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RESEARCH ON THE USE OF SLUDGE FROM THE PITEȘTI WASTEWATER TREATMENT PLANT AS FERTILIZER

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Abstract

Sludge is a by-product, resulting from wastewater treatment. This study research provides the sludge analysis from the Pitești Wastewater Treatment Plant and the possibility of using this sludge in agriculture in its initial state, resulting from the treatment plant or even after any remediation required or appropriate treatment so that it can be used. For these analyses, we used the services of two laboratories, namely: Iași Research Institute for Agriculture and Environment - ICAM, from the "Ion Ionescu de la Brad" Iași University of Life Sciences and WESSLING - testing and consulting laboratory for continuous improvement of quality, safety, environmental protection, and health - the Hungarian laboratory.
The research focused on the presence of heavy metals, antibiotics, and hormones in the sludge and the determination of microplastics in it. The microplastics in the sludge were determined by treating them with 5% HCl sonicated at 25^{0}C and then centrifuging and analyzing the supernatant. The research results show that the sludge obtained from the Pitești Wastewater Treatment Plant cannot be used as fertilizer in agriculture.

***Key words**: sludge, wastewater treatment.*

INTRODUCTION

In the European context, the storage and recycling of sludge generated in wastewater treatment plants are highly contested. Applying sewage sludge to agricultural land can be beneficial as it improves the physical, chemical, and biological properties of soils and enhances crop growth (Dracea et al., 2022). Sludge is a by-product, resulting from wastewater treatment. It is considered a source of energy because it contains elements that must be recycled. Dewatered sewage sludge, depending on stabilization processes, contains on average 50-70% organic matter and 30-50% mineral components (including 1-4% inorganic carbon), 3.4-4.0% N, 0.5-2.5% P and significant amounts of other nutrients, including micronutrients (Fytili & Zabaniotou, 2008; Samolada & Zabaniotou, 2014; Tyagi & Lo, 2013).

Sewage sludge also contains high concentrations of nitrogen and phosphorus and can be considered as a plant fertilizer, but it also contains heavy metals, polychlorinated biphenyls (PCBs), adsorbable organic halides (AOX), pesticides, surfactants, hormones, pharmaceutical products, nanoparticles and many more (Siebielska, 2014; Sandu et al., 2023).

Sludges contain many pathogenic species: bacteria, viruses, and protozoa, which, together with other species of parasitic helminths, can create health hazards for humans, animals, and plants (Fijalkowski et al., 2014; Kacprzak & Stańczyk-Mazanek, 2003).

Currently, sludge is regulated in the European Union legislation as waste resulting from the treatment of domestic and industrial wastewater, which must be treated, recovered, or disposed of.

Sludge management is a complex issue as environmental standards become increasingly restrictive. From this perspective, the wastewater treatment activity must be associated with the usage and/or controlled storage of the sludge resulting from the process. In the European Union, the environmental strategy regarding sludge resulting from wastewater treatment supports the minimisation of production thereof, as well as the implementation of treatment methods with increased efficiency, with a view to recycling.

Reusing sludge in agriculture, forestry, or the restoration of degraded lands, although accepted and preferred in many countries of the world, is also a vulnerable and controversial method that still requires numerous interdisciplinary explorations. Although the fertilizing value of sludge is acknowledged, use thereof faces both hygienic and ethical objections due to the unwanted presence of heavy metals and other categories of pollutants, such as hormones, antibiotics, microplastics, etc.

MATERIALS AND METHODS

Location of the studies

The Wastewater Treatment Plant in Pitești is intended for the treatment of the residual water of Pitești and the industrial units within its radius, excluding the petrochemical platform.

The industrial wastewater connected to the city network, excluding that of the petrochemical platform, comes from industrial enterprises with a very varied production profile and represents about 60-70% of the total flow.

The plant's location was chosen primarily for relief/landscape considerations. It is at the lowest point in the inner city, which provides the advantage of being supplied with wastewater by gravity; no pumping is necessary.

Also, the minor bed of the Argeş River is only 250 m away. Another consideration for choosing the site was the fact that it is located downstream of the city's water intake.

The wastewater treatment plant in Pitești was built in several stages, along with an increase in the number of inhabitants and industrial development, requiring an increase in the treatment capacity.

The technological process of mechano-biological purification (with a tertiary step) of wastewater takes place in three main directions: the water line, the sludge line, and the biogas line.

At the present time, the capacity of the Treatment Plant is a maximum flow rate (Q) of 1,138 l/s mechanically, biologically, and chemically treated water. Household, industrial and meteoric water (from the unitary system) are directed to the city's wastewater treatment plant and have approximately the following composition:

- household water - 60%;
- industrial water - 30-35%;
- seepage water - 5-10%.

Table 1. Purification process flow from the Pitești WWTP

Water line		Sludge line
Mechanical treatment:	Biological treatment:	
Mechanical screens (coarse and fine screens) Sludge filter unit and grease separators Retention tanks Sand separators Primary sludge chambers	Secondary sludge chambers Aeration basins $FeCl_3$ Dosing	Gravitational thickeners Thickened sludge mixing basins Digester Digested sludge storage tanks Sludge water retention tank Polyelectrolyte dosing systems

Sample collection and analysis

The sludge samples were taken after treatment from the Pitești Wastewater Treatment Plant's drying platform on September 13, 2022, in 3 plastic containers weighing between 0.9 and 2.5 kg each (Figure 1).

Figure 1. Sampling

RESULTS AND DISCUSSIONS

Analysis of heavy metals presence

As the Analysis Bulletin from ICAM Iași shows, heavy metals were detected in concentrations exceeding the admissible limits according to the legislation in force, as presented in Table 2 for

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the following elements: zinc, copper, nickel, and lead. However, the concentration values of the other heavy metals are also not negligible.

Table 2. Analysis Bulletin from ICAM Iași

No.	Test name	UM	Values obtained
1.	pH	-	7.08
2.	Moisture	%	40.2
3.	Total nitrogen	%	0.78
4.	Total phosphorus	%	1.14
5.	Total potassium	%	1.37
6.	Organic matter	%	37.29
7.	Fe	%	2.83
8.	Zn	Ppm	1431
9.	Cu	Ppm	247
10.	Mn	Ppm	415
11.	Cd	Ppm	ND
12.	Co	Ppm	11.2
13.	Ni	Ppm	72
14.	Cr	Ppm	126
15.	Pb	Ppm	57

Contamination of agricultural soils with heavy metals adversely affects plant growth and soil microbiome and it is dangerous for food safety and human health (Wang et al., 2019). If concentrations of heavy metals such as copper (Cu), zinc (Zn), nickel (Ni), iron (Fe), and molybdenum (Mo), which are also essential micronutrients, exceed plant requirements, they become a serious environmental threat (Chen et al., 2014). Although other heavy metals such as lead (Pb), chromium (Cr), mercury (Hg), cadmium (Cd), and arsenic (As) are not essential for plant growth, they can adversely affect soil function, plant growth, and human health (Edelstein & Ben-Hur, 2018; Vardhan et al., 2019).

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means the increase over time, in biological organisms, of the concentration of the substance in a quantity comparable to the concentration in the environment. Compounds accumulate in living organisms when they are assimilated and stored faster than they are metabolized or disposed of. Heavy metals cannot be degraded or decomposed to reduce their toxicity but can be transformed into non-reactive and less toxic species (Pandey & Keshavkant, 2021).

Once penetrated into plants, heavy metals enter the food chain and undergo specific processes. This circuit has a series of biological barriers, with limited action, which determine a selective bioaccumulation that defends living organisms against excess. However, there is a great risk of increasing the concentration up to toxicity limits that cause imbalances in the chemical, physical and biological processes in the soil.

Effects of zinc: Zinc is the only metal present in all six classes of enzymes (oxidoreductases, transferases, hydrolases, lyases, isomerases, ligases). It is an essential element for animals and plants. Zinc causes the *phytotoxicity phenomena in contaminated soils*. As the soil pH decreases, the solubility and absorption of zinc increases, and thus, the phytotoxic potential also increases. In acid soils, phytotoxicity is indicated by the presence of ferric chlorosis. The toxicity of zinc can also be caused by the fact that this ion challenges biologically active ions and occupies their binding sites. Typical symptoms in this regard are: *chlorosis, reduction of plant biomass and inhibition of root growth* (Singh et al., 2013).

Effects of copper: Copper – is the metal component of phenol oxidase, ascorbic-acid-oxidase. Copper plays an important role in flowering, fruiting, and ear formation. Copper present in the soil above the natural limits of 1-20 ppm, has negative effects on the percentage of aggregates and the hydro stability of the particles, being susceptible to erosion and compaction. A high concentration of copper causes an increase in the mobile fraction of humus, an increase in hydrolytic acidity, and a reduction in basic cations. In plants, a high Cu concentration (generally > 20 ppm dry matter) reduces the intensity of respiration, slows down the process of chlorophyll formation, and decreases the activity of some ferments.

Effects of nickel: Nickel plays an important role in the life of plants in the synthesis of essential enzymes in the growth and development of plants, such as auxins, cytokines, and gibberellins (Singh et al., 2013). Plants absorb nickel as a Ni^{+2} divalent cation. The required dose is very low, i.e., 1.1 ppm. In excess, nickel is a heavy element and is strongly phytotoxic at a higher concentration. In several plants, Ni produces changes in enzyme activity. The most common symptoms of nickel toxicity in plants are growth inhibition, induction of chlorosis, necrosis, and wilting. Nickel strongly influences the metabolic reaction in plants and has the ability to generate oxygen radicals that can cause oxidative stress. Ni toxicity induces a decrease in the water content of mono- and dicotyledonous species.

Effects of chromium: Chromium compounds are very toxic to plants and act to the detriment of their growth and development. As it is a non-essential element for plant metabolism, chromium does not have specific absorption mechanisms. The toxic effects of chromium are mainly dependent on the metal species, which determines its absorption, translocation and accumulation (Huang et al., 2009).

Effects of lead: Lead in soil negatively influences biological activity by reducing respiratory processes at the root level, as well as by reducing the number of organisms. From the soil, lead passes into plants in amounts directly proportional to the amount of lead available. It acts on: oxidation and photosynthesis processes, limits the amount of water absorbed and intensifies the plant's oxygen requirement, slowing down the pace of crop development, until the crops are compromised (Gisbert et al., 2003).

Effects of cadmium: The toxic effects of cadmium on plant aerial organs include wilting of plants, chlorosis and necrosis of leaves, abnormal stomatal functioning, disruption of gas exchange, hormonal imbalance, production of oxidative stress, and increased peroxidation of membrane lipids. Cadmium usually accumulates in the upper horizons of the soil, in the plowed layer, and migrates with difficulty to the depth. The transition from soil to plants depends on the texture (higher with coarse texture) of the content in organic matter; there is a great affinity for the adsorption of cadmium by organic matter, which can be even 30 times higher compared to mineral soil (Copes et al., 2008; Othman et al., 2009).

The concentration of heavy metals in the sludge is around 0.5 and 2 %, but in some cases, it can increase up to 6% (Vyrides et al., 2017). Over the years, many researchers have studied different processes for the recovery of these heavy metals from sludge. The highest percentages of recovery (> 90%) were obtained using ultrasound (Li et al., 2010). Heavy metals, which are recovered together with proteins, are an inconvenience in the recovery processes, especially if the aim is to use the proteins as nutritional supplements for animals (Tyagi & Lo, 2013; Gherghel et al., 2019).

Most studies show that all these heavy elements in the soil are partially transferred by plants to animals and humans, respectively, leading to health deficiencies.

Analysis of the presence of residues of pharmaceutical substances

Table 3 shows residues of several pharmaceutical substances, some in low concentrations but some in considerable concentrations that depend on the drug from which it comes: antibiotics, analgesics, antimicrobial substances, antidepressants, and contraceptives.

Table 3. Presence of residues of several pharmaceutical substances

No.	Test name	UM	Values obtained
1.	Bisphenol A	mg/kg	0.47
2.	Furosemide	mg/kg	0.02
3.	Ibuprofen	mg/kg	0.03
4.	Triclocarban	mg/kg	0.01
5.	Triclosan	mg/kg	0.02
6.	4-Methoxycinnamic acid 2-ethylhexyl ester	mg/kg	0.21
7.	Amlodipine	mg/kg	0.17
8.	Atorvastatin	mg/kg	0.03
9.	Azithromycin	mg/kg	0.35
10.	Bisoprolol	mg/kg	0.01
11.	Ciprofloxacin	mg/kg	0.14
12.	Diclofenac	mg/kg	0.04
13.	Doxycycline	mg/kg	0.17
14.	Famotidine	mg/kg	0.03
15.	Carbamazepine	mg/kg	0.03
16.	Carvedilol	mg/kg	0.22
17.	Codeine	mg/kg	0.01
18.	Caffeine	mg/kg	0.05
19.	Cotinine	mg/kg	0.01
20.	Levonorgestrel	mg/kg	0.18
21.	Metoprolol	mg/kg	0.09
22.	Miconazole	mg/kg	0.02
23.	Norfloxacin	mg/kg	0.06
24.	Ofloxacin	mg/kg	0.28
25.	Oxytetracycline and 4-Epoxytetracycline	mg/kg	0.09
26.	Progesterone	mg/kg	0.02
27.	Propranolol	mg/kg	0.04
28.	Tetracycline and Epitetracycline	mg/kg	0.18

The substances whose concentration is higher than 0.01 mg/kg are the following:

- **Bisphenol A** is a controversial and highly toxic chemical compound. It comes from plastic products. Being a polymer, polycarbonate is, in turn, composed of several substances (monomers). One of these substances, which is also one of the most used in industry, is represented by **bisphenol A.**

- The ***EPA*** (*Environmental Protection Agency*) defines **bisphenol A** as "*an exogenous chemical substance or combination that alters the structure or function(s) of the endocrine system* *and causes adverse effects*". A 2014 study shows that bisphenol A (abbreviated BPA) is also used to manufacture aluminium pharmaceutical tubes (for ointments, and creams).

- Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID), a type of drug commonly used to relieve pain and reduce fever. Being a frequently used drug, it is normal to be found in the analyzed sludge.

- 4-Methoxycinnamic acid 2-ethylhexyl ester is a hormonal treatment. In women, it is used during pregnancy and breastfeeding.

- Triclosan is a chemical found in toothpaste, soap, and even some toys, which put American experts on alert after a study has showed that the ingredient is associated with the development of cancer cells and hormonal disorders. Animal studies have shown malformations and problems related to infertility. Human studies have demonstrated the presence of triclosan in urine and blood. This means that there can be negative effects for the mother and for those who have a genetic predisposition to certain diseases.

- Amlodipine belongs to the group of medicines called calcium channel blockers. Amlodipine is indicated in the treatment of high blood pressure, angina pectoris or vasospastic angina.

- Azithromycin belongs to a group of antibiotics called macrolides. It is used in the treatment of chest, throat no se, and ear infections. It is a frequently used treatment against the infection with Covid 19 and thus it is understandable why it is found in the list of substances in the studied sludge.

- Ciprofloxacin is part of a group of medicines called quinolone antibiotics that have a broad spectrum of activity against microorganisms that can infect the eye and ear.

- Diclofenac contains diclofenac sodium as an active substance, which belongs to the class of drugs known as non-steroidal anti-inflammatory drugs (NSAIDs) for local use.

- **Doxycycline** is part of the group of drugs known as systemic antibacterials, tetracyclines. Doxycycline is used to treat respiratory tract infections and bacterial infections, including pneumonia.

- Carbamazepine is an antiepileptic with anticonvulsant, sedative and tranquilising properties.

- **Carvedilol** is a beta-blocker which works by relaxing and dilating blood vessels.

- **Levonorgestrel** is a pre-gestational hormone with antiestrogenic action, with various applications in gynaecology. Medicines containing levonorgestrel can be included in the following pharmacotherapeutic classes: emergency contraception, contraceptive pills, and progestogen intrauterine devices.

- **Metoprolol** is a drug from the group of selective beta-blocking drugs. This medicine is used in the treatment of high blood pressure.

- **Norfloxacin** is a new antibacterial derivative from the 4-Quinoline series. It is indicated in the therapy of the upper and lower urinary system.

- **Ofloxacin** is a 2nd generation fluoroquinolone antibiotic. It is used in the treatment of bacterial infections, such as: pneumonia, urethritis, prostatitis and other urinary tract infections.

- **Oxytetracycline** is an antibiotic used in the treatment of various bacterial infections.

- **Progesterone** is a steroid hormone produced by the cells of the ovarian corpus luteum and during pregnancy by the placenta.

- **Propranolol,** the active substance in this drug, belongs to the class of non-selective beta-blocking drugs and is indicated for hypertension.

- **Tetracycline** and **Epitetracycline** are broad-spectrum antibiotics with bacteriostatic action, indicated for the treatment of various infections.

- **Amoxicillin** is an antibiotic that belongs to a group of medicines called "penicillin", the medicine is used to treat infections caused by bacteria.

The treatment of many human and animal diseases relies on access to effective pharmaceutical substances. At the same time, pollution from some pharmaceuticals is an emerging problem, with well-documented evidence of environmental risks. Residues of pharmaceutical products can enter the environment during their manufacture, use and disposal.

Another source of pharmaceutical substances that can end up in wastewater and then in sewage sludge is expired drugs. More than a thousand tons of expired medicines from the population end up either in the sewage system or in the landfill every year.

Current legislation does not provide for minimum or maximum limits because those sludges in which pharmaceutical substances have been detected are not allowed to be used in agriculture.

The toxic effect of pharmaceutical substances on plant tissues and cells varies depending on the concentration; at high concentrations, the entire growth and development process of the plant can be inhibited. After entering the plant, the pharmaceutical substances will be found in the food chain and are already a danger to human and animal health.

Research on the effects of antibiotics on the anaerobic digestion of sludge has shown that most antibiotics can inhibit methane production and methanogenesis rates at low concentrations. A small number of antibiotics (amoxicillin, metronidazole) have a negative effect on the proportion of methane in biogas because these antibiotics inhibit the activity of methanogenic bacteria that convert VFAs (volatile fatty acids) into methane, the percentage of VFAs converted into methane decreases and the CO_2 content grows. Furthermore, the combined effect of multiple antibiotics also inhibits methane production from anaerobic digestion of sewage sludge. In addition, VFA accumulation increases with the progress of anaerobic digestion, which is mainly due to the toxicity of antibiotics to the methanogenesis phase of VFA consumption. However, a few antibiotics (cephalexin, oxytetracycline, sulfamethoxazole, and kanamycin) can have a positive effect on anaerobic digestion by increasing methane production (Qingdao Wu, 2022).

The rate of antibiotic removal and biogas production during anaerobic digestion of sludge can be improved by adding oxidants (ozone, calcium oxide) and catalysts (zero-valent iron, iron ions).

These pretreatments promote the decomposition of antibiotics by improving complex oxidation reactions and electron transfer or increasing the bioavailability of microbial communities, thus achieving the goal of improving the removal rate of antibiotics and increasing methane production. However, the large-scale application of these pretreatment methods requires further environmental and economic studies to improve the methanogenesis performance of antibiotic-inhibited anaerobic digestion of sludge.

Analysis of microplastic presence

The high content of solid particles in the sample, 50 g of the sample was sampled, which was treated as follows: pre-oxidation with H_2O_2, density separation with $CaCl_2$ solution 1.3 g/cm^3, oxidation with Fenton reaction and filtration on Anodisc inorganic filters that transmit IR.

The filters were analyzed with a Thermo Scientific Nicolet iN10 MX FTIR microscope with a pixel size of 25 µm in the transmission mode; 4 scan numbers and a spectral resolution of 8 cm-1 were applied. The spectral data were evaluated with the "simple" software designed for the analysis of microplastics. The data were compared to a library of reference spectra, and particles with > 70% correlation were considered microplastics.

Microplastics are small particles (< 5 mm) of plastic material dispersed in the environment (Calmuc et al., 2023). They have become a cause for concern as they accumulate in soils, rivers, lakes, and the marine environment and in some foods; within a few decades, they have contaminated all oceans and marine species at all levels, from one pole to the other, and even in the deep sea. These can be fragments of plastic objects or plastic microbeads (spherical plastic particles composed of synthetic polymers) that have been increasingly used in industry, cosmetics, or synthetic fibres and found abundantly in sewage sludge.

Additionally, plastics degrade slowly, often over hundreds if not thousands of years. This increases the likelihood that microplastics will be ingested and embedded in the bodies and tissues of many organisms.

Microplastics enter agriculture through sewage sludge - which, when processed, is used as fertilizer, through plastic films that prevent weed growth or protect seeds, or even intentionally as slow-release fertilizers.

Figure 2 shows the sample prepared for FTIR (Fourier Transform Infrared Spectroscopy) analysis.

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Figure 2. Sample prepared for FTIR analysis

Table 4 and Figure 3 show the results of the analysis. The distribution of polymer types is shown in Figure 4, and the distribution of particle sizes in Figure 5.

Table 4. Particle number and polymer type of identified microplastics

		The sum of the particles/ sample	Particles/g Sample dry matter
Microplastics identified (sum of particles/ sample)	Sample mass (g)	50	
	Dry matter content (%)	19.68%	
	PE	149	15.1
	PP	66	6.7
	Polyester	4	0.4
	PA	2	0.2
	Acrylic	3	0.3
	PVC	1	0.1
	PVA	1	0.1
	PVC	4	0.4
	PU	13	1.3
	PS	66	6.7
	ABS	6	0.6
	PTFE	1	0.1
	Cellulose acetate	33	3.4
	Alkyd	130	13.2
	Sum of MPs	**479**	**48.7**

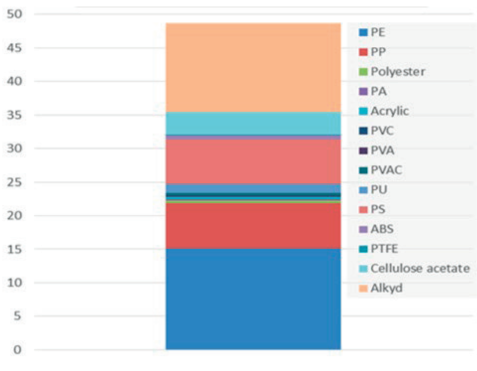

Figure 3. The number of particles and the type of polymer of the identified microplastics

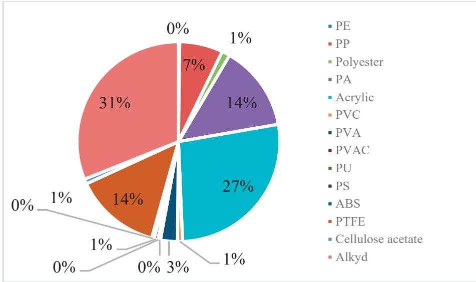

Figure 4. Distribution of polymer types

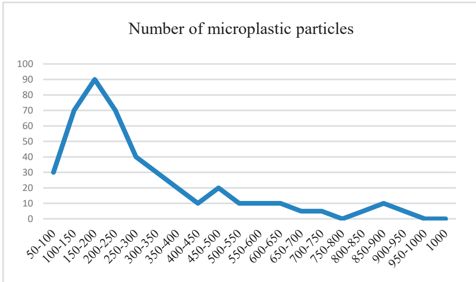

Figure 5. Distribution of particle sizes

Figure 6 present the existence of the types of microplastics detected in the sludge studied and Figure 7 the quantitative and dimensional analysis of the microplastics detected in the sludge studied. Although there are no concrete studies of human ingestion of microplastics, studies of mammals forced in laboratories to ingest these small fragments of plastic have shown that they can pass through cell walls, move through the body, accumulate in the body, and have an impact on the immune system.

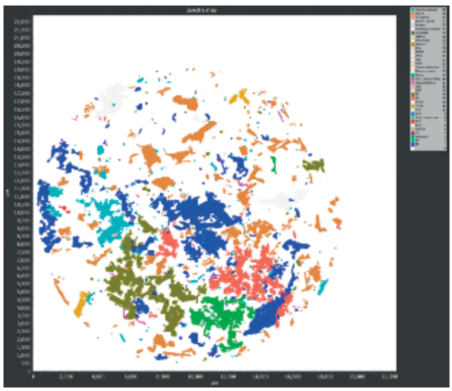

Figure 6. Image with the existence of the types of microplastics detected in the sludge studied

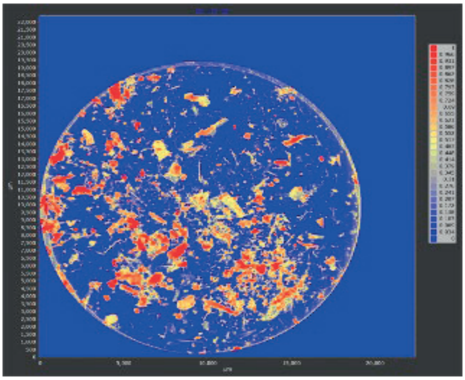

Figure 7. Image with the quantitative and dimensional analysis of the microplastics detected in the sludge studied

The elimination of those small plastic grains from care products (shower gels, face gels, toothpaste), the elimination of single-use plastic products, the ban of plastic films and slow-release fertilisers in agriculture, and companies that produce plastic films should be responsible for their recycling, are among the solutions proposed by specialists, which could solve the problem of microplastics in agricultural land.

CONCLUSIONS

This study research provides for the sludge analysis from the Pitești Wastewater Treatment Plant and the possibility of using this sludge in agriculture in its initial state, resulting from the treatment plant or even after any remediation required or appropriate treatment so that it can be used.

The major objective of sludge treatment in the treatment plant is to avoid the negative impact of environmental pollution and human health. The quality of the sludge differs a lot depending on the origin of the urban wastewater that enters the process, being almost impossible to predict the composition, implicitly their management.

Experimentally, a toxic potential of the anaerobically stabilized sewage sludge could be found at all analyzed levels of organization (prokaryote and eukaryote), especially at high concentrations of use.

Classified as biodegradable waste, anaerobically stabilized sewage sludge is a by-product of sewage treatment plants, whose pathogenic potential presents a health risk for humans but also for the environment. Ecotoxicological effects can manifest in a short, medium or long time, simultaneously with the bioaccumulation effect of heavy metals or other categories of present pollutants.

Long-term spreading of sludge on agricultural land can lead to the accumulation of contaminants (i.e., heavy metals) in agricultural soil and can affect the entire ecosystems. Even if the level of accumulation might not exceed the currently accepted values, scientific research on soil and flora interactions allows us to understand their risk to the environment.

The final conclusions of this study:

The studied sludge has concentrations for some heavy metals that exceed the values allowed by the legislation to which we refer, i.e., Order no. 344/2004.

The presence of pharmaceutical substances derived from antibiotics and hormones causes high toxicity of the sludge, and its use on agricultural land presents a real danger for the entire food chain: for soil, soil water, plants, animals, and people.

The presence of microplastics in a considerable number and of a great variety in the analyzed sludge leads us to the same conclusion, namely that the analysed sludge from Pitești WWTP cannot be used in agriculture.

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