	Cd	0.11
	Ni	3.8	Ni	4.35	Ni	4.6
	Cu	5.6	Cu	6.5	Cu	6.73
	Zn	21.1	Zn	21.72	Zn	22.15
25 t/ha	Pb	9.7	Pb	10.11	Pb	10.42
	Cd	0.10	Cd	0.112	Cd	0.23
	Ni	4.68	Ni	5.16	Ni	5.46
	Cu	6.3	Cu	7.02	Cu	7.41
	Zn	22.15	Zn	22.9	Zn	23.11

Table 9. *Cont.*

Dosage of Applied Sludge (t/ha)	Control Soil Untreated with Sludge		Soil Treated with Euphore-Type Sludge		Soil Treated with Dry Raw Sludge from Treatment Plant Platform	
	Metal	**Quantity mg/kg Dry Substance**	**Metal**	**Quantity mg/kg Dry Substance**	**Metal**	**Quantity mg/kg Dry Substance**
30 t/ha	Pb	10.1	Pb	10.71	Pb	11.08
	Cd	0.11	Cd	0.12	Cd	0.13
	Ni	5.20	Ni	5.78	Ni	6.16
	Cu	6.8	Cu	7.55	Cu	7.85
	Zn	23.12	Zn	23.61	Zn	23.92
35 t/ha	Pb	10.6	Pb	11.12	Pb	11.34
	Cd	0.13	Cd	0.14	Cd	0.15
	Ni	5.82	Ni	6.33	Ni	6.71
	Cu	7.25	Cu	7.66	Cu	8.08
	Zn	24.2	Zn	24.52	Zn	24.96

The rapeseed was sown with about 55–60 seeds/sqm on September 1, 2019 at a distance between rows of about 15 cm.

The fertilization was done in multiple phases according to the following scheme:

- Basic autumn fertilization at sowing and autumn foliar fertilization at the stage of 6–8 leaves.
- Phase fertilization I at the rosette stage, 8–11 leaves and phase fertilization II at the stage of the incipient floral buds.
- Spring foliar fertilization at the stage of green and yellow floral buds.

The experiments performed were multifactorial. For Factor a, the applied sludge doses were 5, 10, 20, and 30 t/ha. For Factor b, the sludge application systems were under plowing at the establishment of the crop and then once a year to the soil surface. For Factor c the control variant was soil with sludge.

In the experimental plots with the two crops, sprinkler watering was applied by means of the drum and hose system with a Rain Sky-model 50 F with a 150 range.

The establishment of watering norms was made taking into account the critical phenophases of development of the studied plants: flowering, fruiting/formation, and filling of seeds.

For the rapeseed crop, two watering norms were applied, $m_1 = 375$ m^3/ha (10.IV) and $m_2 = 400$ m^3/ha (29.V), and for the soybean crop the watering norms were $m_1 = 500$ m^3/ha (2.V) and $m_2 = 550$ m^3/ha (25.VII).

The lower watering norms applied to rapeseed are due to their more efficient use of water accumulated during the cold season and earlier harvesting, towards the end of June and early July, compared to soybeans that are harvested in September.

The average crop production and oil content of the rapeseed are shown in Table 10 for all nine experimental variants. As can be seen, the best percentage of rapeseed production is on the soil treated with Euphore-type sludge, with 5200 kg/ha, compared to that of the soil treated with dry sludge on the platform, which was about 4600 kg/ha, and that on the control soil, which was only 2356 kg/ha.

Table 10. Average crop production and oil content of the rapeseed.

Dosage of Applied Sludge (t/ha)	Control Soil Untreated with Sludge		Soil Treated with Euphore-Type Sludge		Soil Treated with Dry Raw Sludge from Treatment Plant Platform	
	Production kg /ha	Oil Content of Rapeseed %	Production kg/ha	Oil Content of Rapeseed %	Production kg /ha	Oil Content of Rapeseed %
5			T2 = 4250	T2 = 46.1	T6 = 4046	T6 = 41.4
10	T1 = 2356	T1 = 37.5	T3 = 4920	T3 = 46.5	T7 = 4223	T7 = 42.2
20			T4 = 5050	T4 = 47.2	T8 = 4450	T8 = 43.1
30			T2 = 5200	T5 = 48	T9 = 4600	T9 = 44

Rapeseed oil production, O, was computed with the following equation:

$$O = S \cdot C / 100 \tag{6}$$

where S is the seed crop production (kg/ha) and C is oil content (%).

The values for S and C were taken from Table 10, and the values calculated for O are entered, in descending order, in Table 11.

Table 11. Values for average rapeseed oil production, in descending order.

Rank, *r*	1	2	3	4	5	6	7	8	9	Mean
Variant	T5	T4	T3	T9	T2	T8	T7	T6	T1	-
Average oil production, O_r, (kg/ha)	2496	2383.6	2287.8	2024	1959.25	1917.95	1782.11	1675.04	883.5	1934.36
Standard error, σ_r, (%)	9.94	22.04	25.74	26.82	28.08	18.84	20.05	21.58	22.77	21.76

Because the same values were considered as those in the case of rapeseed crop production, for the following basic data, $\alpha = 5\% = 0.05$ and $N_V = 9$; $v = 27$ the same values resulted for both standardized critical values for functions $\gamma_p = \gamma(p)$ and $R_p = R(p)$ from Table 4 and for all sizes entered in Table 12 $\gamma_p = \gamma(p)$.

Table 12. The values for the sizes $\left(\Delta_{i,j}\right)_k$, $(R_P)_k$ and $\left(\Delta_{i,j}\right)_k - (R_p)_k$ related to case 3.2.

Difference between Pairs of Variants, k	30
Values for difference between pairs of variants, $\left(\Delta_{i,j}\right)_k$ (Kg/ha)	41.30
Values for shortest critical range, $(R_P)_k$, (Kg/ha)	63.18
Values for difference $\left(\Delta_{i,j}\right)_k - (R_p)_k$, (Kg/ha)	−21.88
Variant for superior rank, i ($i = 5$)	T9
Variant for inferior rank, j ($j = 6$)	T8

The values for the sizes, $\left(\Delta_{i,j}\right)_k = (O_i)_k - (O_j)_k$, $(R_P)_k$ and $\left(\Delta_{i,j}\right)_k - (R_p)_k$, related only to case 3.2., are summarized in Table 11.

Thus, the conclusions of the Duncan test for the average rapeseed oil production are as follows:

- of the $p = 9$ treatment variants, 2 variants are insignificant, and 7 are significant;
- insignificant treatment options are T8 and T9;
- significant treatment options are T1, T2, T3, T4, T5, T6, and T7.

Similar to the application regarding soybean crop production, with degrees of freedom $v = 27$, for the normal deviation t, the same values were obtained: $t_{5\%} = 2.05$, $t_{1\%} = 2.77$, and $t_{0.1\%} = 3.69$.

Then, for the corresponding standard deviation $\sigma_d = 293.62$, $DL_{5\%} = 533.20$, $DL_{1\%} = 720.47$, and $DL_{0.1\%} = 959.76$. Finally, with the data centralized in Table 13, the classification of variants T2, T3, ... , T9 was performed. $\Delta O_r = O_r - O_{Nv}$

Table 13. Centralization of the data necessary for the classification of variants by the DL test.

Rank, r	1	2	3	4	5	6	7	8
Difference of production, $\Delta O_r = O_r - O_{Nv}$	1612.5	1500	1404.3	1140.5	1075.75	1034.45	898.61	791.54
$sign(\Delta O_r - DL5\%)$	+	+	+	+	+	+	+	+
$sign(OS_r - DL1\%)$	+	+	+	+	+	+	+	-
$sign(OS_r - DL\ 0.1\%)$	+	+	+	+	-	-	-	-
Significance	T5:FS	T4:FS	T3:FS	T9:FS	T2:DS	T8:DS	T7:DS	T6:S

The results for DL test in Table 13 are compatible and complementary to those in the Duncan test.

In Table 14 the average values of the agrochemical characteristics of the soil in the experimental field at the end of the vegetation period are presented. As can be seen, the best values are for the soil treated with Euphore-type sludge (V2), for which there is an increase in the amount of humus up to 3.4% in the Am horizon, compared to 2.03% (V3) in the variant fertilized with 25 t/ha. The total nitrogen content of the soil was also influenced by the application of urban sludge, the values being between 0.088–0.160 mg/100 g for the variants with untreated soil and 0.23–0.21 mg/100 g for the variants where urban sludge was applied. The total phosphorus analyzed for the soil from the experimental variants had low values in the untreated variants, 1.8–2.2 mg/100 g, and in the variants in which sludge was applied, a relatively proportional increase was found with the applied dose, with values of at 4.2 to 9.5 mg/100 g.

Table 14. Average values of agrochemical soil characteristics in the experiment.

Chemical Indicators that were Determined	Unit of Measurement	Values of the Indices		
		Dose of Sludge Applied: 20 t/ha		
		Control Soil, Untreated with Sludge, V1	Soil Treated with Euphore-Type Sludge, V2	Soil Treated with Dry Raw Sludge from Treatment Plant Platform, V3
pH		7.34	7.52	7.85
Total nitrogen	mg/100 g	0.16	0.23	0.21
P_2O_5	mg/100 g	2.2	9.5	4.2
K_2O	mg/100 g	14.9	24.5	18.6
Pb	mg/kg	8.9	10.1	13.7
Cd	mg/kg	0.60	0.61	0.65
Cr	mg/kg	65.9	68.6	70.4
Ni	mg/kg	4.1	4.3	4.8
Cu	mg/kg	16.1	16.6	17.3
Zn	mg/kg	12.3	14.42	15.2

Field—for the applied dose of 20 t/ha of sludge.

Regarding the pH, in the untreated variants, it had values between 7.32 and 7.34, and in the treated variants it varied between 7.52 and 7.85. The content of heavy metals in the soil at the end of the period was intended to study the effect of urban sludge on the soil, and it was within the normal limits cited in the literature.

We considered that the soil reaction from the experimental variants was influenced by the mechanical dilution resulting from the sludge-soil sewage mixture and a higher rate of mineralization of the organic material from the sludge used in the experimental variants. Old manure obtained from animal waste fermentation also has a slight alkaline reaction and causes a slight increase in the pH values of acid soils [41–43].

The slight alkaline reaction of the soil in the experimental variants may be due to some mineral and organic substances that form stable organo-mineral complexes in the soil and lead to the blockage of hydrogen ions from the salt and organic acid buffer systems [44,45].

In assessing the effect of applying treatments to correct the soil reaction, both pH and H+ ions modifications must be taken into account. At equal pH ranges, but ranging from different limits, the concentration of H+ ions has different values. The pH values change very easily in the range between 6 and 8.

4. Conclusions

The sludge from urban wastewater treatment is a source of macro and micronutrients that can be used in agriculture. The Euphore-type sludge introduced into the soils contains 2.55 more K, in the form of organic complexes accessible to plants, and 1.1% more phosphate and nitrogen, than those found in naturally dried sludge.

The positive response of crops to the application of sludge from wastewater varies with the type of crop and soil conditions. The average soybean production obtained for the soil treated with Euphore-type sludge is about 30.6% higher than that of the control soil and about 12% higher compared to that of the soil treated with dry raw sludge.

Following the application of sludge processed at a Euphore plant, the content of heavy metals recorded in the soil and plants does not exceed the maximum permissible limits.

We recommend the application of sludge processed with a Euphore plant on agricultural land as it contributes to the improvement of some soil properties and to the increase of soybean production. The Pb, Cd, Cu, Ni, and Zn content of roots, stems, and berries are lower than the maximum allowable limits.

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