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THE USE OF DIGESTATE IN GREEN AGRICULTURE

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This paper evaluates the importance of natural fertilizers for green agriculture. The digestate that results from biogas plants is another valuable material extracted through anaerobic digestion. Digestate mainly consists of undigested feedstock, microbial organisms, and microbial metabolites with high biological value. Digestate composition and quality strongly depend on those of the raw materials used in the anaerobic digestion. The amount of readily accessible macro and micronutrients found in digestate and its bioactive substances required for plant growth, results in a beneficial crop fertilizer. The usage of digestate as a fertilizer represents one of the most efficient ways to this day.

Keywords: Digestate, Biogas, Green Agriculture, Environmental Protection

1. Introduction

Agriculture is one of the most important economic sectors in Europe which had its production valued at around €434 billion in 2018. The production value of livestock represented almost 40% of total agricultural production (€172 billion), highlighting the socioeconomic relevance of the sector (*Eurostat 2019*). Anaerobic digestion (AD) is commonly used in Europe for the treatment of food and farm waste [1,2]. The AD process is a biological mechanism during which bacterial and archaeal communities convert carbon-rich organic waste into biogases, primarily methane and carbon dioxide [3]. Another byproduct of the AD process is a nutrient-rich digestate (NRD). NRD is rich in carbon, nitrogen (N), phosphorus (P), and other macro and micronutrients [4]. NRD is primarily used as organic fertilizer and is directly applied to farmland [5-7].

However, the use of digestate as a soil fertilizer increases the risk of nutrient runoff and penetration of groundwater resources, leading to soil and water eutrophication [8]. The suitability of digestate for various uses depends heavily on

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its composition and consistency, and the local nutrient situation. As previously mentioned, digestate is a valuable biofertilizer, rich in plant nutrients and with great potential as a replacement for mineral fertilizers worldwide.

Agricultural management differs considerably between regions in the world, due to the variation, for example, in climate conditions, in management technologies, and the length of the growing season. At present, there is a paucity of evidence on the sustainability of agricultural biomass use for bioenergy in Northern European countries, but this pathway could be a meaningful part of a circular bioeconomy. The success of the bioeconomy, and especially the circular bioeconomy, will depend on the achievement of environmental, social, and economic benefits [9].

The present study is focused on observing the effects that a non-treated solid digestate had on a type of soil and what differences appear between a digestate-fertilized soil and a commercial-fertilized one, at a heavy metal level using an XRF device. This paper is part of the first step in a Ph.D. thesis which aims to study the present focus in Romania in regard to the usage of digestate as an alternative, environmental-friendly fertilizer in daily agriculture processes, as well as demonstrating its benefits and availability. The novelty of the research consists in the local investigations on a Romanian soil Dâmbovița county, Săbiești village), where the soil composition could be improved by adding solid digestate usually a waste resulted from a biogas plant.

2. Materials and methods

In the first part of the current study, a series of experimental tests were made in order to analyze the quality and agriculture value of a soil that was treated for 3 months with solid digestate and compare it with the quality of the soil treated with synthetic fertilizer and with that of untreated soil. The soil samples were taken from Dâmbovița county, Săbiești village, where the specific soil type in that area of the county is close to that of loess. Throughout history, in that region, due to the presence of a gravel blanket of variable thickness, stand loessoid or meadow deposits formed. Over time, the most fertile soils in the county were formed on those deposits. The loess is largely composed of fine sand, siliceous and clayey dust. Given the history and the predominant type of soil, it was expected to find large quantities of Silicon [Si] in the final composition of the soil samples.

The soil samples were collected from different parts of a well-determined and selected area. All individual samples, except for 2 were spread on a plastic sheet and mixed thus creating one big sample. This collective sample was then divided into four squares equal to two opposite squares selected to create a new sample, as can be seen in Fig. 1.

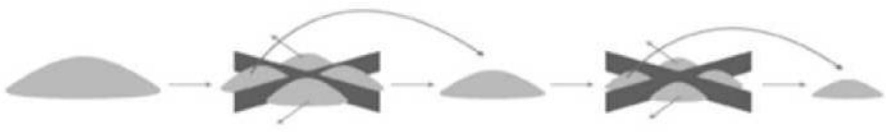

Fig.1. Soil selection method

This process was repeated until a sample of the appropriate size for laboratory testing remained (at least 100g). This process was done to create a homogenous composition of the soil.

In the end, 6 soil samples of approximately 100g each were created, which were then divided into two to be mixed/treated as follows:

- 2 samples of soil mixed with digestate;
- 2 samples of soil mixed with normal, commercial used fertilizer;
- 2 raw/untreated soil samples.

Each soil sample was watered every two weeks and a new batch of fertilizer and digestate was added to the composition, almost 20g of solid digestate and 15ml of commercial fertilizer. Before starting the set of analyzes, the 6 samples were subjected to a weighing process from which it was extracted between 10g and 10.4 g (Fig. 2), which were then dried in an oven at a constant temperature of 100°C (Fig. 3).

Fig. 2. Weighing of the soil samples

Fig. 3 Drying the samples in the oven

The set of analyzes to which the 6 soil samples were subjected is:

- determination of pH;
- determination of electrical conductivity;
- volumetric analysis for the determination of Ca in the soil;
- determination of the percentage of heavy metals with the XRF (X-ray fluorescent) method.

The 10g of dry and grinded soil were divided into two sets, one set was used to determine the heavy metals by XRF method, and the other for pH and electrical conductivity. The sample of digestate used to fertilize the soil samples was subjected to a liquid-solid separation process; the liquid fraction being stored in a basin on-site and used as fertilizer for crops. Part of the solid fraction was dried and packaged; the rest is stored on the digestate platform. In order to use digestate as a valuable biofertilizer in agriculture and forestry, as well as for it to be able to be integrated into the farm's fertilization scheme, it is necessary to know its chemical composition and properties. For this reason, representative samples must be taken from all the quantities of digestate produced and the N, P, and K content determined, as well as the values of dry matter (DM), volatile matter (VM), and their pH. If the biogas plant uses co-digestion of organic residues, the presence of heavy metals and persistent organic contaminants in the digestate must also be determined. Their concentration must not exceed the limits established by law. For it to be applied safely and to fertilize and condition the soil, the digestate must be free of pathogens, prion particles, as well as physical impurities. An XRF analysis of the digestate was made to determine and observe the presence of heavy metals.

Fig. 4 Seed planting with Jiffy peat pellets

After the first 3 months of treating the soil samples, commercial flower seeds were planted in them to visually analyze the growing process of plants in different soil types. For starters, the seeds were planted in Jiffy peat pellets, intended for the production of vegetable and flower seedlings (*Fig. 4*), and then replanted in the treated soil samples. Jiffy peat pellets are basically very well pressed peat, sterilized with steam and fertilized with the microelements necessary for good early development of the plants.

3. Results and discussion

3.1. XRF analysis of the solid digestate

In Table 1 we can see the results of the XRF analysis of the digestate sample. To be able to perform this analysis, 10g of the sample was selected and left to dry in the oven at a constant temperature of 100°C. After drying the sample was subjected to a process of uniformity by grinding.

Table 1

XRF, results of the solid digestate

Formula	Concentration (%)	Stat. Error (%)	±	LLD (ppm)	Analyzed layer (gm)	LLD (%)
Ca	25.17	0.25%	0.0624216	525.7	35	0.05257
K	16.92	0.26%	0.0434844	299.7	58	0.02997
P	4.39	0.69%	0.0304227	52	25.5	0.0052
S	4.229	0.55%	0.02330179	36.1	28.6	0.00361
Mg	1.9	1.65%	0.03135	149.1	8.7	0.01491
Si	1.08	1.67%	0.018036	60.7	18.5	0.00607
Fe	0.555	0.94%	0.0052059	35.8	76	0.00358
Al	0.336	3.59%	0.0120624	69.7	12.5	0.00697
Cl	0.292	3.00%	0.00876	71.6	32	0.00716
Ba	0.14	9.15%	0.01281	320.8	29.4	0.03208
Sr	0.0554	1.27%	0.00070358	16	0.69	0.0016
Ti	0.054	6.74%	0.0036396	92.5	30	0.00925
Mn	0.0477	4.43%	0.00211311	41.4	61	0.00414
Zn	0.0347	2.93%	0.00101671	22.5	168	0.00225
Cu	0.011	8.31%	0.0009141	25.2	138	0.00252

Fig. 5 Heavy metals present in the Digestate

In the XRF analysis's result of the digestate (*Table 1*), you can see the increased percentage of calcium and potassium, which means that this digestate is a good fertilizer for plants where they can extract the nutrients they need from the soil. The nutrients in the digestate are considerably more available than in the raw suspension, which means that it is easier for plants to use them. All the nitrogen, phosphorus, and potassium present in the raw material will remain in the digestate because none of these elements are present in the biogas which resulted from the energy plant.

3.2. pH and electrical conductivity determination

To facilitate the determination of pH and electrical conductivity in the soil, after drying the samples, followed a step of grinding the samples for uniformity and then wetting them with distilled water. The samples were numbered from 1 to 6 and were subjected in turn to pH and electrical conductivity testing. pH is an indicator of the balance of nutrients available in the soil, while electrical conductivity provides information on the amount of nutrients available in the soil. The optimal pH for agricultural soil is 6.5 (slightly acidic), which allows the development of micro-organisms and the assimilation of nutrients by plants. Regarding the electrical conductivity, the optimal values are in the range of 200-1200 pS/cm. Based on the results presented in *Table 2,* the following were found:

- untreated soils have a very strong acidic pH (pH <5) and low electrical conductivity (<200 pS/cm). These indicate a lack of nutrients available to plants and the fact that elements such as iron, aluminum, and manganese can be found in the forms available to plants, and useful elements such as phosphorus, potassium, calcium, magnesium are hardly available to plants.
- soils treated with fertilizer have slightly acidic pH, with higher values compared to untreated soil (~ 6) and higher electrical conductivity (300- 400 pS/cm), indicating a higher amount of nutrients available in the soil.
- soils treated with digestate also have a slightly acidic pH and very high electrical conductivity (>500 pS/cm), with the presence of salts (sodium, magnesium, potassium).

Table 2

Electrical conductivity and soil pH determination

Soil sample	Weight [g]	pH	CE [pS/cm|	Observations
Digestate 1	10,024	5,91	527	Slightly acidic with the presence of salts (sodium,
Digestate 2	10,451	6,3	608	Slightly acidic with the presence of salts (sodium,
Com. Fertilizer 1	10,190	5,93	335	Slightly acidic

Com. Fertilizer 2	10,093	5,88	409	Slightly acidic
Untreated 1	10,225	4,74	167	Very strong acidic
Untreated 2	10,115	4,82	159	Very strong acidic

Observations were noted according to the following classification of soils by pH (in water):

- very strong acidic – pH <5
- strongly to moderately acidic – pH 5.01 – 5.80
- slightly acidic – pH 5.81 – 6.80
- neutral – pH 6.81 - 7.20

3.3. Calcium (Ca) determination

Calcium, along with other basic cations (Mg^{2+}, K^{+}), compensates for the negative charges of the soil colloidal complex, constituting the dominant cation in ensuring the degree of saturation in the bases. Acidic soils contain less calcium than alkaline ones. In these soils, calcium precipitates iron, aluminum and manganese cations in the form of hydroxides Fe(OH)3, Al(OH)3 and Mn(OH)2, thus reducing the toxicity caused by excess H^{+}, Fe^{2+}, Al^{3+} and Mn^{2+}.

Following the procedures of the **SR ISO 6058:2008** standard, an analysis of the samples for the volumetric determination of the amount of calcium (Ca) present, was performed. In general, a certain ratio of nutrients is desired in the soil to ensure a balanced nutrition for the plants. Thus, the ideal Ca:Mg ratio in the soil is between 5:1 and 8:1, the Ca:K ratio is 13:1, and the Mg: K ratio is 2:1.

To 1g of soil sample, we added 100ml of distilled water in two phases. In the first phase, we added 25ml of water over the sample, stirred for homogenization and then filtered the solution obtained. After completing the filtration process, we diluted the solution with another 75ml of distilled water. Thus, after obtaining the final solution, we added NaOH solution until reaching pH 12-13 and 0.1g of MUREXID mixture (indicator), preparing the sample for the titration process with EDTA solution until obtaining a purple color.

To calculate the amount of calcium in the soil, we used the standard formula:

$$\rho_{Ca} = \frac{1000 \times 0.4008(V_s - V_b) \times r}{V_a}$$

Where,

Va - the volume of the analyzed sample

Vb - the volume of EDTA solution used for titration of the control sample Vs - the volume of EDTA solution used for sample titration r - number of dilutions (ignored in this case)

0.4008 - the amount of Ca in mg, corresponding to 1ml 0.01m EDTA solution.

The results obtained from the titration of the samples are present in *Table 3*.

Table 3

Volumetric Calcium determination

Soil sample	**Titrated [ml]**	**Calcium [mg/l]**	**Percentage [%]**
Digestate 1	0,05	0,2004	2
Digestate 2	0,1	0,4008	4
Com. Fertilizer 1	0,2	0,8016	8
Com. Fertilizer 2	0,1	0,4008	4
Untreated 1	0,05	0,2004	2
Untreated 2	0,1	0,4008	4

3.4. XRF soil analysis

The method consists of producing the X-ray spectrum characteristic of the sample to be analyzed, using an X-ray beam as the excitation source. The incident beam must have a high intensity because the fluorescence X-rays are approximately 1000 times less intense than those obtained by direct electron bombardment. Also, to excite the fluorescence of an element, the primary radiation must have a shorter wavelength (longer energy) than those of the discontinuities that appear in the absorption spectrum of that element. Qualitative analysis is done based on the position of fluorescence peaks in the spectrum, and quantitative analysis is done by determining the intensity of characteristic radiation emitted by an element. To obtain correct results, it is of great importance to properly prepare the samples for analysis [10].

In *Table 4* we can see the results of the XRF analysis of a soil sample treated with digestate and the high percentage of silicon, which is due to the soil type-specific for the area from which it was taken.

Table 4

XRF results for the soil x digestate mix

Formula	Concentration (%)	Stat. Error (%)	±	LLD (ppm)	Analyzed layer (gm)	LLD (%)
Si	24.21	0.37	0.089577	78.9	11.3	0.00789
Al	5.97	0.78	0.046566	69.2	11.9	0.00692
Fe	4.33	0.25	0.010825	73.7	98	0.00737
K	2.2	0.77	0.01694	42.1	19.8	0.00421
Ca	0.86	1.22	0.010492	63.8	23.7	0.00638
Ti	0.75	1.15	0.008625	37	39	0.0037
Mg	0.67	2.84	0.019028	132.2	8.2	0.01322
Na	0.57	7.89	0.044973	286.2	5.3	0.02862

Zr	0.13	0.89	0.001157	15.1	0.89	0.00151
Mn	0.13	1.81	0.002353	23.5	78	0.00235
Sr	0.05	2.2	0.0011	7.9	0.66	0.00079
Rb	0.03	2.71	0.000813	9.6	0.56	0.00096
Zn	0.01	4.87	0.000487	13.3	161	0.00133

In *Table 5* where we can see the XRF results of the soil sample treated with fertilizer, phosphorus (P) appears in the part of heavy metals that are found in higher proportions (0.52%). We know that in acidic soils phosphorus is retained by absorption in hard-to-change forms through iron and aluminum hydroxides. The appearance of phosphorus in the results, at that percentage, indicates the presence of organic matter, the organic ions releasing the phosphate ions fixed on the soil particles. This confirms the use of organic fertilizers in the mixture of that sample.

Table 5

XRF results for the soil x commercial fertilizer mix

Formula	Concentration (%)	Stat. Error (%)	±	LLD (ppm)	LLD (%)	Analyzed layer (gm)	LLD (%)
Si	23.37%	0.38%	0.087871	63.7	0.00637%	11.70	0.006370
Al	6.16%	0.77%	0.047124	67.5	0.00675%	12.30	0.006750
Fe	4.78%	0.24%	0.011233	73.2	0.00732%	104.00	0.007320
K	2.57%	0.70%	0.017964	32.3	0.00323%	21.70	0.003230
Ca	1.22%	1.01%	0.012322	66.0	0.00660%	25.50	0.006600
Ti	0.70%	1.19%	0.008330	36.2	0.00362%	41.00	0.003620
Mg	0.63%	2.91%	0.018333	126.9	0.01269%	8.40	0.012690
Na	0.54%	8.05%	0.043470	294.5	0.02945%	5.40	0.029450
P	0.52%	2.63%	0.013676	80.8	0.00808%	6.00	0.008080
Zr	0.20%	1.01%	0.002020	17.7	0.00177%	0.91	0.001770
Mn	0.12%	1.94%	0.002328	23.3	0.00233%	83.00	0.002330
Sr	0.09%	1.33%	0.001197	9.0	0.00090%	0.67	0.000900
Rb	0.03%	2.86%	0.000858	10.6	0.00106%	0.57	0.001060

The sample of untreated soil was taken from an area with unmaintained and uncultivated agricultural land for almost two years. This is also observed in the results obtained (Table 2 and 6) by the low amounts of minerals and salts, but also by determining the pH which is strongly acidic.

Table 6

XRF results for the raw soil sample (untreated)

Formula	Concentration (%)	Stat. Error (%)	±	LLD (ppm)	LLD (%)	Analyzed layer (gm)	LLD (%)
Si	24.61%	0.36%	0.089580	72.1	0.00721%	12.50	0.007210
Al	5.78%	0.78%	0.045315	60.9	0.00609%	13.20	0.006090
Fe	4.40%	0.24%	0.010604	69.6	0.00696%	110.00	0.006960
K	2.18%	0.76%	0.016546	35.6	0.00356%	21.90	0.003560
Ti	0.74%	1.14%	0.008436	33.4	0.00334%	43.00	0.003340
Mg	0.63%	2.85%	0.017955	112.3	0.01123%	9.00	0.011230
Ca	0.62%	1.42%	0.008804	61.4	0.00614%	26.20	0.006140
Na	0.47%	8.38%	0.039386	244.2	0.02442%	5.80	0.024420
Mn	0.16%	1.61%	0.002576	22.8	0.00228%	87.00	0.002280
Zr	0.13%	0.95%	0.001238	13.4	0.00134%	0.98	0.001340
Sr	0.04%	2.67%	0.001068	8.3	0.00083%	0.72	0.000830
Rb	0.03%	2.80%	0.000840	9.3	0.00093%	0.61	0.000930
Y	0.03%	5.39%	0.001617	15.1	0.00151%	0.84	0.001510

The results obtained from the XRF analysis highlight the following aspects:

• The main elements of the soil are silicon, aluminum, iron, and potassium. Soil treatment has no significant effects on the content of these elements.

• The main elements of the digestate are calcium, potassium, magnesium, silicon, and phosphorus. These are useful elements for the soil and plants.

• The calcium content of the soil treated with digestate is higher compared to the untreated soil. However, much higher values are recorded in the case of soil treated with fertilizer, as the increase in calcium content may be related to a high content of organic matter.

• The magnesium content does not change significantly after treating the soil with digestate or fertilizer.

• From the point of view of Zn, we can conclude by highlighting the same increasing trend of concentration in the soil treated with conventional fertilizer, compared to that treated with digestate.

• The concentration of manganese in the treated soils exceeds the normal limit provided in Order 756/1997 for the approval of the Regulation on environmental pollution assessment, of 900 mg/kg, being registered values in the range 1200-1700 mg/kg.

• The rubidium content is high in both untreated soil samples (300 mg/kg for sample 1 and 400 mg/kg for sample 2) and for the treated ones. Rubidium is generally found in heavily polluted areas. At acidic pH, rubidium is found in a slightly changeable form. Treating the soil with fertilizer or digestate does not affect the rubidium content of the soil.

• Similar to rubidium, strontium is leachable at acidic pH. And in this case, the values recorded are high (400 mg/kg for sample 1 and 300 mg/kg for sample 2, respectively).

• At low pH values, as is the case of the analyzed samples, the solubility of some elements such as iron, manganese, potassium, rubidium, and strontium increases, favoring their leaching and bioaccumulation by plants.

All these are in relatively normal quantities, above the detection limit of the XRF method, of ppm quantities. The margin error of the analysis compared to the percentages obtained is acceptable, as it is somewhere below 1% for the main metals.

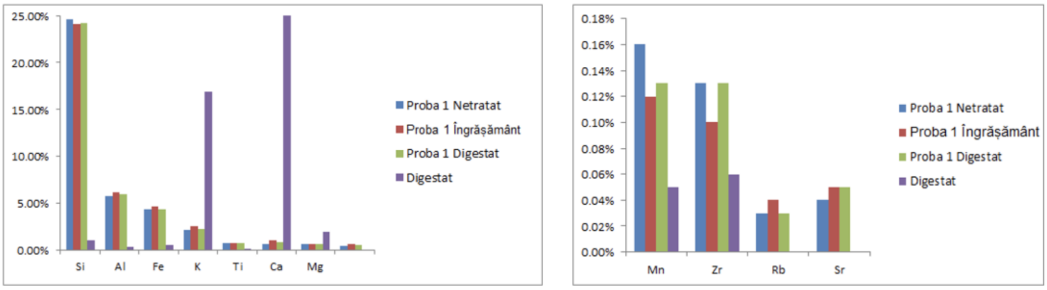

Fig. 6: XRF results comparison between soil samples

4. Conclusions

In the analysis, when determining the Ca in the soil by volumetric method compared to the results obtained by the XRF method, a discrepancy could be observed because, volumetrically, Mg is determined in the same way which means that in the results we have Ca and Mg, hence the percentage obtained. After the end of the analysis set, it was observed that the soil has mainly the same characteristics and falls within normal and favorable parameters for agriculture. There were found high percentages of heavy metals such as Si, Ca, Fe, Al, K, Ti, but also traces of Zr, Mn, Rb, and Zn.

The biggest error was recorded when determining the percentage of Na^+ in the soil, where the device displayed an error between 7 - 13%. In the samples treated with digestate, we noticed an increase in the level of pH and electrical conductivity, which would indicate the presence in larger quantities of mineral salts. However, the XRF analysis showed that the percentage of salts such as K^+, Mg^+, and Na^+ are in the same ratio as in the rest of the samples. The two soil samples to which was added as a digested amendment obtained by anaerobic fermentation from biogas plants had a lower concentration of Fe than those to which conventional fertilizer was applied, which is explained by the addition of additional Fe in the fertilizer formula. Moreover, the addition of digestate has the advantage that in its composition Fe is found in a percentage of over 70% in the form of ferrous phosphate $Fe_3(PO_4)_2$, a form with low plant availability.

Although XRF analysis showed a higher concentration of Mg in the soil on which it was added digested, it should be noted that its speciation prevails when we talk about the possibility of plant phytoextraction. Thus, from the point of view of the bioavailability of heavy metals, the addition of digestate prevails over the use of conventional fertilizer.

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