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Digestion Procedure and Determination of Heavy Metals in Sewage Sludge—An Analytical Problem

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Abstract: Huge amounts of sewage sludge produced globally is a substantial environmental threat and require rational handling. Application in agriculture is an economical and relatively simple method of sludge management, however, it is associated with restrictions regarding metals content. According to EU regulations, the total amounts of Cd, Cu, Cr, Pb, Ni, and Zn have to be analyzed by the AAS technique requiring effective destruction of the organic matrix. Currently used methods of sewage sludge digestion may be biased when applied without optimization. The aim of the presented work was to evaluate the efficiency of the organic substances destruction in either raw or stabilized sludge. Three mineralization procedures were evaluated, namely: (A)—drying and microwave digestion; (B)—ignition and microwave digestion; (C)—drying and conventional digestion. For matrix destruction, a mixture of concentrated HNO_3 and HCl (3:1 *v*/*v*) was used. Metals were determined by flame atomic absorption spectrometry (FAAS). No limits of metal concentration were overdrawn. Generally, the method (B) was the most effective. Results obtained for Cu, Cd, and Zn after digestion by method (A) and (B) were comparable. Methods (B) and (C) yield complete decomposition of the matrix. As result, the precision of measurement substantially increases.

Keywords: sewage sludge; municipal wastewater treatment plant; heavy metals; FAAS method

1. Introduction

Sewage sludge is a by-product of wastewater treatment. During the wastewater treatment processes, products are separated into liquid and solid phases. Among the solid residues, the largest volume is sewage sludge. The raw sludge contains less than 12% solids [1]. The population growth, the upgrading of new municipal sewage treatment plants and modernization of old facilities result in an increase in sludge production. Therefore, the possibility of its processing is of great interest in the EU. The EU strategy consists in the gradual reduction of the load of stored sludge by means of their reuse, energy recovery or recycling. On 4 March 2019, the European Commission adopted a report on the implementation of the Circular Economy (CE) Action Plan [2]. According to the concept of the CE, the actions will aim to prevention of waste, achieve "closing the loop" of product lifecycle by recovery and reuse. Waste should be treated as secondary raw materials. Sewage sludge fits perfectly into the CE concept as a source of elements, chemical compounds, water and energy [2,3]. Sludge recovery brings significant benefits for environment and economy.

Sludge management includes the following methods e.g., landfilling, thermal processes, application to agricultural land, composting, wasteland reclamation and silviculture, use in the construction industry or recovery of rare earth metals [1,4–10]. In 2014, total sewage sludge generated in Poland from industrial and municipal wastewater treatment plants was 967.4 thous. Mg of dry matter. Major methods for sludge management were (in 2014): agriculture (128.2 thous. Mg), land reclamation (117.0 thous. Mg), cultivation of plants intended for compost production (48 thous. Mg), incineration (164.4 thous. Mg), landfilling (135.2 thous. Mg) [11]. The widely used waste treatment technologies are the thermal processes and the use of sludge in agriculture.

There are numerous methods of sewage sludge thermal treatment. Drying and biodrying allow for reducing operating costs. Incineration is the most popular way of thermal decomposition of toxic organic compounds and pathogens, significant reduction of waste volume, minimization of odor generation. An alternative technology are pyrolysis and gasification. Their final products are widely used in the industry. Wet oxidation may be applied primarily in industrial wastewater treatment plant. As case studies, four technologies for sewage sludge management in Italy were described [12]. Wet-oxidation system was adopted to municipal plants, but it does not provide a sufficiently low level of nitrogen. Combined biological and conventional processes were used for biomass reduction (so-called cannibalization). Pyrolysis is the third type of sewage sludge treatment. Final products are used to heat the process water and a sewage sludge thermal drier, although it is necessary to optimize the technological parameters. Co-combustion is used successfully in cement works. In Poland, the innovative Bionor Sludge wastewater treatment technology has been used [13]. Biomass is composting in high-temperature conditions, the final product can be applied as fertilizer for soil improvement or as a source of energy. Therefore, it is part of the CE strategy.

Sewage sludge contains organic compounds and plant nutrients. The Council Directive 86/278/EEC [14] pays particular attention to the use of sludge in agriculture and encourages Member States to use this recycling technology. However, this method of waste management is acceptable provided that "*the use of sewage sludge must not impair the quality of the soil and of agricultural products*". The use of sewage sludge in agriculture is an economical method of its utilization, it favors the rapid growth of plants, prevents soil erosion, improves the soil structure and enriches it with micronutrients [4]. On the other hand, its composition is very complex and depends on the origin and load of wastewater and also on the applied methods of wastewater treatment. High fluctuation of chemical composition of sewage sludge is characteristic of small communities. During the day large variations of total nitrogen, COD and BOD were observed [15]. Sludge may contain some biological and chemical toxins, like pathogens, heavy metals, poorly biodegradable organic compounds e.g., chlorinated hydrocarbons, dyes or heterocyclic compounds. Due to a high concentration of nutrients and contaminants, the utilization of sludge in agriculture is still widely discussed. After sludge application to land, nutrients are transported with rainfall into the groundwater. Due to the high content of readily soluble inorganic substances, the use of sewage sludge in agriculture may cause soil salinity. Heavy metals form sparingly soluble compounds with soil constituents but some of the cations (e.g., cadmium) are very easily leached and consequently pollute the groundwater, may be taken up by plants and enter the food chain. Long-term accumulation of heavy metals in soil may subsequently cause water pollution and soil degradation [16–19]. The risk of biomagnification of metal in the food chain depends on the properties of the element, its form and the mechanism of binding to the sludge [1]. Therefore, sewage sludge may be used as a good, cheap fertilizer or soil conditioner provided that the composition of sludge and soils on which it will be used is regularly checked and correct sludge doses are used [7,14].

According to current regulations [14,20–22], sludge can be used in agriculture because of its valuable agronomic properties. In the sludge used for some agricultural, composting and land reclamation purposes, the maximum amounts of some heavy metals are strictly limited. In Poland, obligatory regulations [22] set the maximum allowable values of trace elements in municipal sludge recycled for agriculture at 750 mg/kg (Pb), 500 mg/kg (Cr) (not regulated by the European legislation [14]), 20 mg/kg (Cd), 16 mg/kg (Hg), 300 mg/kg (Ni), 2500 mg/kg (Zn) and 1000 mg/kg (Cu). The above-mentioned limits concern the total amounts of contaminants and these quantities correspond to the lower limit set by the Sewage Sludge Directive [14]. It is commonly known that total metal contents in soil, sludge or fertilizer are not the best indicator of their mobility, bioavailability and toxicity. Environmental risk of heavy metals depends on their chemical speciation, chemical composition of sewage sludge, soil properties etc. However, there are no directives concerning the analysis of more soluble forms of heavy metals in sludge. Despite a large number of literature data presenting different schemes for the release of metals (single and sequential extractions), there are no comparable methods of analysis [1,6,23–27]. The forms of metal determine the environmental risk resulting from the use of sludge [28]. According to the Regulation of Minister of the Environment [22], lead, cadmium, mercury, nickel, zinc, copper and chromium must be determined after samples digestion using a strong acid (*aqua regia* or other mixtures of concentrated acids). The reference analysis must be performed by atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES). The limit of detection should be no greater than 10% of the limit value for an appropriate metal. The Polish Standard [29] recommends conventional or microwave extraction of sludge with *aqua regia* for matrix destruction.

The study reported in the paper was undertaken: (i) to compare and assess the efficiency of sewage sludge digestion methods and (ii) to estimate the quality of sewage sludge from a modernized municipal wastewater treatment plant in the context of further application of the wastes in agriculture. The sample preparation is a crucial step which ensures the quality of the whole analytical process. Several procedures as used for the decomposition of sewage sludge and other samples with substantial organic matrix contributions (thermal or microwave destruction with different types of reagents) are reported in the scientific literature [30–37]. The authors of those works addressed the issue of environmental samples complexity with a special attention paid to organic carbon and silica. The factor which significantly influences the retention of heavy metals in a sample is the organic matter. The composition of organic fraction may be quite complicated indeed. Some of these compounds are stable, resistant to oxidation and coordinate metal cations substantially. It is, therefore, necessary to develop a general, analytically efficient method which releases a majority of metals from the matrix. The research objects of our work were raw sewage sludge and lime-stabilized sludge. Three digestion procedures were based on the use of a HNO_3 and HCl mixture. The concentration of the total amounts of trace elements were determined by FAAS.

2. Materials and Methods

All heavy metals were analysed in excess sludge samples from the biological unit of the municipal wastewater treatment plant (population equivalent (PE) 9073) located in the Lodz Voivodeship (Central Poland). In 2017 the plant has a daily flow 865 m^3/d and the total annual flow 315,880 m^3. Eight sludge samples were taken in winter directly from a filter press (unstabilized sludge—samples No. 1, 3, 5, 7) and after the process of their stabilization with calcium oxide (samples No. 2, 4, 6, 8). Samples were dried at 60 °C, ground and passed through a 1 mm stainless steel sieve, stored in closed, polyethylene (PE) bottles, in the dark, at ambient temperature [38]. Organic matter content was determined by the weight lost after drying at 105 °C for 6 h and then ignition at 600 °C in a muffle furnace for 6 h [30]. Sludge pH was determined by the potentiometric method in 1 mol/dm^3 KCl solution (sample:KCl ratio 1:2.5 *m/v*) [31], using pH-meter Mettler Toledo Delta 350. In order to determine the amount of heavy metals, dried sludge samples were mineralized with a mixture of concentrated acids (HNO_3 d = 1.4 g/cm^3 and HCl d = 1.18 g/cm^3) in ratio 3:1 *v/v*. Three digestion procedures (A, B, C) were carried out.

Method A (microwave acid digestion)—0.5 g of the dried (105 °C) sample was digested with 6 cm^3 of concentrated HNO_3 and 2 cm^3 of concentrated HCl in closed polytetrafluoroethylene (PTFE) vessels in a microwave oven (UniClever BM—1z, Plazmatronika, Poland). A three-stage protocol (as below) was used. After digestion the solution with a solid phase was placed into the 100 cm^3 volumetric flask, filled to the mark with Type I (ISO 3696) deionized water of resistivity > 10 MΩ·cm and filtered through a filter paper (pore size 8 µm, medium porosity) to a PE bottle.

Method B (microwave acid digestion)—0.5 g of the roasted (600 °C) sludge was mineralized and treated according to Method A.

Microwaves operation parameters as applied in methods A and B

	heating time [min]	pressure [atm]	power [%]
Step 1	5	17–20	60
Step 2	10	24–27	80
Step 3	10	27–30	100

Method C (wet acid digestion in an open system)—Sewage sludge was dried to constant weight at 105 °C. Then 1 g aliquot of each sludge was digested using a mixture of 12 cm^3 HNO_3 and 4 cm^3 HCl. Samples were boiled for 2 h in covered beakers on a hot plate. All solutions with undissolved residual phases were transferred into the 100 cm^3 volumetric flasks and filled to the mark with deionized water followed by filtration through medium filters as above to the PE bottles.

Digests as obtained by A, B and C procedures were stored for no longer than 24 h in the temperature of about 8 °C prior to FAAS analysis.

Heavy metal (Cd, Cu, Ni, Pb, Zn) contents were determined directly in respective solutions by FAAS (the GBC 932 plus spectrometer) with the air-acetylene flame and hollow cathode lamps (HCL) as light sources. To reduce matrix effects on the determination of chromium, digests were diluted with 1% solution of $LaCl_3$ in a ratio 4:1 (*v*/*v*).

The following spectrometer parameters were used:

	Cd	Cr	Cu	Ni	Pb	Zn
Lamp current [mA]	4	7	4	4	10	5
Slit [nm]	0.5	0.2	0.5	0.2	1.0	1.0
Wavelength [nm]	228.8	357.9	324.7	232.0	217.0	213.9

All reagents were of analytical grade. Standard stock solutions of metals (1.0000 mg/dm^3 as nitrate salts in 0.5 mol/dm^3 nitric acid) were obtained from Merck. Standard solutions were prepared by appropriate dilution of stock standards with deionized water. All other reagents were purchased from POCh (Poland).

3. Results and Discussion

Our results clearly indicate that the content of organic matter in the raw sewage sludge under study is relatively stable (73–75%) and decreases after the addition of calcium oxide on average of 10–15%. Similar values were also reported in the literature [24]. Only in sample No. 4 (sludge stabilized with lime), the organic matter content decreased by almost 30% as compared to the raw sample No. 3, and finally amounts to 43.6%. The pH of raw sludge was 5.3–5.7 and this range is consistent with the literature data [31]. One of the most commonly used methods of stabilizing sludge is the addition of lime [1,4]. Calcium oxide also promotes the immobilization of many heavy metals in the sludge. On the contrary to the raw sludge, the lime-treated samples showed high variations of pH (8.6–12.6).

Heavy metals determinations in samples mineralized with HNO_3/HCl mixture as applied in all three procedures are reported in Table 1. This mixture is recommended as one of the most effective for decomposition of the organic matrix [32,35–37]. According to Polish regulations, the error of heavy metals determination in sludge should not be higher than 10% of the respective allowable values, i.e., 75 mg/kg of Pb, 50 mg/kg of Cr, 2 mg/kg of Cd, 30 mg/kg of Ni, 250 mg/kg of Zn and 100 mg/kg of Cu [22]. Table 2 presents statistical evaluation of the results obtained by methods A, B, C for samples No. 3 (raw sludge) and No. 4 (sample stabilized with CaO). The results of metals determination for the sludge dried (105 °C) and then decomposed by microwaves (method A) are burdened with the highest errors (high relative standard deviation (RSD) values for Cr, Ni, Pb, Cd). This particularly applies to the unstabilized sludge with a high organic content. The conventional digestion of dried sludge (method C) and microwave digestion of roasted sludge (method B), combined with the extended heating time promotes complete decomposition of the matrix. As a result, the precision of measurement substantially increases.

Table 1. Range of metal content in sewage sludge.

Sludge		Content [mg/kg]					
		Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Method A							
raw	range	3.7–4.4	9.0–11.6	126.9–143.5	12.7–22.7	27.6–35.7	843.1–986.5
	median	3.85	10.20	132.55	15.80	31.85	875.55
stabilized	range	5.1–8.4	4.1–9.1	85.2–143.5	17.9–29.2	37.2–69.1	547.8–869.2
	median	5.25	7.00	106.45	19.90	42.10	681.35
Method B							
raw	range	3.0–3.8	10.8–14.8	121.2–136.9	14.6–27.9	30.7–34.1	836.7–1010.7
	median	3.60	11.85	124.50	20.30	32.15	886.6
stabilized	range	5.0–7.7	8.5–11.2	86.1–121.7	19.5–71.3	47.3–82.0	575.0–898.3
	median	5.20	9.45	100.80	21.60	50.50	704.05
Method C							
raw	range	2.3–3.5	9.9–12.7	108.0–122.1	12.6–13.8	29.1–32.5	780.4–907.9
	median	2.55	10.70	111.90	13.15	30.75	792.2
stabilized	range	9.9–12.7	7.1–8.9	69.3–104.2	15.7–23.7	36.3–55.8	487.2–761.5
	median	10.70	8.40	86.80	16.90	39.75	601.2

Table 2. Statistical assessment (n = 5)—methods A, B, C.

Method A						
Sample no. 3	Cd	Cr	Cu	Ni	Pb	Zn
confidence interval for the mean [mg/kg]	4.44 ± 0.77	11.04 ± 2.39	137.68 ± 4.51	22.68 ± 5.52	27.60 ± 9.73	879.56 ± 107.34
standard deviation [mg/kg]	0.54	1.68	3.17	3.88	6.84	75.43
RSD [%]	12.16	15.22	2.30	17.11	24.78	8.58
Sample no. 4	Cd	Cr	Cu	Ni	Pb	Zn
confidence interval for the mean [mg/kg]	8.44 ± 1.14	4.10 ± 1.10	85.20 ± 3.70	29.24 ± 2.29	69.14 ± 10.73	547.76 ± 57.75
standard deviation [mg/kg]	0.80	0.77	2.60	1.61	7.54	40.58
RSD [%]	9.48	18.78	3.05	5.51	10.91	7.41
Method B						
Sample no. 3	Cd	Cr	Cu	Ni	Pb	Zn
confidence interval for the mean [mg/kg]	3.50 ± 0.31	11.94 ± 2.26	127.14 ± 1.39	27.90 ± 0.97	32.86 ± 0.84	913.00 ± 22.84
standard deviation [mg/kg]	0.22	1.59	0.98	0.68	0.59	16.05
RSD [%]	6.11	13.32	0.77	2.44	1.80	1.76
Sample no. 4	Cd	Cr	Cu	Ni	Pb	Zn
confidence interval for the mean [mg/kg]	7.72 ± 0.81	11.22 ± 1.28	86.14 ± 0.51	71.26 ± 6.25	81.98 ± 0.83	575.08 ± 9.43
standard deviation [mg/kg]	0.57	0.90	0.36	4.39	0.58	6.63
RSD [%]	7.38	8.02	0.42	6.16	0.71	1.15
Method C						
Sample no. 3	Cd	Cr	Cu	Ni	Pb	Zn
confidence interval for the mean [mg/kg]	2.32 ± 0.26	11.04 ± 0.78	110.78 ± 2.11	13.22 ± 0.44	30.02 ± 1.05	797.54 ± 17.00
standard deviation [mg/kg]	0.18	0.55	1.48	0.31	0.74	11.95
RSD [%]	7.76	4.98	1.34	2.34	2.47	1.50
Sample no. 4	Cd	Cr	Cu	Ni	Pb	Zn
confidence interval for the mean [mg/kg]	6.02 ± 0.37	8.84 ± 1.04	69.32 ± 2.03	23.70 ± 0.85	55.84 ± 3.09	487.20 ± 7.68
standard deviation [mg/kg]	0.26	0.73	1.43	0.60	2.17	5.40
RSD [%]	4.32	8.26	2.06	2.53	3.89	1.11

Figure 1 shows the contents of six toxic metals (Cu, Cd, Zn, Pb, Ni and Cr) under study. Higher content of cadmium, lead and nickel in the sludge stabilized with lime (samples No. 2, 4, 6 and 8) and the resulting greater immobilization of these elements is probably caused by the alkaline reaction of sewage sludge. At high pH, the solubility of the metal compounds decreases and the cations are less prone to leaching from the waste. On the other hand, the concentrations of copper, chromium and zinc determined in the stabilized sludge were lower. The reason may be the partial leaching of metals from the strongly alkaline sludge during its storage [39,40]. Differences in metal mobility (and thus their bioaccumulation) may result from several factors related to the complex chemical composition of sewage sludge and the pH of either fresh or stabilized sludge. Metals that easily form complexes with organic anions as present in the raw sludge are prone to leaching after lime stabilization due to the increased solubility of metal-organic complexes at high pH. This result was observed after either addition of lime to sewage sludge, or the use of stabilized sludge in alkaline soil [39]. A higher content of lead and chromium in comparison with the sludge after stabilization was found in several samples from a municipal wastewater treatment plant located in industrial areas in southern Poland [24]. In turn, Długosz and Gawdzik [41] found a significant decrease in the content of copper and zinc in the lime-stabilized sludge.

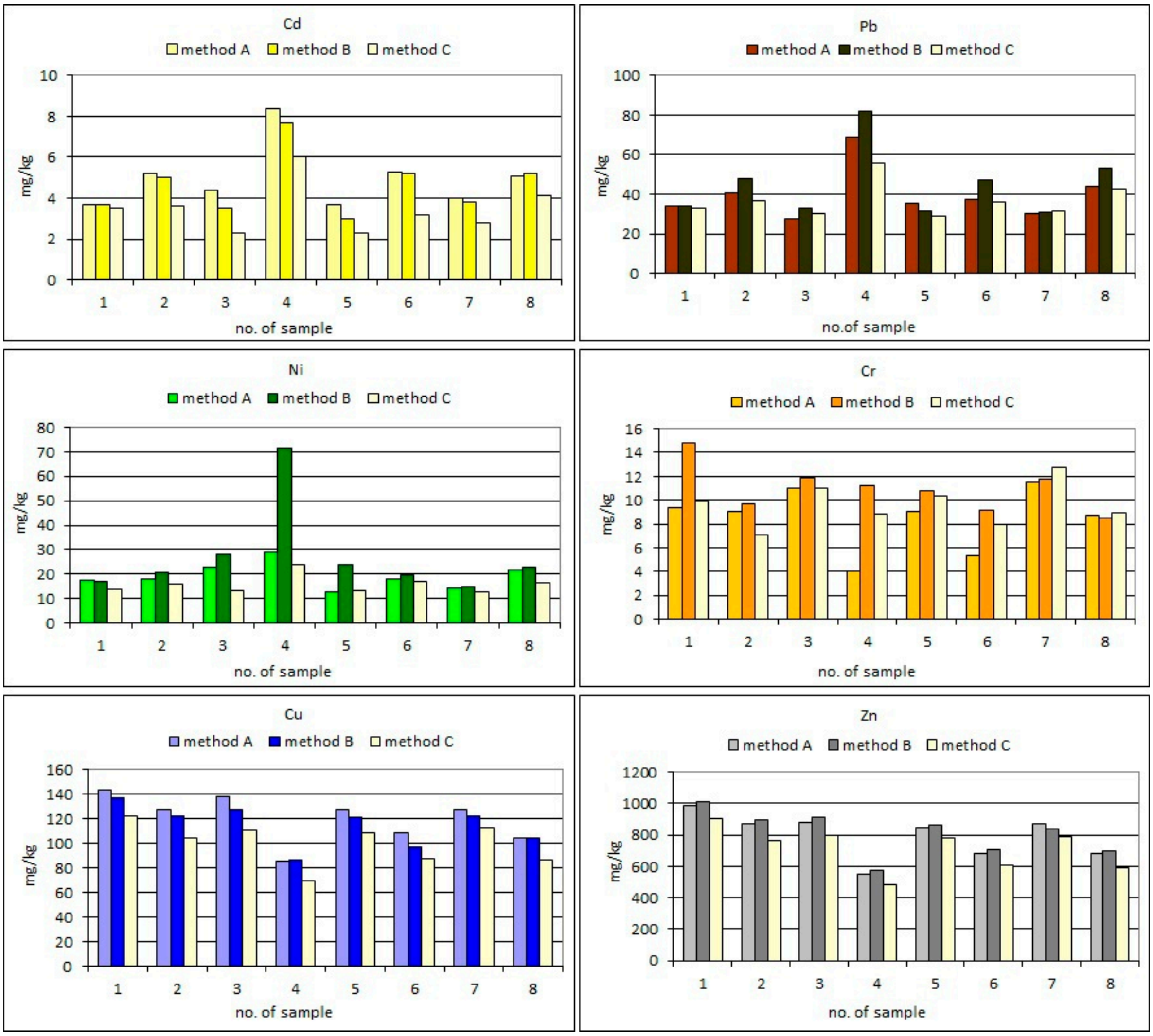

Figure 1. Comparison of the heavy metal contents after digestion by methods A, B, and C.

Results presented in this paper clearly indicate that there is no singly efficient digestion method which by default can be applied to sewage sludge. The yield of extraction depends on the metal properties and the method used [23,26,33]. Higher metal recoveries were obtained using the microwave digestion methods as compared to the sample decomposition in the open system. This is in agreement with the observations of Nemati [36]. During digestion in an open system, loss of analyte due to its volatility and contamination of the sample should be taken into account [34]. As shown in the studies of the plant samples digestion [33], the critical parameter is the content of organic matter. In the case of decomposition of sewage sludge, organic substances are the main components of the matrix. Also, the destruction of other types of matrix creates problems with the choice of the digestion method [34,36,42]. Generally, digestion of samples by method B (microwave mineralization of roasted sludge) allows extraction of the highest amounts of zinc, lead, nickel and chromium in both raw and stabilized sludge. The thermal destruction of organic matter facilitates further digestion of matrix by acids and final release of metals. No complete destruction of samples was achieved by any investigated method. However, small amounts of the residual fraction that remain after decomposition contain silica, which does not exhibit strong sorption properties with respect to metals. It can, therefore, be assumed that the total content of metals accumulated in the sludge is released during the sample destruction with the mixture of HNO_3 and HCl. The comparable results were achieved using both method A and B for determination of copper, cadmium, zinc and lead. Methods A and C give similar results for lead (raw sludge) and zinc, slightly larger differences occur for copper. But there is no relationship between the chromium or nickel contents and sludge digestion by A, B or C methods. The comparison of the results obtained by microwave and conventional methods indicates that for copper and zinc all those methods can be used. Regardless of the decomposition method applied, the metal contents occur in the following order: Zn > Cu > Pb > Ni > Cr > Cd either in raw or lime-stabilized sludge. This order is slightly different from those previously reported [24], but it is very similar to that described by Spanos et al. [43] and Sánchez et al. [44]. Depending on the source of sewage, differences in Cr, Ni and Pb content are observed. The high content of zinc and copper as observed in this study is an advantage, due to their properties as micronutrients. The content of cadmium is always the lowest in all investigated sludge [24,25,45]. Compared with the results obtained by Tatła et al. [24], sludge analyzed by us contains a much lower amount of chromium. The reason is the lack of significant sources of chromium emission in the area covered by the research. In all samples, allowable metal contents were not overdrawn [22]. Therefore, stabilized sludge can be safely used in agriculture. Also, environmental risk involved was pointed out by Carabassa et al. [7], who concluded that nitrate inflow to surface water reservoirs may lead to uncontrolled eutrophication. Fortunately, due to the intense nitrate uptake by plant roots during the growing season, this risk may only occur within the first four months after the sludge has been applied.

Despite the fact that samples of sludge were collected in short intervals of time from a small sewage treatment plant, a certain temporal variability of the metal contents is observed. Similar relations span over longer time were found in other works [15,43,44]. The content of metals (except for Cr) in sample No. 4 differs significantly from those in other samples. The lowest content of Cu and Zn, as well as the highest content of Pb, Cd, and Ni, were found in the sludge No. 4. In the other samples, variations are smaller. The statistical analysis has been applied widely to identify the sources of contaminants. Pearson correlation coefficients (R) indicate the relationship between copper and zinc (R = +0.771) in the raw sludge. A high positive correlation could be related to domestic-commercial origin of these elements [43]. In the stabilized sludge, the correlation coefficients are high or moderate and amount to R = +0.945 (Cu/Zn), R = +0.879 (Pb/Ni), R = +0.872 (Pb/Cd), R = +0.677 (Ni/Cd), R = −0.768 (Cd/Cu), R = −0.762 (Pb/Cu), R = −0.754 (Cd/Zn) R = −0.657 (Pb/Zn), R = −0.606 (Ni/Cu), R = −0.547 (Ni/Zn). Higher correlations in stabilized sludge are due to complex processes occurring in the sludge, e.g., gradual decomposition of the organic matrix, sorption of metal cations from the environment by an alkaline sludge or leaching of easily soluble metal compounds with organic substances [1,4]. The negative correlation between metals may be explained by their origin from multiple sources (e.g., commercial, micro-industrial units, domestic) and greater variation in the pollution load [27,43].

4. Conclusions

Several factors, including chemistry of sludge (organic matter, forms of metals), the acids used or digestion conditions influence the yield of a sample mineralization. It was found that there is no general method for the destruction of the samples matrices. Efficient method of digestion is the treatment of roasted sludge with a HNO_3/HCl mixture under high pressure (method B) which enables extraction of the highest amounts of elements with good recovery. Microwave acid digestion in a closed system allows to decompose samples more quickly than that with conventional mineralization. The digestion process is expedited through elevated pressure and temperature, but the reaction system requires special safety devices, which involves increased purchase costs of the apparatus. On the other hand, microwave mineralization uses smaller volume of reagents, which reduces exploitation costs. An important advantage of the mineralization in the closed system is reduction of release of harmful gases and losses of volatile analytes as well as avoiding contamination of the sample during preparation for analysis. In addition, microwave digestion provides more controlled and homogenous conditions of decomposition. Stable conditions and a relatively short time of the mineralization process make the microwave digestion in a closed system an important way to prepare samples for quality control in industrial laboratories. Microwave systems are implemented for waste treatment (asbestos, biological waste) and exhaust gases, therefore the results of our investigation are also important for improving the efficiency of removing organic pollutants from sewage sludge.

Differences in the content of metals in the lime-stabilized sludge and without the addition of lime were observed. They are likely to be caused by diverse solubilities of metal-organic matter complexes at a range of pH levels (samples with/without CaO). The presented study demonstrated that the recommended levels of heavy metals in the sewage sludge under investigation were not overdrawn and it may be used in agriculture. Therefore, it is crucial to adjust the pH of particular sludge to the generally accepted levels. There is an obvious need for standardization of analytical methods as applied to sewage sludge. Agriculture created promising and highly effective methods for sludge utilization. However, it requires high safety standards as applied to the food. Mineralization is one of the expensive and time-consuming procedures applied during metal determination. In fact, it is a very important source of errors which may bias final results. Obviously, it should be enhanced in terms of either reliability or economics of analytical process.

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