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The influence of stabilization technology on selected properties of municipal sewage sludge

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ABSTRACT

This article assesses the properties of municipal sewage sludge stabilized using various stabilization technologies. Raw, stored, lime-stabilized, and stabilized sludge through aerobic composting were evaluated. The study assessed the chemical properties of the sludge, including pH and sorption capacity; available of P, K, and Mg; organic carbon and total nitrogen content; and selected heavy metals. The study revealed that the studied sewage sludge was characterized by a slightly acidic pH, high sorption capacity, and high content of available of P, K, and Mg, with low heavy metal content, qualifying it for agricultural use. The organic carbon content in lime- and aerobically stabilized sludge allows it to be classified as organic fertilizers, while stored sludge is classified as organic-mineral fertilizers. Stored sewage sludge had the lowest total nitrogen content and the highest carbon-to-nitrogen ratio. Raw sewage sludge has potential as an agricultural fertilizer, but its effectiveness and safety depend on its quality, processing method, and appropriate application. Pretreatment is recommended before agricultural application. Assessment of the properties of sewage sludge has shown that it can be used as a substitute for mineral fertilizers.

Keywords: municipal sewage sludge, stabilization, chemical properties.

INTRODUCTION

Sewage sludge is a byproduct of sewage treatment plants and must be properly used and managed. Sewage sludge management encompasses several key aspects and poses a serious economic, social, and environmental problem. Sewage sludge generated in massive quantities poses a challenge for humans, requiring energy-intensive and costly treatment processes in sewage treatment plants and safe disposal methods [1]. Over 10 million tons of dry sewage sludge are produced annually in the European Union, as confirmed by a European Commission report. The implementation of the EU Directive on Urban Wastewater Treatment 91/271/EEC and the introduction of advanced technologies in the development of treatment plants are a result of these enormous volumes. Landfilling sewage sludge is considered the least desirable method of managing this waste, due to its impact on the economy (occupancy of landfills, transportation costs), the environment (accumulation of heavy metals in soil and release of greenhouse gases), and society (social acceptance, soil loss, public health) [2, 3]. A safe sewage sludge management method is based on the assessment of the sludge's properties, which depend on the operating conditions of the treatment plant and the effectiveness of the sludge stabilization processes, as well as the quality of the treated wastewater [4]. The term "sewage sludge" commonly refers to sewage sludge stabilized through treatment processes, characterized by properties that meet regulations regarding its beneficial use [5]. The circular economy strategy prioritizes the reuse of sewage sludge, especially its use for agricultural purposes. Using sewage sludge in agriculture allows for the replacement or reduction of chemical fertilizers, which translates into both environmental and economic benefits [6]. Directly, using conventional methods for sewage sludge disposal or incineration, nearly 40% of the dry solid waste produced annually in the European Union was recycled in agricultural activities [7], including Poland (20%), and in other countries such as Australia (55%), Spain (64%), and the United Kingdom (79%) [8]. Limitations on the use of sewage sludge in agriculture include threats to soil and water quality and odor problems. Sludge treatment processes in wastewater treatment plants, including hygienization and stabilization, are crucial [3]. Recycling into the ground is currently recognized as one of the most beneficial and economical methods of municipal sewage sludge management [9]. The suitability of municipal sewage sludge for agricultural use is assessed based on its fertilizing properties, including the content of organic carbon and total nitrogen, phosphorus, potassium, and the presence of contaminants that may limit its use [10]. Municipal sewage sludge contains valuable fertilizing components, such as organic carbon (200–400 g/kg DM), total nitrogen (20–60 g/kg DM), phosphorus (10–30 g/kg DM), and potassium (1–10 g/kg DM) [11, 12], making it potentially useful in agriculture. However, it can also contain contaminants such as heavy metals (e.g., cadmium, lead, mercury), organic compounds (e.g., PAHs, PCBs), pharmaceutical residues, microplastics, and pathogens, which may limit its use. Therefore, before use, sludge must meet quality standards and be appropriately processed (e.g., stabilized and hygienized). The aim of the study was to evaluate the fertilizing properties of municipal sewage sludge stabilized using various technologies.

MATERIALS AND METHODS

Samples of municipal sewage sludge stabilized using various methods were collected from selected sewage treatment plants in Poland (Figure 1). The characteristics of the sewage treatment plants and sludge studied are presented in Table 1. The study included: raw sludge (treatment plants from Słupsk and Swarzewo), sludge subjected to chemical stabilization by liming with CaO (treatment plants from Zamość and Stalowa Wola), sludge stabilized aerobically in the composting process (from the treatment plants in Stalowa Wola and Tarnobrzeg), and sludge dried by storage for 6 years in a sludge lagoon (treatment plants in Kielce and Końskie).

The tests were conducted on representative sludge samples collected and prepared according to the adopted methodology [13]. A representative sludge sample for testing was obtained by combining and thoroughly mixing 15 primary samples collected simultaneously from different locations in the sludge to be tested. A composite sample was prepared from the collected primary samples by thoroughly mixing them in

Figure 1. Location of municipal sewage treatment plants covered by sewage sludge studies. A. Słupsk, B. Swarzewo, C. Kielce, D. Zamość, E. Tomaszów Lubelski, F. Tarnobrzeg, G. Stalowa Wola, H. Końskie

Table 1. Characteristics of sewage treatment plants and sludge

Type of sewage sludge		Sampling location	Treatment plant parameters	
			RLM (population equivalent)	Capacity m^3/day
SS-R1	Raw sewage sludge	Słupsk	330640	19647
SS-R2	Raw sewage sludge	Swarzewo	130000	14000
SS-L1	Lime-stabilized sewage sludge	Zamość	250000	40000
SS-L2	Lime-stabilized sewage sludge	Tomaszów Lubelski	63420	7600
SS-S1	Aerobically stabilized sewage sludge	Tarnobrzeg	61277	4760
SS-S2	Aerobically stabilized sewage sludge	Stalowa Wola	88240	17500
SS-D1	Sludge stored for 6 years in a heap	Kielce	289000	51000
SS-D2	Sludge stored for 6 years in a heap	Końskie	21250	1851

a container. For this purpose, the mixed sample was formed into a cone shape and divided into four parts of equal thickness and diameter, taking into account the irregular shape. Opposite quarters were retained and recombined. This process was repeated until the final two quarters formed the required sample mass. After thorough mixing, the sewage sludge was collected in a prepared plastic container or sterile bag. The mass of the test sample was approximately 1 kilogram. The sludge was then dried, averaged again, and sieved through a 0.2 mm sieve.

Laboratory tests determined:

- potentiometric pH in H_2O and 1 mol/dm^3 KCl [14],
- hydrolytic acidity (Hh) using the Kappen method in 1 mol/dm^3 CH_3COONa [15],
- base cations (S) using the Pallmann method in 0.5 mol/dm^3 NH_4Cl^- (pH 8.2) [16],
- sorption capacity (T=S+H) and the degree of saturation of the sorption complex with base cations (V = 100 S/T) were calculated,
- content of available forms of phosphorus, potassium using the Egner-Riehm method, and magnesium using the Schachtschabel method [17–19],
- organic carbon content using a TOC analyzer using the TOC-VCSH, SSM-5000A apparatus [18],
- total nitrogen content using the modified Kjeldhal method using a KjeltechTM 8100 distillation unit [19],
- heavy metal content (Cu, Zn, Pb, Cd) – the collected sediment sample, after drying, averaging, and grinding, was wet mineralized in a mixture of concentrated nitric acid and perchloric acid in a 5:4 ratio. A 0.5 g aliquot of the sediment was poured over 18 ml of the acid mixture and mineralized in a mineralizer. After mineralization, the sample was transferred to a 25 ml flask and filled to the mark with deionized water. The heavy metal content was determined by ICP-AES using a Leeman PS 950 apparatus [20].

RESULTS AND DISCUSSION

The high variability of the chemical composition of municipal sewage sludge depends on the properties of the wastewater and the treatment and processing technology. A characteristic feature of sewage sludge is its relatively high hydration, ranging from 99% in the case of raw sludge to 85–55% in dewatered sludge. Moisture values below 10% are observed only in thermally dried sludge [21]. Sewage sludge is characterized by heterogeneous chemical composition, varying contents of aldehydes, ketones, organic acids, hydrocarbons, heavy metal concentrations, and microbiological contamination [22]. High content of heavy metals and harmful organic compounds poses a significant problem related to the environmental use of municipal sewage sludge [23, 24] and the presence of pathogenic organisms – pathogenic bacteria of the Enterobacteriaceae genus (e.g., Salmonella, Shigella), fungi (especially dermatophytes), viruses, and eggs of parasites of the gastrointestinal tract of humans and animals [25]. The use of sewage sludge for environmental purposes involves the use of methods that change its chemical composition, improve its physical properties, and improve its sanitary condition [26]. The basic processes used in sewage sludge processing include thickening, stabilization, dewatering, drying, and incineration [21]. Sewage sludge stabilization can be carried out through chemical, thermal, and biological processes, resulting in changes in the biological and chemical composition of the sludge. Increasing the effectiveness of sewage sludge stabilization is achieved through the use of methods that increase the sludge's biodegradability [21]. Sludge stabilization processes change the hazardous properties of sludge components, transforming hazardous waste into non-hazardous waste [27]. Studies have shown that the properties of the assessed sewage sludge varied depending on the stabilization technology used. The reaction of municipal sewage sludge was slightly acidic, with pH in 1 mol KCl.dm^{-3} ranging from 5.5 to 6.5. Only sewage sludge stabilized with lime (SS-L1) had an alkaline reaction, pH in 1 mol KCl.dm^{-3} was 7.9 (Figure 2). Most other authors also confirm the obtained research results. Studies of the physicochemical properties of various sewage sludge from individual European Union countries showed that the pH of sewage sludge ranged from acidic to alkaline [28–30]. The results of research by Polish authors also confirm that the pH of municipal sewage sludge ranges from acidic to neutral and/or alkaline [32–35]. However, sewage sludge stabilized with CaO was characterized by a lower pH than in the studies of other authors. Our own studies showed a pH below 8.0 for individual sediments; while studies by other authors showed a pH above 8.0 [37, 38]. However, the mixture formed after the addition of CaO has favorable physical properties from the point of view of transport, storage, and spreading on the field surface [38].

The sorption capacity of municipal sewage sludge varied depending on the degree of sludge processing and ranged from 12.91 cmol(+)·kg^{-1} (SS-D2) to 33.66 cmol(+)·kg^{-1} (SS-R1). The absorption capacity of sewage sludge is primarily driven by its organic matter content, cation exchange capacity, and pH. These influence how effectively the sludge can retain and supply nutrients to plants. The presence of exchangeable calcium, magnesium, and potassium contributes significantly to its fertilizer value, enhancing soil structure, plant nutrition, and buffering capacity. Therefore, sludges rich in these cations and with high CEC are particularly valuable as soil amendments. Landfilled municipal sewage sludge had a lower sorption capacity (Table 2). Analyzing the share of exchangeable cations in sorption capacity, it should be noted that the degree of sludge processing affected the share of cations in the total sorption capacity (Table 2).

The exchangeable calcium content ranged from 3.41 cmol(+).kg^{-1} in raw sewage sludge (SS-R1) to 3.89 cmol(+).kg^{-1} in lime-stabilized sewage sludge (SS-L2). Exchangeable magnesium contributed the largest share of sorption capacity. Its content ranged from 4.01 cmol(+).kg^{-1} in stabilized sewage sludge (SS-D2) to 13.66 in stabilized sludge (SS-S1). The exchangeable potassium content in the analyzed municipal sewage sludges ranged from 1.18 cmol(+).kg^{-1} in stored sludge (SS-D2) to 6.66 cmol(+).kg^{-1} in lime-stabilized sewage sludge (SS-L2). The exchangeable sodium content ranged from 1.31 cmol(+).kg^{-1} in the sludge (SS-D2) to 4.74 cmol(+).kg^{-1} in the lime-stabilized sludge (SS-L2). The hydrogen content ranged from 1.80 cmol(+).kg^{-1} in the sludge (SS-L1 and SS-L2) to 7.50 cmol(+).kg^{-1} in the raw sludge (SS-R1). A clear effect of the sludge processing degree on the H^+ ion content in the sorption complex was observed. The lowest H^+ ion content was found in the lime-stabilized sludge, and the highest in the raw sludge. The evaluated sewage sludges were characterized by a high degree of saturation of the

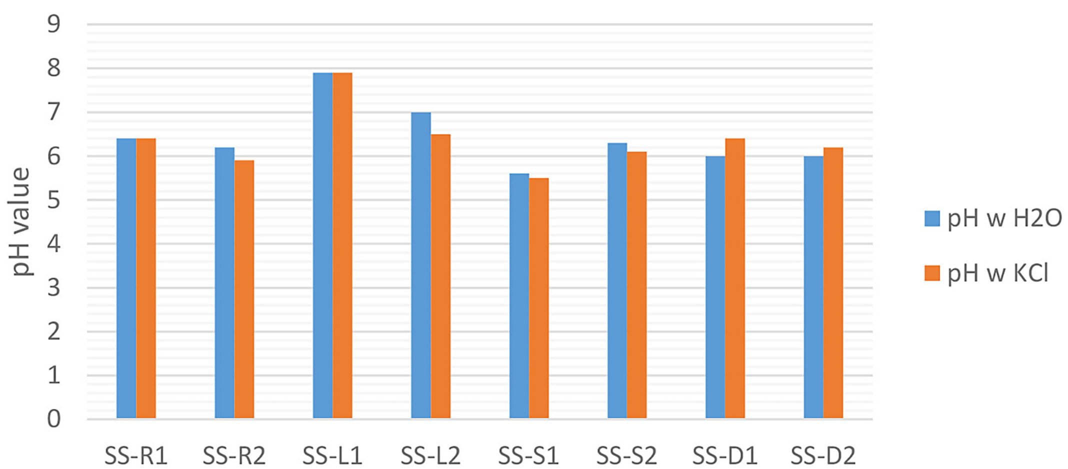

Figure 2. Reaction of municipal sewage sludge. SS-R1,R2 – raw sewage sludge; SS-L1,L2 – limed sewage sludge; SS-S1,S2 – stabilized sewage sludge; SS-D1,D2 – stored sewage sludge

Table 2. Sorption properties of municipal sewage sludge

No.	Type of sewage sludge	Exchangeable cations				Sorption properties			
		Ca^{++}	Mg^{++}	K^+	Na^+	H^+	S=[Ca+Mg+K+Na]	T=S+H	V=100S/T
		cmol (+)·kg^{-1}							%
1.	SS-R1	3.41	13.42	6.13	3.21	7.50	26.16	33.66	77.72
2.	SS-R2	3.56	12.43	4.04	4.04	7.25	24.07	31.32	76.85
3.	SS-L1	3.56	8.64	4.18	1.53	1.80	17.92	19.72	90.87
4.	SS-L2	3.89	4.33	6.66	4.74	1.80	19.63	21.43	91.60
5.	SS-S1	3.64	13.66	2.79	1.99	5.98	22.09	28.07	78.70
6.	SS-S2	3.82	7.70	3.03	3.48	3.38	18.03	21.41	84.21
7.	SS-D1	3.64	6.39	2.74	1.65	2.25	14.42	16.67	86.50
8.	SS-D2	3.61	4.01	1.18	1.31	2.80	10.11	12.91	78.31
Minimum		3,41	4.01	1.18	1.31	1.80	10.11	12.91	76.85
Maximum		3,89	13.66	6.66	4.74	7.50	26.16	33.66	91.60
Average		3,64	8.82	3.84	2.74	4.10	19.05	23.15	83.10
Standard deviation		0,15	3.93	1.83	1.29	2.43	5.20	7.23	6.04

sorption complex with alkaline cations (Table 2). The highest degree of saturation of the sorption complex with alkaline cations was characterized by the lime-stabilized sludge (V = ca. 90%). Similar results were obtained by other authors [40–42].

Test results of available forms of potassium, phosphorus, and magnesium, as well as the fertilizer suitability of the sludge, are summarized in Table 3. The available phosphorus content in the assessed sewage sludge ranged from 122 mg.kg^{-1} to 292.1 mg.kg^{-1}. The total phosphorus content in sewage sludge varies widely (from approximately 1 to over 3%) [30], but only a small portion occurs in compounds available to plants. The amount of available potassium forms in the assessed sewage sludge was low, ranging from 18.1 to 61.1 mg.kg^{-1}. Numerous authors point out the deficient content of this nutrient in sewage sludge [42]. The content of available forms of magnesium in sewage sludge depended on the origin of the sewage sludge. The lowest content was found in stored sewage sludge (SS-D2), while the highest in raw sewage sludge (SS-R1) (192 mg.kg^{-1}) and lime-stabilized sludge (SS-L1 and SS-S2) (over 180 mg.kg^{-1}). One of the main components of sewage sludge is the significant content of organic matter. The content of organic matter in sewage sludge is determined by the chemical composition of treated sewage, the course of the treatment process, and the degree of sludge processing, which is confirmed by numerous scientific studies [43–46]. The amount of organic carbon in the tested sewage sludge ranged widely – from 234 g.kg^{-1} to 480 g.kg^{-1} (Table 3), and depended on the type of treatment plants tested and the degree of sludge processing (raw sludge, sludge with lime added, stabilized sludge, and stored sludge). In raw sewage sludge, the organic carbon content was similar and ranged from 462 g.kg^{-1} to 480 g.kg^{-1}. The amount of organic carbon in sewage sludge stabilized with lime ranged from 336 g.kg^{-1} to 462 g.kg^{-1}. Stabilization of sewage sludge with lime had a beneficial effect on the Corg content, which is related to the effect of calcium on reducing the intensity of organic matter mineralization [47]. In stored sewage sludge, the amount of organic carbon ranged from 234 g.kg^{-1} to 330 g.kg^{-1}. It cannot be clearly stated whether these contents resulted from the type of treated sewage or from the storage process. Żukowska et al. [48] found that 6 years of storage of sewage sludge from the municipal-industrial treatment plant in Końskie significantly reduced the Corg content, which qualified it as organic-mineral waste. In turn, most fresh and stabilized sewage sludge is classified as organic waste. Differences in organic carbon content in the assessed sewage sludge were accompanied by changes in total nitrogen content. Its content ranged within a very wide range of 11.55–51.52 g.kg^{-1} (Table 3). These results are confirmed by numerous studies, which indicate a high nitrogen content in municipal sewage sludge [42,49]. The lowest total nitrogen content was found in landfilled sewage sludge (11.55–17.78 g.kg^{-1}). The total nitrogen content in raw sludge ranged between 40.25 g.kg^{-1} and 46.76 g.kg^{-1}. The

Table 3. Content of available forms of P, K, Mg, Corg., Nog., and C:N in municipal sewage sludge

No.	Type of sewage sludge	Available ingredients			Organic matter and nutrients		
		P	K	Mg	Corg.	Nog.	C:N
		mg·kg-1			g·kg-1		
1.	SS-R1	287.8	27.2	192.0	462	40.25	11.48
2.	SS-R2	244.2	54.6	166.0	480	46.76	10.27
3.	SS-L1	248.0	18.1	77.7	336	23.80	14.12
4.	SS-L2	196.2	25.9	31.0	462	51.52	8.97
5.	SS-S1	259.0	57.1	181.0	414	36.68	11.29
6.	SS-S2	122.0	16.5	186.0	420	35.56	11.81
7.	SS-D1	292.1	61.1	74.2	234	11.55	20.26
8.	SS-D2	157.0	54.5	57.9	330	17.78	18.56
Minimum		122.00	16.50	31.00	234.00	11.55	8.97
Maximum		292.10	61.10	192.00	480.00	51.52	20.26
Average		225.79	39.38	120.73	392.25	32.99	13.35
Standard deviation		61.59	19.10	66.59	85.15	14.05	4.04

amount of total nitrogen in lime-stabilized sewage sludge ranged between 23.80–51.52 g.kg^{-1}. The differences found in the calculated C:N ratio were a consequence of differences in the organic carbon and total nitrogen content in the assessed sludge. In most of the assessed sewage sludge, the C:N ratio ranged from approximately 8 to approximately 11, and these values were typical for humus horizons in mineral soils. Slightly higher C:N ratio values were found in sewage sludge stabilized with lime (SS-L1). The highest C:N ratio values were found in stored sludge (SS-D1 and SS-D2). It can be assumed that in these facilities, during the process of nitrogen release during the mineralization of organic matter, a simultaneous process of intensive leaching of mineral nitrogen compounds occurred. In addition to organic matter and plant nutrients, sewage sludge may contain varying amounts of heavy metals, which is confirmed by other authors in their works [29, 30]. The concentration of heavy metals in sewage sludge depends on the quality of treated wastewater and the treatment technology. The heavy metal content in the analyzed sewage sludge varied

Table 4. Heavy metal content in municipal sewage sludge

No.	Type of sewage sludge	Heavy metal content			
		Cu	Zn	Pb	Cd
		mg·kg-1			
1.	SS-R1	163.0	676	59.3	1.7
2.	SS-R2	178.0	625	28.1	1.7
3.	SS-L1	77.8	672	28.4	1.2
4.	SS-L2	29.2	341	22.8	0.7
5.	SS-S1	130.0	686	68.3	2.2
6.	SS-S2	164.0	825	39.3	2.8
7.	SS-D1	89.4	636	49.4	2.1
8.	SS-D2	141.0	459	79.8	2.0
Reference values for sewage sludge used for agricultural purposes (Dz. U. Nr 137, poz. 924)		1000	2500	750	20.0
Minimum		29.20	341.00	22.80	0.70
Maximum		178.00	825.00	79.80	2.80
Average		121.55	615.00	46.93	1.80
Standard deviation		51.59	149.31	20.82	0.64

(Table 4). The copper content in municipal sewage sludge ranged from 29.2 mg.kg^{-1} (SS-L2) to 178 mg.kg^{-1} (SS-R2), which are within the permissible limits [50]. The highest copper content was found in raw sewage sludge, landfilled sewage sludge, and sewage sludge from treatment plants contaminated with industrial wastewater. The total zinc content ranged from 341 mg.kg^{-1} (SS-L2) to 825 mg.kg^{-1} (SS-S2) (Table 4). These values were significantly lower than the reference values [48]. The lead content, similar to that of other heavy metals, was lowest in limed sewage sludge (SS-L2) (22.80 mg.kg^{-1}). The highest lead content was found in the stored (SS-D2) and stabilized (SS-S1) sewage sludge, at 79.8 and 68.3 mg.kg^{-1}, respectively. These values were significantly lower than the permissible limits [50]. The total cadmium content ranged from 0.74 mg.kg^{-1} (SS-L2) to 2.77 mg.kg^{-1} (SS-S2) and was considered low [50].

Regardless of the differences found in the content of the assessed heavy metals, it should be noted that these contents were significantly lower than the reference values contained in the Regulation on Municipal Sewage Sludge [50] and, based on this criterion, the assessed sewage sludge can be used for environmental purposes.

CONCLUSIONS

The conducted research indicates that the technologies used to stabilize sewage sludge influence its fertilizing properties. Regardless of the stabilization technology, sewage sludge had a slightly acidic reaction, high sorption capacity, and high content of available forms of phosphorus, potassium, and magnesium, which qualify it for agricultural use. Under current EU and national regulations on agricultural fertilizers, including Regulation (EU) 2019/1009 of the European Parliament and of the Council and the Fertilizers and Fertilization Act, for a material to be classified as an agricultural fertilizer, it must contain minimum amounts of essential nutrients in an available form. For phosphorus in the form of phosphorus oxide (P_2O_5), the minimum content is 2%; for potassium in the form of potassium oxide (K_2O), the minimum content is 2%; for magnesium in the form of magnesium oxide (MgO) soluble in 2% citric acid solution, the minimum content is 2%; and for calcium in the form of calcium oxide (CaO), in the case of calcium fertilizers, the minimum content is 10%. In the context of assessing the suitability of municipal sewage sludge for agricultural use, the content of these nutrients in the analyzed material is crucial. If the sludge contains available forms of phosphorus, potassium, magnesium, and calcium in amounts exceeding the specified limits, it can be considered a valuable organic or organomineral fertilizer. Such sludge not only provides plants with essential nutrients but also improves the physicochemical and biological properties of the soil. Organic carbon content in sewage sludge ranged widely – from 234 g.kg^{-1} (stored sludge) to 480 g.kg^{-1} (raw sludge) – and depended on the origin and degree of sludge processing. The Corg content in CaO^{-} and oxygen-stabilized sludge allows the assessed sludge to be classified as organic fertilizers, while the stored sludge can be classified as organic-mineral fertilizers. CaO^{-}stabilization of sewage sludge, which reduced the mineralization rate, favorably affected the nitrogen content and its ratio to organic carbon (C:N). The lowest nitrogen content and the highest carbon-to-nitrogen ratio were found in landfilled sewage sludge, as the mineralization of organic matter was accompanied by the release and intensive leaching of nitrogen compounds. The heavy metal contents assessed varied, but regardless of the stabilization technology, they were significantly lower than reference values. The properties of the analyzed sewage sludge confirm that its use as a fertilizer could be a substitute for synthetic fertilizers. Consequently, this will reduce the demand for natural raw materials used to produce mineral fertilizers. The evaluated sewage sludge, with the exception of the landfilled sludge, was characterized by a significant organic carbon content, therefore its introduction into soils may promote carbon sequestration in the soil. Lime-stabilized and composted sewage sludge demonstrated good fertilizing properties. Due to its high content of organic carbon and total nitrogen, the use of lime-stabilized sewage sludge may contribute to increased emissions of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O), which reduces its fertilizing potential as they are greenhouse gases.

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