Influence of sonication on changes in micro- and macro-elements content and availability of organic matter in stabilized sewage sludge used for agricultural purposes

Dariusz Boruszko

Bialystok University of Technology, 45A Wiejska Str., 15-351 Bialystok, Poland, Tel. +48 85 746 96 44; email: d.boruszko@pb.edu.pl (D. Boruszko)

Received 2 December 2019; Accepted 17 March 2020

ABSTRACT

The manuscript presents experiments and results of research aimed at determining the influence of sonication on the availability of organic matter and biogenic compounds as well as micro- and macro-elements of stabilized sewage sludge used for agricultural purposes. The research material consisted of sewage sludge collected from three sewage treatment plants located in the Podlaskie Voivodeship. The research was carried out on sludge from an earthworm patch (vermicompost) and reed lagoon (dehydrated and stabilized sludge) from the Municipal Wastewater Treatment Plant in Zambrów, ATAD stabilized sludge from the Municipal Wastewater Treatment Plant in Wysokie Mazowieckie and digested sludge from the Mlekovita Dairy Wastewater Treatment Plant in Wysokie Mazowieckie. The research was conducted in 2017/2018 in the Departments of Technology and Systems of Environmental Engineering and the Department of Chemistry, Biology and Biotechnology of the Białystok University of Technology. The process of sewage sludge disintegration was con-ducted using ultrasonic atomizer Sonics VCR-130 (USA). In order to establish the effect of ultrasonic disintegration, the following parameters were determined in sludge samples before and after disintegration: pH, dry mass, dry organic mass, dry mineral mass, total carbon (TC), total organic carbon (TOC), total inorganic carbon (TIC), total phosphorus, total nitrogen, ammonium nitrogen, and micro- and macro-elements. The analyses were carried out in accordance with the applicable standards. Based on the conducted research, it was shown that the application of ultrasounds individually shaped the final content of the tested parameters in the sludge. The highest content of biogenic compounds (nitrogen and phosphorus) was found in fermented sludge from one of the largest dairy sewage treatment plants in Europe in Wysokie Mazowieckie. The content of phosphorus was 4.81 g/kg DM, while nitrogen was at 14.55 g/kg DM. The content of microelements (heavy metals) in all stabilized sewage sludge treated with the ultrasonic field did not exceed the permitted concentrations specified in Directive 86/278/EEC. From the results of the Spearman's correlation matrix, it can be concluded that, in the sewage sludge stabilized in the processes of vermicomposting and sewage sludge stabilized in reed beds during an ultrasound, both micro- and macro-elements, as well as biogenic compounds and organic substances, are in one large group of variables so their "behaviors" are similar. However, in the sediments stabilized in the fermentation process and with ATAD technology, the grouping of the examined parameters into two groups, "behaving" slightly differently, is clearly visible.

Keywords: Sewage sludge; Ultrasonic disintegration; Heavy metals; Organic substances; Biogenic compounds

Presented at the 14th Conference on Microcontaminants in Human Environment, 4–6 September 2019, Czestochowa, Poland 1944-3994/1944-3986 © 2020 Desalination Publications. All rights reserved.

1. Introduction

Currently, in Poland, the energetic and fertilizing potential of sludge is underestimated and unused in relation to the available technological possibilities and the state of knowledge and science. The basic problem of sludge management is a very negative perception of sludge as a huge threat to our health and life.

An approach based on the product method, which includes risk analysis of using sludge, is observed in many countries with high research and development potential, such as the USA, UK, France, Denmark, Spain, and others. There, the fertilizing potential is usually used more than the thermal potential. The strategies planned in EU countries aim to maintain a high level of utilization of sludge fertilization potential in agriculture while increasing the importance of stabilization and hygienization processes. In parallel with biological methods, thermal transformation plants are being developed, especially in the system of regional co-incineration plants. The development of both strategies is also determined by restrictions (or practically total bans) on the storage of sludge containing more than 5% organic matter.

Among those techniques, disintegration gained the biggest popularity. The research on applying the ultrasounds technique for sewage sludge treatment showed the great potential of this disintegration method based on the cavitation phenomenon, mainly in intensifying the process of anaerobic fermentation. The ultrasound's wave frequency range is between 20 kHz and 1 GHz. [1,2]. Ultrasonic interaction leads to processes that usually cause irreversible macroscopic changes in the core. Primary mechanisms of this interaction are cavitation, radiation pressure, and acoustic pressure. These processes cause secondary phenomena, such as dispersion, ultrasonic coagulation, depolymerization, heat phenomena, oxidation, reduction, degassing, and others [3]. Most researchers claim that ultrasonic cavitation is mostly responsible for the disintegrating character of the ultrasonic wave. This phenomenon is based on the occurrence of empty spaces (cavities) in liquids and their disappearance, as well as resonant vibrations of gas vesicles [4].

In operational practice, the ultrasonic disintegration process is most often used as a process supporting the stabilization of sewage sludge. There are no literature reports on the possibility of increasing the susceptibility of sewage sludge to agricultural use by increasing the availability of easily assimilable substrates through the use of ultrasound.

According to the current regulations in force in the EU member states, sewage sludge can be used in agriculture only if relevant legal regulations are in force in a given country. The permitted concentrations of heavy metals in individual countries must therefore not exceed the concentrations specified in Directive 86/278/EEC 1986, but may, of course, be more rigorous [5]. Many countries, such as Austria, Denmark, Sweden, and Switzerland, have stricter requirements. In Poland, too, the previous regulations on municipal sewage sludge [6,7] provided for partially lower limit values for heavy metals in sewage sludge used in agriculture than those currently in force [8]. In addition, all domestic regulations specify that exceeding the limit values for only one heavy metal excludes sewage sludge from agricultural use. The presence of heavy metals in sewage sludge, along with other toxic pollutants and sanitary conditions, is the basic criterion for its suitability for environmental use. In practically all legal regulations in Europe and worldwide, the permitted concentrations of heavy metals in sewage sludge refer to their general forms (total concentrations) [5,9–12].

2. Material and methods

2.1. Materials

The sewage sludge under examination was collected from a patch with earthworms (vermicompost) and a reed bed (dewatered and stabilized sludge) at Municipal Wastewater Treatment Plant in Zambrów, ATAD stabilized sludge from Municipal Wastewater Treatment Plant in Wysokie Mazowieckie and digested sludge from Dairy Wastewater Treatment Plant Mlekovita in Wysokie Mazowieckie.

2.2. Experimental procedure

Sewage sludge disintegration process was conducted with the use of an ultrasonic atomizer Sonics VCR-130 (USA) with a frequency of 20 kHz. Sewage sludge was exposed to ultrasounds of 20 kHz frequency in four periods of 5, 10, 15, and 20 min, with maximum vibration power and amplitude equal to 88% of the rated amplitude. Five research series were conducted for each type of sludge, which is a total of 20 research series.

In order to determine the effectiveness of ultrasonic disintegration, such parameters as pH, dry mass, organic dry mass, total carbon, organic carbon, and non-organic carbon were measured in the samples before and after sonification. Samples of sewage sludge had a capacity of 50 mL. Samples of sewage sludge were dried at 105°C until they reached a constant mass in an air circulation dryer. The inductively coupled plasma mass spectrometry triple quadrupole spectrometer was used to determine the microelements content.

2.3. Analytical methods

Dry matter, organic matter, total organic carbon (TOC), total carbon (TC), nitrogen, phosphorus, micro- and macroelements were determined by using Standard Methods [13].

Dry mass – about 5 g of the sample was dried at 105°C to achieve constant mass and then weighed. Water content and dry mass were determined by difference.

Dry organic mass – the sample dried to constant mass was burned for 4 h at 550°C. Dry organic mass was calculated from the difference in masses.

TC – about 10 mg of dried and homogenized sample was weighed. The sample was analyzed on an Analytik Jena Multi N/C 3100 carbon analyzer with a solid samples adapter.

TOC – about 10 mg of dried and homogenized sample was weighed, 2 drops of 10% HCl were added, and waited for the gas release to finish. Two drops of concentrated HCl were added and dried at 105°C for 3 h. Next, an Analytik Jena Multi N/C 3100 with a solid sample attachment performed analysis on the apparatus for carbon determination. Kjeldahl nitrogen (N), the sum of organic and ammonia nitrogen, was determined in the analyzed sludge. The sludge sample was dried and homogenized. It was then alkalized using a 35% solution of NaOH and mineralized in the presence of the catalyst $CuSO_4 + K_2SO_4$ using ammonium distillation. The determination of ammonia nitrogen was carried out using the distillation method.

For determining the phosphorus concentration, the sample was dried, homogenized, and then mineralized using a mixture of the concentrated acids $HCIO_4$ and HNO_3 . In the obtained solution, PO_4^- ions were determined calorimetrically in the reaction with ammonia molybdate in the presence of glycerine with dissolved $SnCl_2$.

Sewage sludge samples were treated in a HACH mineralizer with the use of sulfuric acid and hydrogen peroxide in a mixture of nitric and hydrochloric acid in a ratio of 1:3. For further analysis, mineralizers were filtered through MN 616 G paper filter.

Determination of cadmium, nickel, and total chromium content was done in samples of mineralizers with the use of an atomic absorption spectrometer Perkin-Elmer 4100 ZL with transversely heated graphite cuvette and Zeeman-effect background correction.

The determination of mercury content was done in samples of mineralizers by means of the cold steam technique with the use of an atomic absorption spectrometer Perkin-Elmer 4100 ZL equipped with add – on device FIAS-200.

The determinations of zinc, lead, and copper contents were done in samples of mineralizers with the use of an atomic absorption spectrometer Varian SpectrAA 20 Plus by means of flame atomization.

Determinations of the test samples were performed in triplicate.

2.4. Statistical methods

Tables 1 and 2 show the test results as arithmetic means from three repetitions. The standard deviation of the tested parameters was no more than 5%.

Mathematical-statistical calculations presented in the paper were made using common computer software and spreadsheets. To study the relationship between quantitative parameters and describe the strength of the correlation in the case of a small number of observations, Spearman's rank correlation coefficient was applied [14]. In order to verify whether there was a statistically significant change, the ANOVA rank Kruskala–Wallisa test was used for each pair of observations [15].

To determine interdependencies in the parameters group and describe the intensity of their intercorrelations, correlation matrixes were built. A Spearman correlation matrix was constructed for the parameters group. The results were explored graphically [16]. A selection of suitable criteria allowed the determination of a small number of parameters behaving in a similar way in each of the sewage sludge stabilization processes. After the grouping process, a certain number of variables groups were graphically labeled according to the following criteria:

Table 1

Physicochemical parameters in sludge during ultrasonic disintegration

Type of sludge sonification time	Changes in physicochemical parameters in sewage sludge during sonication								
	TC	TOC	IC	$\mathbf{P}_{\mathrm{tot}}$	N _{tot}	Dry matter	Organic matter	pH in H_2O	
			g/kg DM			%	% DM	_	
Vermicomposting	266.50	234.47	32.03	1.22	1.85	52.42	41.27	5.50	
5 min	276.45	256.37	20.08	1.34	1.90	50.32	43.90	5.45	
10 min	304.34	270.22	34.12	1.46	1.99	46.99	44.12	5.50	
15 min	324.40	278.10	46.30	1.49	2.01	46.26	44.72	5.45	
20 min	335.87	287.32	48.55	1.63	2.10	45.43	45.56	5.43	
STRB	332.87	284.40	48.47	1.77	3.22	25.46	57.82	5.64	
5 min	342.32	278.98	63.34	1.78	3.22	25.11	57.89	5.70	
10 min	356.90	270.28	86.68	1.79	3.24	24.56	58.11	5.68	
15 min	366.07	264.70	101.37	1.88	2.25	24.03	58.28	5.95	
20 min	370.45	258.90	111.55	1.93	3.29	23.56	58.34	5.87	
ATAD	369.61	318.33	51.28	1.56	3.95	24.24	61.40	7.70	
5 min	378.42	319.32	59.10	1.50	3.92	23.80	61.65	7.78	
10 min	389.09	317.39	71.70	1.51	3.90	22.97	61.56	7.89	
15 min	462.84	315.30	147.54	1.42	3.84	22.60	61.52	8.22	
20 min	471.22	314.88	156.34	1.38	3.59	22.32	60.34	8.21	
Fermentation	330.20	255.94	74.26	4.81	14.55	2.18	61.98	8.40	
5 min	345.34	256.98	88.36	4.02	14.00	2.23	62.32	8.45	
10 min	356.81	257.13	99.68	3.90	13.70	2.33	62.30	8.50	
15 min	376.59	258.80	117.79	3.80	13.25	2.34	62.14	8.53	
20 min	390.37	260.10	130.27	3.63	12.64	2.37	63.04	8.55	

	Changes in macro-elements and microelements in sewage sludge during sonication											
Type of sludge	S	Mg	Ca	Fe	Mn	Cr	Ni	Cu	Zn	Pb	Cd	Hg
sommed to the	g/kg DM						mg/kg DM					
Vermicomposting	19.61	18.46	15.28	25.73	565.38	53.86	23.43	314.65	1,439.11	53.38	0.44	0.25
5 min	20.45	20.13	18.21	23.55	550.70	53.08	26.70	445.80	1,737.80	52.32	0.45	0.30
10 min	24.47	21.34	23.57	23.67	532.21	52.05	29.03	460.41	1,750.38	52.18	0.47	0.33
15 min	30.05	32.67	26.80	20.79	507.90	52.04	31.20	520.50	2,207.07	51.30	0.48	0.34
20 min	31.50	39.69	32.27	17.67	422.75	51.56	42.50	826.80	2,764.79	51.03	0.53	0.37
STRB	17.77	22.85	19.42	24.32	551.13	45.08	24.11	274.65	1,440.65	51.92	0.32	0.32
5 min	18.45	26.73	22.11	28.15	542.04	46.79	26.70	456.71	1,672.30	51.21	0.40	0.31
10 min	20.33	29.04	23.56	29.80	520.70	48.90	29.43	523.90	1,904.50	50.59	0.45	0.30
15 min	27.55	30.47	25.80	30.45	495.15	50.55	32.20	702.21	2,113.57	50.45	0.57	0.29
20 min	35.86	40.65	29.92	34.18	421.38	60.35	43.80	828.95	2,758.14	49.88	0.56	0.31
ATAD	12.97	35.71	17.76	30.30	909.00	63.35	37.58	593.70	2,537.15	75.58	1.74	0.15
5 min	12.99	30.21	19.04	27.55	889.05	60.34	34.50	490.33	2,107.33	70.31	1.34	0.15
10 min	13.15	25.44	20.06	20.35	878.44	47.50	30.23	437.19	1,976.20	62.33	1.20	0.22
15 min	15.67	19.44	23.55	15.80	812.39	42.22	19.82	369.06	1,700.50	50.21	0.96	0.23
20 min	18.19	14.58	27.13	4.59	767.75	21.49	11.93	236.32	1,307.33	24.33	0.27	0.23
Fermentation	16.33	11.37	19.94	30.64	973.25	65.84	41.00	636.85	2,653.85	81.32	1.54	0.14
5 min	16.61	11.32	20.56	28.50	870.30	45.32	40.13	578.40	2,130.47	76.40	1.23	0.17
10 min	18.22	13.23	22.57	23.40	850.20	40.34	29.60	520.48	2,066.20	69.49	1.08	0.15
15 min	20.12	13.22	25.05	15.89	813.62	34.69	19.34	478.50	1,872.18	60.24	0.90	0.16
20 min	25.40	14.44	26.27	4.33	757.15	19.38	12.69	335.66	1,323.33	33.46	0.26	0.17

Table 2 Selected microelements and macro-elements in sludge during ultrasonic disintegration

- the number of variables groups must be the smallest possible (which means maximizing the number of variables in each group),
- in each group there can only be variables with a Spearman correlation coefficient > 0,
- if statistically, unimportant correlation coefficients appear in a group, their number should be the smallest possible (not bigger than 30%),
- despite the possibility of manual selection of variables in a group, the task was performed by an algorithm in order to obtain independency of possible mistakes in results interpretation. An assessment of how one parameter from a group behaved in time, allowed a prediction of how the other parameters from that group would behave.

In the presented pictures (Fig. 2), the size and color (of a circle) stand for the values of Spearman *S* correlation coefficients:[TS: Image symbol inside the text]

 $\bullet - S = +1$

$$-S = -1$$

A bigger circle and more intensive color denote that Spearman correlation coefficients approach border values of +1 and -1.

Statistical analysis was conducted in a statistical environment R (3.3.0 version called "Supposedly Educational"), with

the use of the basic package and additional packages pspearman (version 0.3–0) and corrplot (version 0.77) [17–19].

3. Results and discussion

3.1. Results

The sludge exposed to ultrasonic disintegration was stabilized in various ways and came from different wastewater treatment plants. Tables 1 and 2 show the results of research on sewage sludge stabilized during ultrasonic disintegration. Results analysis allows to claim that post-fermentation sludge was the most hydrated (2.18% DM), whereas vermicompost had the greatest amount of dry mass of 52.42% DM. The content of organic substances ranged from 41.27% DM in vermicompost to 61.98% DM in post-fermentation sludge. The content of TOC was on a similar level in the examined sludge, which is from 234.47 g/kg DM in vermicompost to do 318.33 g/kg DM in aerobically stabilized sludge (ATAD).

The highest content of biogenic compounds (nitrogen and phosphorus) was found in fermented sludge from one of the largest dairy sewage treatment plants in Europe in Wysokie Mazowieckie. The content of phosphorus was 4.81 g/kg DM, while nitrogen was at 14.55 g/kg DM.

The content of macro-elements (S, Mg, Ca, and Fe) in stabilized sewage sludge was at a similar level and ranged from 12.97 g/kg DM for sulfur in sludge stabilized with ATAD technology to 35.71 g/kg DM for calcium in sludge stabilized with ATAD technology. The content of microelements (heavy metals) in all stabilized sewage sludge treated with the ultrasonic field did not exceed the permitted concentrations specified in Directive 86/278/EEC 1986 [5]. Therefore, sewage sludge from dairy sewage treatment may be used in agriculture for fertilization and reclamation. Numerous studies presented in the literature related to the problem of sludge management show that sludge from dairy treatment plants has a low content of heavy metals compared to municipal sludge in Poland and abroad [20,21]. Based on previous studies on the content of selected macro-elements (calcium, magnesium, nitrogen, and phosphorus), many authors show higher concentrations of these macro-elements in dairy sludge than in municipal sludge [22,23].

Fig. 1 depicts the changes in the percentage share of TOC and total inorganic carbon (TIC) in relation to TC with various times of ultrasonic disintegration. In reference to all sewage sludge, there is a similar tendency of an increasing inorganic carbon percentage share along with the increase of sonification time. Also, a short sonification time (5 min) initially caused an insignificant increase of the organic carbon percentage share. The highest increase in the inorganic carbon percentage share after 20 min of sonification was observed for sewage sludge stabilized in reed beds (STRB) from 13.9% to 33.2%. whereas the lowest increase occurred in post-fermentation sludge from 12.0% to 14.5%. Research conducted by Zhang et al. [24] among others, confirms that the shear force which causes organic substance disintegration occurs during sonification.

For each of the examined sewage sludge types, various disintegration effects were observed in reference to particular parameters. The tested sludge samples varied in terms of dry mass content (Vermicomposting – 52%, STRB – 25%, ATSO – 24%, Fermentation – 2%), which is considered to be the main factor in determining disintegration effectiveness. Although the dry mass concentration recommended in publications is between 2% and 3%, it was not confirmed in the conducted tests [25].

3.2. Statistical analysis

To determine any interdependencies in the parameters group and to describe the intensity of their intercorrelations, Spearman correlation matrixes were built. After constructing the matrixes, a hierarchical clustering algorithm of variables was applied in order to determine sub-groups of variables that behave alike. As a result of applying a hierarchical clustering algorithm and appropriate selection of the number of groups, the following groups of variables that behave alike were recognized.

Fig. 2 presents the results for all research series in the conducted experiment.

The *X* mark in the middle of the area (circle) denotes that in the Spearman correlation coefficient relevance test with Benjamini–Hochberg correction (for multiple testing), the *p*-value is larger than 0.05. The value of this coefficient is then statistically insignificant.

In order to construct the Spearman matrix, the examined values of organic and mineral substances, carbon, and the content of macro-elements, as well as the total content microelements (heavy metals) for sewage sludge stabilized with various methods, were taken into account.

As a result of analyzing the Spearman correlation matrix, the following groups of variables were obtained which behave alike during ultrasonic disintegration of sewage sludge stabilized with various methods:

- for sludge processed with vermicompost:
- group I all groups variables without dry mass and Fe. for sludge stabilized through STRB:
- group I all groups variables without dry mass, TOC and nitrogen.
- for sludge stabilized with ATAD technology:
- group I total carbon, Ca, and S,
- group II all microelements (heavy metals), Fe, Mg, N, and dry mass.
- for post-fermentation sludge:



Fig. 1. Changes in the percentage share of total organic carbon (TOC) and total inorganic carbon (TIC) in relation to total carbon (TC) with various times of ultrasonic disintegration.



Fig. 2. Spearman correlation matrixes for all research series in the conducted experiment.

- group I all microelements (heavy metals), Fe, P, and N,
- group II total carbon and organic carbon, dry mass, S, and Ca.

Another statistical analysis of the obtained results was based on applying the ANOVA Kruskal–Wallis test. The results of the K–W test were graphically presented in the form of a diagram in Fig. 3 (frame with moustache) for the biggest correlated group of variables obtained as a result of statistical equations of the Spearman correlation matrix (Fig. 2). The obtained K–W test results are statistically significant as they have p < 0.05.

The obtained results of these statistical tests point to a strong similarity of most of the examined parameters in stabilized sewage sludge with sonification time both as dependent and independent data.

From the results of the Spearman's correlation matrix it can be concluded that in the sewage sludge stabilized in the processes of vermicomposting and STRB during ultrasound, both micro- and macro-elements, as well as biogenic compounds and organic substances, are in one large group of variables so their "behavior" is similar. However, in the sediments stabilized in the fermentation process and with the ATAD technology, the grouping of the examined parameters into two groups "behaving" slightly differently is clearly visible.

Application of the ANOVA Kruskal–Wallis test allowed to state that the use of ultrasounds resulted in an increase in the sum of microelements in sewage sludge stabilized with vermicomposting and STRB processes. However, in the case of sludge stabilized in the fermentation process and ATAD, the use of ultrasounds caused a decrease in the content of the sum of heavy metals. The behaviors of heavy metals in different sewage sludge processing methods vary greatly according to numerous studies.

3.3. Discussion

The heavy metal content of sewage sludge is very often associated with microelements present in the environment. It should be emphasized that in the group of seven heavy metals tested in sewage sludge there are microelements that are essential for plants and are characterized by high quantities. This contributes to a positive agricultural assessment

Vermicomposting

ATAD



Fig. 3. Results of the ANOVA Kruskal-Wallis test. STRB: sludge treatment reed bed; ATAD: aerobic digestion of sewage sludge.

of sewage sludge, in particular the finished products based on it (compost), as a potential and important source of soil micronutrient supplementation. Many authors point out that with an increase in crop intensity there is a possibility of the frequent occurrence of microelements deficiency in the soil, especially in the case of a drastic reduction in the use of mineral fertilizers [26–28].

The group of eight microelements essential for plants includes, among others, metals such as nickel, copper, zinc, manganese, and iron. Of course, compared to macroelements, they are absorbed in much smaller amounts. The assimilation of microelements is also influenced by their mobility resulting from the type of connections with other groups of compounds (minerals, carbonates, hydroxides, and organic matter), soil pH and oxidation-reduction potential [29,30]. Based on previous studies, according to many research authors in Europe and the United States, it is the pH that constitutes the basic factor determining the potential availability of heavy metals. Heavy metal cations are more mobile in an acidic environment [31,32].

Based on previous studies conducted on the properties of sewage sludge, it was stated that the forms of heavy metals and other chemical substances contained in sewage sludge have an impact on the availability and absorption of these elements. Therefore, the examination of only the total amount of heavy metals in sewage sludge, despite it being a commonly used indicator of the degree of sludge pollution, does not really determine the degree of absorbability for plants nor the potential mobility of metals in the environment. Therefore, it does not determine the potential risk heavy metals pose on the environment [33,34].

Many factors determine the release of heavy metals from sludge into the environment. Apart from the chemical form of metal itself, the changes in the composition of sewage sludge as a result of the applied treatment processes in a sewage treatment plant and the changes occurring over time in different fertilization conditions are also important. Organic and inorganic substances that undergo transformations in sewage sludge have a direct impact on their sorption capacity and concentration of heavy metals [35,36].

Sewage sludge can be a buffer matrix for the release of metals into the environment. Based on previous studies it has been shown that the decomposition of organic matter is one of the most important factors associated with the release of heavy metals into the environment, which may have a harmful effect on groundwater. For some heavy metals the release to the environment may occur immediately after the sediment is added to the soil, and for others only after a certain period of time which may be limited by the presence of phosphates and oxides of Fe and Mn in sludge [37,38].

Some authors believe that the total concentration of a given heavy metal in soil has an effect on its availability (mobility), while others show that the total metal concentration does not affect its mobility [39–41].

The results point to the fact that there are factors (such as ultrasonic disintegration) that might influence not only the content, but more importantly the mutual composition of organic substances, biogenic compounds, and heavy metals. Applying ultrasounds is a crucial factor in evaluating the toxicity and availability of macro- and micro-elements in sewage sludge.

4. Conclusions

The conducted research was complex. The obtained results and experiments point to the necessity of continuation and further development of research concerning changes in the content of stabilized sewage sludge during sonification. In this aspect, the importance of recognizing the role of a varied physio-chemical content of sewage sludge and degradation of macro- and micro-elements should be stressed. Determining the impact of the amount of organic substance and carbon contained in sewage sludge on changes in heavy metals within that sludge during sonification is of particular importance.

The permitted content of heavy metals in various environmental elements is determined within the European Union and in most countries in the world by suitable legal regulations. Due to various properties of particular heavy metals, different concentration values are permitted depending on the type of environmental matrix.

Sewage sludge from dairy treatment plants, although treated as municipal sewage sludge, exhibits different properties and physio-chemical content. Treated dairy sewage sludge is characterized by a high content of organic substances and low heavy metals content.

Applying ultrasounds with 20 kHz frequency and four different exposure time periods shaped the final content of the examined macro- and micro-elements in sewage sludge in an individual manner.

It was observed that under the influence of ultrasounds significant changes might occur in heavy metals, organic substances, and biogenic compounds content in sewage sludge.

All applied ultrasound duration periods caused a decrease in the content of organic carbon in sewage sludge, to the highest degree in vermicompost, while to the lowest degree in fermented dairy sewage sludge.

Acknowledgments

The research was carried out within the framework of the work No. WZ/WBilŚ/8/2019 and funded by the Ministry of Science and Higher Education.

References

- K.Y. Show, T.H. Mao, D.J. Lee, Optimisation of sludge disruption by concation, Water Res., 41 (2007) 4741–4747.
 X. Feng, J.C. Deng, Q. Yu, H.L. Li, Physical and chemical
- [2] X. Feng, J.C. Deng, Q. Yu, H.L. Li, Physical and chemical characteristics of waste activated sludge treated ultrasonically, Chem. Eng. Process., 48 (2009) 187–194.
- [3] C.M. Braguglia, M.C. Gagliano, S. Rossetti, High frequency ultrasound pre-treatment digestion of sludge: effect of floc structure and microbial population, Bioresour. Technol., 110 (2012) 43–49.
- [4] S. Gao, Y. Hemar, M. Ashokummar, S. Paturel, G.D. Lewis, Inactivation of bacteria and yeast using high-frequency ultrasound treatment, Water Res., 60 (2014) 93–104.
- [5] Directive 86/278/EEC, Council Directive on the Protection of the Environment and in Particular of the Soil, When Sewage Sludge is Used in Agriculture, Off. J. Eur. Communities, L 181 (1986) 6–12.
- [6] Regulation of the Minister of Environment from 9th of September 2002 on Standards of the Quality of the Soil and Standards of the Quality of the Earth (Dz.U. 2002 no 165 pos. 1359) (in Polish).
- [7] Regulation of the Minister of Environment from 23th of July 2008 on Criteria and the Mode of Evaluating of the State of Underground Waters (Dz.U. 2008 no 143. pos. 896) (in Polish).
- [8] Regulation of Minister of Health on the Quality of Water Intended for the Human Consumption (Dz. U. 2010 no 72. pos. 466) (in Polish).
- [9] MAFF, Review of the Rules for Sewage Sludge Application to Agricultural Land: Soil Fertility Aspects of Potentially Toxic Elements, PB1561, Her Majestry's Stationary Office, London, 1993.
- [10] EPA, Environmental Guidelines: Use and Disposal of Biosolids Products, New South Wales Environment Protection Authority, Sydney, 1997.
- [11] Working Document on Sludge, 3rd Draft, Council of the European Community, Brussels, 2000.
- [12] Working Document on Sludge and Biowaste, Council of the European Community, Brussels, 2010.
- [13] APHA/AWWA/WEF, Standard Methods for the Examination of Water and Wastewater, 21th ed., American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA, 2005.
- [14] M. Sobczyk, Statistica, Publishing Company PWN, 2011 (in Polish).
- [15] S. Siegel, Non-Parametric Statistics for the Behavioral Sciences, McGraw-Hill, New York, NY, 1956.
- [16] M. Friendly, Corrgrams: exploratory displays for correlation matrices, Am. Stat., 56 (2002) 316–324.
- [17] R.T. Core, R: A Language and Environment for Statistical Computing, R Foundation for Statistical Computing, Vienna, Austria, 2016. Available at: https://www.R-project.org/
- [18] P. Savicky, Spearman's Rank Correlation Test, R Package Version 0.3–0. 2014. Available at: https://CRAN.R-project.org/ package=pspearman
- [19] T. Wei, V. Simko, Visualization of a Correlation Matrix, R Package Version 0.77. 2016. Available at: https://CRAN.Rproject.org/package=corrplot
- [20] W. Dabrowski, Studies upon heavy metals contents in sewage sludge and reject water produced from its treatment in dairy wastewater treatment plants, Ecol. Chem. Eng., 15 (2008) 1041–1047.
- [21] C. Rosik-Dulewska, U. Karwaczyńska, T. Ciesielczuk, Leaching of Soluble Components from Fertilizers Based on Sewage Sludge and Ashes, Pawłowski, Dudzińska, Pawłowski, Eds., Environmental Engineering III, Taylor & Francis Group, London, 2010, pp. 417–423.
- [22] D. Boruszko, A. Butarewicz, Impact of effective microorganisms bacteria on low-input sewage sludge treatment, Environ. Prot. Eng., 41 (2015) 83–96.
- [23] E. Dusza-Zwolińska, Z. Zabłocki, B. Mieszczerykowska-Wójcikowska, Content of magnesium and other fertilizer compounds in stabilized sludge from the municipal sewage treatment plant, J. Elementol., 14 (2009) 63–70.

- [24] G. Zhang, P. Zhang, J. Gao, Y. Chen, Using acoustic cavitation to improve the bio-activity of activated sludge, Bioresour. Technol., 99 (2008) 1497–1502.
- [25] D. Boruszko, Applying ultrasonic in the PAHs degradation in sewage sludge. Desal. Water Treat., 134 (2018) 15–22.
- [26] C.P. Jordao, C.C. Nascentes, P.R. Cecon, R.L.F. Fontes, J.L. Pereira, Heavy metal availability in soil amended with composted urban solid wastes, Environ. Monit. Assess., 112 (2006) 309–326.
- [27] I. Walter, F. Martinez, V. Cala, Heavy metal speciation and phototoxic effects of three representative sewage sludges for agricultural uses, Environ. Pollut., 139 (2006) 507–514.
- [28] D. Boruszko, W. Dąbrowski, P. Malinowski, Organic matter and heavy metals content modeling in sewage sludge treated with reed bed system, E3S Web Conf., 22 (2017), doi: 10.1051/ e3sconf/20172200021
- [29] M. He, G. Tian, X. Liang, Phytotoxicity and speciation of copper, zinc and lead during the aerobic composting of sewage sludge, J. Hazard. Mater., 163 (2009) 671–677.
- [30] J. Kumpiene, A. Lagerkwist, C. Maurice, Stabilization of As, Cr, Cu, Pb, Zn in soil using amendments – a review, Waste Manage., 28 (2008) 215–225.
- [31] B. Chefetz, P.G. Hatcher, Y. Hadar, Y. Chen, Characterization of dissolved organic matter extracted from composted municipal solid waste, Soil Sci. Soc. Am. J., 62 (1998) 326–332.
- [32] R.L. Chaney, S.L. Brown, J.S. Angle, *In situ* Remediation Reclamation Restoration of Metals Contaminated Soil Using Tailor-Made Biosolid Mixtures, In: Proceedings of the Symposium on Mining, Forest and Land Restoration: The Successful ISE of residuals Biosolids Organic Matter for Reclamation Activities Rocky Mountain Water Environment Association, Denver, CO, 2000.

- [33] Q.-Y. Cai, C.-H. Mo, Q.-T. Wu, Q.-Y. Zeng, A. Katsoyiannis, Concentration and speciation of heavy metals in six different sewage sludge-composts, J. Hazard. Mater., 147 (2007) 1063–1072.
- [34] A. Karaca, Effect of organic wastes on the extractability of cadmium, copper, nickel and zinc soil, Geoderma, 122 (2004) 297–303.
- [35] G. Merrington, I. Oliver, R.J. Smernik, M.J. McLaughlin, The influence of sewage sludge properties on sludge borne metal availability, Adv. Environ. Res., 8 (2003) 21–36.
- [36] L.Z. Zhou, J.W.C. Wong, Effects of dissolved organic matter from sludge and sludge compost on soil copper sorption, J. Environ. Qual., 30 (2001) 878–883.
- [37] T.L. Logan, B.J. Lindsay, L.E. Goins, J.A. Ryan, Field assessment of sludge metal bioavailability to crops: sludge rate response, J. Environ. Qual., 26 (1997) 534–550.
- [38] D. Boruszko, Research of effective microorganisms on dairy sewage sludge stabilization, J. Ecol. Eng., 20 (2019) 241–252.
- [39] P. Baveye, M.B. McBride, D. Bouldin, T.D. Hinsely, M.S.A. Dahdoh, M.F. Abdel-Sabour, Mass balance and distribution of sludge-borne trace elements in a silt loam soil following long-term applications of sewage sludge, Sci. Total Environ., 277 (1999) 13–28.
- [40] D. Boruszko, Fractionation of selected heavy metals in sludges from treatment of sewage sludge low-input methods, Annu. Set Environ. Prot., 15 (2013) 1787–1803.
- [41] J. Kujawska, K. Wójcik-Olivieira, Effect of vermicomposting on the concentration of heavy metals in soil with drill cuttings, J. Ecol. Eng., 20 (2019) 152–157.