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VALORISATION OF SEWAGE SLUDGE HUMIC COMPOUNDS IN THE ASPECT OF ITS APPLICATION IN NATURAL ENVIRONMENT

The valorization of sewage sludge (SS) has been presented originating from four wastewaters treated in wastewater treatment plants (WWTPs) located in the Wielkopolska province. In the SS samples collected in two successive years, the quantity and quality of humic substances (HSs), fulvic and humic acids (FAs, HAs), amounts of organic carbon (TOC), organic matter (OM), labile carbon (CL), and water extracted organic carbon (WEOC) were determined. It was investigated how the defined parameters depend on the size of the installation and select those which in a routine SS analysis facilitate rapid assessment of their quality and suitability for application in the natural environment. Regardless of WWTP size and the year of analysis, SS was characterized by a significant share of easily decomposable compounds such as FAs and WEOC. The statistical analysis showed significant usefulness of CL, FAs, and HAs in the evaluation of SS quality and usability.

1. INTRODUCTION

Sewage sludge (SS) is the semi-solid or liquid residue generated during the treatment of municipal wastewaters, which has to be discarded periodically from the system to ensure optimal performance of biological treatment processes. Taking into account the quality of the aquatic environment, wastewaters treated in wastewater treatment plants (WWTPs) must be cleaned perfectly in terms of removing all pollutants, especially those that are biogenic, thus new and more effective methods of wastewater purification are also applied. Additionally, at present, very rapid urbanization and agglomeration processes are taking place, enhancing wastewater infrastructure development, playing a major role in increasing the mass of SS generated in individual countries. This

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tendency has been observed starting from the 20th century and is confirmed by the Eurostat data for the EU state members [1].

Also, in the nearest future, the remarkable gain of generated SS should be considered, because based on the current forecasts a rapid increment of global population size is expected. Nowadays, it is evident that the generated mass of SS poses real and serious environmental problems, and proper methods of SS utilization are required. Currently, the most popular methods of SS management in the EU include landfill, thermal disposal, agricultural application, or co-composting for compost production. The landfill is the least desirable way of SS utilization and for example in Poland according to the Polish legal regulations [2] such wastes from 2016 may not be deposited at landfills. A review conducted by Sharma et al. [3] indicates that alternative methods of SS management such as agriculture application, thermal disposal, or other methods are more popular in European countries. In Poland, in 2018, out of the total SS mass generated almost 30% were used in the natural environment such as agriculture, land reclamation, or cultivation of plants intended for composting [4].

The use of SS for natural purposes is a very important strategy to comply with the Landfill Directive [5] and to the principles of circular economy [6]. Sharma et al. [3] cited several papers discussing the benefits of sewage sludge in terms of its effect on various soil properties, both physical, chemical, physicochemical, and biological. The beneficial effect of SS is closely related to its chemical composition. Sewage sludge has been repeatedly recognized as a valuable source of organic matter (OM) and nutrients essential for plants [7–9]. A majority of studies regarding SS are focused on an analysis of nutrients in the aspect of their mobility and uptake efficiency by plants. At the same time, the statement concerning SS abundance in organic matter is very general without detailed and precise research. The organic carbon components in SS include water-soluble organic substances such as starch, sucrose, oligosaccharides, fructose, and amino acids. Thanks to this, the water-soluble organic compounds are direct materials and energy sources for microorganisms [10]. Additionally, Lv et al. [11] proved that water-extractable organic matter is the most active fraction of organic waste and subject to change, thus it may directly reflect the organic matter transformation process. Considering the soil application of SS, information on the quality of humic substances is needed.

Special attention is focused on the susceptibility of humic compounds to chemical and microbiological processes, which lead to their solubility and mobility. Humic substances (HSs) are the most abundant and reactive components of organic matter. It is well documented that HSs consist of hydrophobic molecules with an aromatic structure and branched aliphatic chains with functional groups, such as hydroxyl, methoxy, methyl, methylenic, carboxylic, carbonyl, quinone, and amine – derived basic groups [12]. Humic acids (HAs) and fulvic acids (FAs) represent the majority of humic substances [10, 13, 14]. Similarly, one can describe differences between HAs and FAs in SS. Anielak et al. [15] proved that HAs have a more complex structure than FAs, because of their higher molecular weight and a lower number of oxygen-containing groups compared to FAs.

Moreover, HAs contained many acidic functional groups and have a considerable cation exchange capacity, thus absorbing various nutrients. This is why they play an important role during sludge treatment because they are directly involved in the release of nutrients, cation exchange capacity, pH buffer capacity, and heavy metals retention. It was recognized that the removal of humic substances in effluents from WWTPs was mainly dependent on the absorption by activated sludge and discharge of excess sludge, rather than degradation by microorganisms. Some humic substances were also precipitated with flocculants and then removed in primary clarifiers [13]. Regardless of this fact, HSs are considered to be important recalcitrant compounds of sewage sludge organic matter and thanks to this their role is especially emphasized for land utilization.

Although the use of SS as the organic amendment is well documented, very few studies have been conducted on the quality and quantity of SS humic substances. Apart from this general information, scarce and limited data is available considering more in-depth studies on various humic parameters. To date, changes of water extracted organic carbon (WEOC) or labile carbon (CL) in SS has not been fully studied. Therefore, this study was focused on the valorization of SS originating from four various WWTPs applying the same wastewater purification method, but differing in the size of installations. Next to the determined amounts of organic matter, total organic carbon, also more sophisticated analyses dedicated to humic substances, labile carbon, and water extracted organic carbon were performed. Thus it was assumed in the study that the size and wastewater capacity of WWTPs can influence the quality and quantity of analyzed SS parameters. Besides, an attempt was made to indicate the most useful parameter which would most reliably evaluate SS quality and facilitate the assessment of its suitability for soil application.

2. MATERIALS AND METHODS

Materials. The sewage sludge used in this study was collected from four various WWTPs located in the Wielkopolska province (western part of Poland). Each of the WWTPs works in the same modernized Bardenpho system with the removal of carbon, nitrogen, and phosphorous compounds in a process of low load activated sludge. All selected WWTPs meet the required parameters of wastewater purification and their efficiency, expressed as a percentage of reduction of individual parameters is high, exceeding 96%. The difference between individual WWTPs relates to their designed size expressed as the equivalent number of inhabitants (ENI), average capacity of wastewater (Q) reaching the installation, and thus the mass of SS generated. The basic characteristics of WWTP parameters are given in Table 1. According to ENI, the values SS1 and SS2 represent big installations, whereas SS3 and SS4 small ones.

All the sewage sludge samples were collected in the same period, at the beginning of October in 2018 and 2019. Samples were gathered after the completed process of waste management at WWTPs, i.e., following degassing, equalization, dewatering, and compaction. The fresh mixed mass of individual SS was transported from WWTPs to the laboratory, where the material was desiccated in a laboratory dryer at 105 °C. Then, the samples were ground in a mill to obtain a homogeneous and even structure as a fine powder and stored in plastic bags at 4 °C for chemical analysis.

Table 1

Basic parameters of WWTPs from which the sewage sludge was collected

Sewage sludge	ENI	Average capacity Q [$m^3 \cdot day^{-1}$]	Approximate mass of generated sewage sludge [$t \cdot year^{-1}$]
SS1	1 200 000	200 000	17 000
SS2	63 330	8000	3500
SS3	51 500	6000	730
SS4	28 500	5000	550

Methods. Dry matter of SS was obtained from a 100-g fresh matter sample of waste after the 24-h drying process at 105 °C. For the organic matter of SS, samples of 1 g of dried matter were incinerated for 5 h at 550 °C. The total nitrogen (N_{tot}) of SS was determined with the standard Kjeldahl procedure. The selected properties of the analyzed sewage sludge are presented in Table 2.

In the sewage sludge samples, the total organic carbon (TOC) was determined by wet combustion [16] and labile carbon (CL) by $KMnO_4$ oxidation [17]. Cold (CWEOC) and hot (HWEOC) water-extractable organic carbons were determined according to the method presented by Ghani et al. [18] with the final determination of organic carbon by wet combustion [16]. The sum of CWEOC and HWEOC was expressed as water-extractable organic carbon (WEOC). Humus fractionation was determined according to the method proposed by Kononova and Bielczikova [19], in which humic substances were assayed in a mixture of 0.1 $mol \cdot dm^{-3}$ $Na_4P_2O_7$ + 0.1 $mol \cdot dm^{-3}$ NaOH solution. The fulvic acids fraction (FAs) was separated after precipitation of humic acids at pH 1.5 (HAs). Carbon (CFAs and CHSs) in the obtained fractions was oxidized by 0.1 $mol \cdot dm^{-3}$ $KMnO_4$ in the H_2SO_4 medium [20]. Humic acids carbon (CHAs) was calculated by subtracting CFAs from CHSs. The optical density ($Q_{4/6}$) of the obtained fractions was determined at 465 nm and 665 nm.

Statistical analysis. To monitor the value variability of the studied parameters and to indicate the most useful parameter (or a group of parameters) for a qualitative evaluation of various sewage sludge, several statistical analyses were conducted. To show the observed ranges of each of the eight parameters (CL, CHSs, CHAs, CFAs, TOC, CWEOC, HWEOC, and WEOC) through all sludge SS1, SS2, SS3, and SS4 taken together, boxplots were determined, i.e., box graphs. On the boxplots, the minimum value, maximum value, median, and quartile are shown for each parameter, separately for 2018 and 2019. Moreover, the *t*-student test was run to compare the average value of the parameter in 2018, μ_{2018}, with the average value in 2019, μ_{2019} (through all sewage sludge taken together), i.e., the null hypothesis H_0 was tested, i.e., that the average value of a parameter tested is equal to the average value of this parameter in both years under study (regardless of the sludge tested):

$$H_0\colon \mu_{2018} = \mu_{2019}$$

against the alternative hypothesis H_1, which states that these are not the average values of the examined parameter that differ in years, i.e., hypothesis 1

$$H_1\colon \mu_{2018} \neq \mu_{2019}$$

To determine which parameter is characteristic of a given sludge in the years under study, another analysis was performed. For the established *i*th sludge ($i = 1, 2, 3, 4$), the average value of the parameter in 2018 was compared with the average value in 2019. For this purpose, the null hypothesis was tested that the average values (of the established tested parameter for the *i*th sludge) were equal in both years under study:

$$H_0\colon \mu_{2018}^{\mathrm{SSi}} = \mu_{2019}^{\mathrm{SSi}}, \quad i = 1, 2, 3, 4$$

against the alternative hypothesis H_1, which states that the mean values of the examined parameter (for the *i*th sludge) differ between the years, i.e., hypothesis 2

$$H_1\colon \mu_{2018}^{\mathrm{SSi}} \neq \mu_{2019}^{\mathrm{SSi}}, \quad i = 1, 2, 3, 4$$

Each of the eight parameters was tested independently for each of the four sludges. 32 independent analyses were performed employing the *t*-student test (hypothesis 2). Moreover, it was checked whether the average values of the tested parameter are the same for all four sludges: SS1, SS2, SS3, SS4, for each year independently (separately for years 2018, 2019, and each parameter). In detail, for each of the eight parameters, the analysis of variance (ANOVA) was carried out independently, i.e., the null hypothesis was tested: that the average values (of the examined parameter) are equal for each of the four sludges:

$$H_0\colon \mu_{\mathrm{SS1}} = \mu_{\mathrm{SS2}} = \mu_{\mathrm{SS3}} = \mu_{\mathrm{SS4}}$$

against the alternative hypothesis H_1, stating that not all averages are equal, i.e., it is a negation of H_0, hypothesis 3:

$$H_1\colon {\sim}H_0$$

If we do not reject the null hypothesis in the ANOVA (hypothesis 3), we can, with some error, assume that the average values of the examined parameter for each of the four sludges are equal (hypothesis H_0). If we reject H_0, we know that the average values for all sludges are not equal. Then it is reasonable to perform Tukey's analysis. This test can answer the question of whether although not all averages are equal, it is possible to distinguish homogeneous groups among these four sludges, i.e., the average content of the tested (determined, one) parameter in one sludge does not differ significantly from the average content of this parameter in another sludge, although it differs significantly from the content in the other sludge. Then, the first two sludges constitute one group, the so-called homogeneous group.

Apart from examining the value of particular parameters and changes in the size of the values of single parameters, it is very interesting to see how these parameters interact and how they change in time. The same parameters for different sludges may take very different values. However, the relationships (correlations) between them may be the same. For example, if the value of one of them increases, the other increases proportionally, or the other decreases proportionally.

Because the following parameters appear to be dependent on each other in the following way: CFAs + CHAs = CHSs, and CWEOC + HWEOC = WEOC, no correlation analysis was performed for them. Moreover, for pairs (x, y) of correlated parameters, estimates of simple regressions of the form can be determined (Regression model):

$$y = \beta_0 + \beta_1 x$$

where the regression parameter β_1 shall be interpreted as follows: if parameter x increases by one unit, parameter y increases (decreases) by β_1 units.

3. RESULTS

The values of most analyzed parameters were comparable for the SS1 and SS2, as well as SS3 and SS4. Generally obtained values for SS1 and SS2 (and with one exception for the C:N values) were lower compared to those specified for SS3 and SS4 (Tables 2 and 5).

The present study focused on the following parameters: CL, CHSs, CFAs, CHAs, TOC, CWEOC, HWEOC, and WEOC. The obtained data were subjected to detailed statistical analysis. Statistical analysis conducted for four sewage sludge treated together (hypothesis 1) confirmed that the values of many parameters assessed for sewage sludge from 2018 differ significantly compared to the values specified in the sludge from 2019, their quantitative variability should be stated in the years of the study (Fig. 1). The exceptions were the amount of CHAs (p-value = 0.4904) and TOC (p-value = 0.1589). The CL (p-value = 0.0986) and WEOC (p-value = 0.0658) values were not much different. Comparisons with the t-test, p-values, and boxplot charts should be considered for information only.

Table 2

Selected properties of the analyzed sewage sludge

Sewage sludge	OM (g·kg^{-1})	TOC (g·kg^{-1})	N_{tot} (g·kg^{-1})	C:N	HSs $Q_{4/6}$	HAs $Q_{4/6}$	CHAs:CFAs
SS1	620–730 672.22±41.2	329.8–340.1 329.6±6.1	48.8–54.1 51.4±2.0	6.4	2.55	4.83	0.18
SS2	650–700 670±19.4	323.4–352.7 333.7±14.1	47.8–53.2 50.4±2.0	6.6	2.00	4.06	0.16
SS3	650–850 762.2±83	406.1–440.9 420.1±15.5	70.4–76.8 73.0±2.7	5.8	4.63	5.74	0.32
SS4	520–840 767.8±98.6	393–729 408.9 ±15.5	66.3–76.7 70.6±4.5	5.8	4.20	5.49	0.32

OM, TOC, N_{tot}: first row – range of values, second row – mean value±standard deviation.

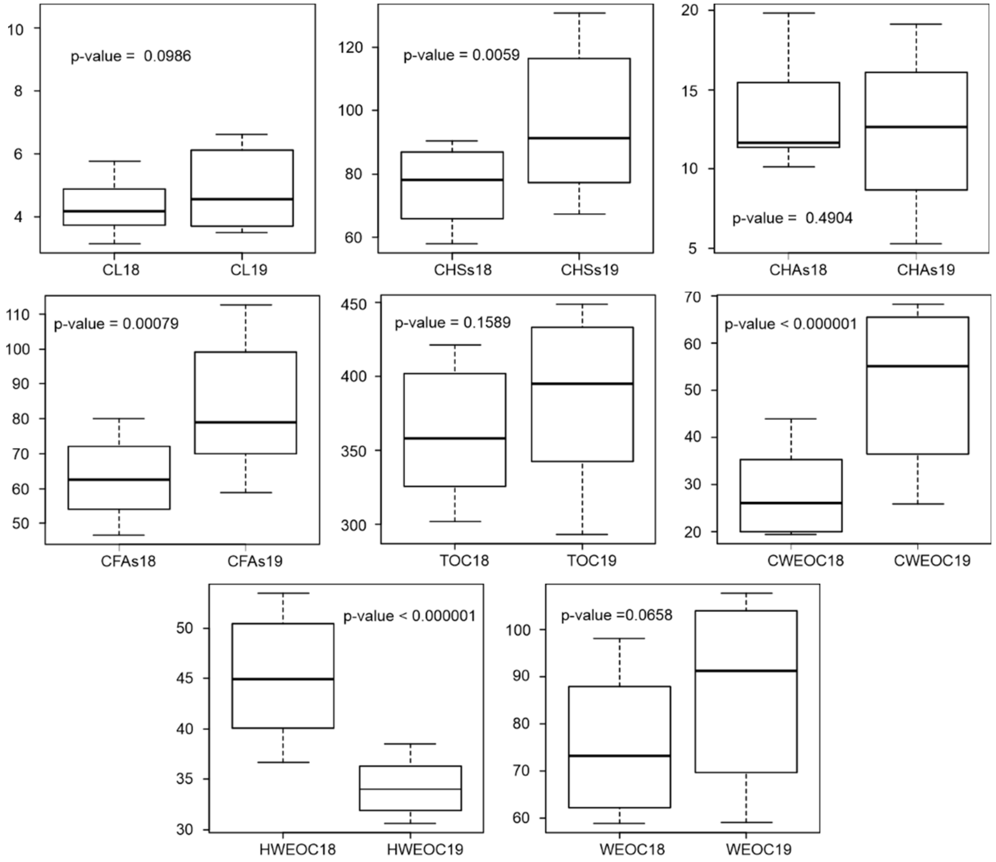

Fig. 1. Box-plots for the tested parameters; ranges of parameter sizes in 2018 and 2019 through all sludges taken together; the *p*-value from the comparison analyses was recorded calculated using the *t*-student test (hypothesis 1) for each pair of comparisons

In connection with the above, the charts in Fig. 1 illustrate the ranges of the tested parameter in a given year, averaged for the tested sludge (four sludge treated together), cannot be used to draw detailed and accurate conclusions about the quantitative changes of individual parameters in each sludge.

More detailed results (Table 3) are provided by another analysis (hypothesis 2). Numbers in bold indicate the values of *t*-Student statistics for the parameter whose value was unchanged during the years of the study. And so for the SS1, the parameters whose quantities were not subject to quantitative changes were CL and TOC. Hence, these two parameters can be treated as characterizing the SS1. In the case of SS2 and SS3, it was proved that CL and CHAs were characterized by invariant values. In the case of SS4, each parameter had on average significantly different values in 2018 compared to 2019. The contents of CL, CHSs, CHAs, and CFAs in 2018 were the least statistically significantly different compared to the results obtained in 2019 ($\alpha = 0.1$).

Table 3

Results of the *t*-student test (hypothesis 2) – the comparison of the average values for 2018 and 2019 for the analyzed sewage sludge

CL	CHSs	CHAs	CFAs	TOC	CWEOC	HWEOC	WEOC
SS1							
–0.65	-9.36^{a}	4.54^{c}	-10.51^{a}	**0.89**	-7.76^{a}	15.99^{a}	2.68^{c}
SS2							
0.003	-4.38^{b}	**1.11**	-5.3^{c}	-4.83^{b}	-46.22^{a}	7.14^{a}	-17.73^{a}
SS3							
–1.65	-23.91^{a}	**0.86**	-32.47^{a}	-3.71^{b}	-22.43^{a}	22.32^{a}	-8.90^{a}
SS4							
-2.38^{d}	-2.71^{d}	-2.35^{d}	-2.26^{d}	-6.24^{a}	-57.7^{a}	36.63^{a}	-33.16^{a}

Superscripts denote the following levels of significance: a – $\alpha = 0.001$, b – $\alpha = 0.01$, c – $\alpha = 0.05$, d – $\alpha = 0.1$.

Table 4

F-statistics values from ANOVA variance analysis (hypothesis 3) for comparison of SS1–SS4 sewage sludge

Year	CL	CHSs	CHAs	CFAs	TOC	CWEOC	HWEOC	WEOC
2018	14.18^{a}	53.74^{a}	50.17^{a}	54.77^{a}	102.7^{a}	227.8^{a}	130.2^{a}	355.8^{a}
2019	9.197^{b}	226.3^{a}	24.99^{a}	258.1^{a}	57.11^{a}	2185^{a}	51.43^{a}	1697^{a}

Degrees of freedom for compared objects (sewage sludge) for each of the 16 analyzes $df = 3$, degrees of freedom for the error $df = 12$. Superscripts denote the following levels of significance: a – $\alpha = 0.001$, b – $\alpha = 0.01$.

Significant differences between parameter values of individual SS also were assessed by ANOVA (Table 4). Based on the results from Table 4, it can be concluded that in all of the 16 analyzes tested, the null hypothesis saying that equality of the average values of the tested parameter for each sewage sludge was rejected (hypothesis 3). This means that the average CL parameter values are not the same for all four sewage sludge in 2018 (significance at $\alpha = 0.001$ (a)) and that the average CL values are not the same for all four sewage sludge in 2019 (significance for level $\alpha = 0.01$ (b)). The same conclusion regarding testing the average values of the tested parameter for various SS can be drawn for all other parameters: CHSs, CHAs, CFAs, TOC, CWEOC, HWEOC, and WEOC for each year treated independently (Table 4).

Table 5

Average values of parameters [g·kg^{-1}] for the analyzed sewage sludge in 2018 and in 2019

2018											
Sludge	CL mean	Group	Sludge	CHSs mean	Group	Sludge	CHAs mean	Group	Sludge	CFAs mean	Group
SS3	5.05	a	SS4	89.20	a	SS3	18.56	a	SS4	77.52	a
SS4	4.92	a	SS3	81.16	b	SS4	11.68	b	SS2	63.35	b
SS2	3.80	b	SS2	74.72	b	SS1	11.64	b	SS3	62.60	b
SS1	3.52	b	SS1	59.47	c	SS2	11.37	b	SS1	47.83	c
Sludge	TOC mean	Group	Sludge	CWEOC mean	Group	Sludge	HWEOC mean	Group	Sludge	WEOC mean	Group
SS3	409.91	a	SS3	41.92	a	SS3	52.29	a	SS3	94.22	a
SS4	389.58	b	SS4	30.63	b	SS4	48.73	b	SS4	79.36	b
SS1	329.83	c	SS1	20.80	c	SS1	40.18	c	SS1	60.98	c
SS2	314.42	c	SS2	20.07	c	SS2	39.29	c	SS2	59.35	c
2019											
Sludge	CL mean	Group	Sludge	CHSs mean	Group	Sludge	CHAs mean	Group	Sludge	CFAs mean	Group
SS4	8.04	A	SS3	129.31	A	SS3	17.73	A	SS3	111.58	A
SS3	5.87	AB	SS4	97.63	B	SS4	10.30	B	SS4	83.34	B
SS2	3.80	B	SS2	87.60	C	SS2	10.13	B	SS2	77.48	C
SS1	3.66	B	SS1	68.35	D	SS1	7.25	B	SS1	61.10	D
Sludge	TOC mean	Group	Sludge	CWEOC mean	Group	Sludge	HWEOC mean	Group	Sludge	WEOC mean	Group
SS3	436.77	A	SS3	67.44	A	SS3	37.15	A	SS3	104.58	A
SS4	429.86	A	SS4	63.78	B	SS4	35.81	A	SS4	99.59	B
SS2	355.82	B	SS2	45.90	C	SS2	32.25	B	SS2	78.15	C
SS1	319.08	C	SS1	26.57	D	SS1	31.36	B	SS1	57.93	D

Homogeneous groups of sludges for 2018 are indicated by lowercase letters a, b, c, and for 2019 by capital letters A, B, C, D. Tukey's HSD test results

Therefore, it made sense to perform the Tukey test analysis, the results of which are given in Table 5. Based on Tuckey's analysis, the homogenous groups were elaborated

(Table 5). Considering the obtained findings from 2018, SS3 is characterized by the highest amounts of CL, CHAs, TOC, CWEOC, HWEOC, and WEOC. Simultaneously, the lowest amounts of CL, CHSs, and CFAs were determined for SS1. Whereas SS2 showed the lowest amounts of CHAs, TOC, CWEOC, HWEOC, and WEOC. It should be underlined that SS3 and SS4 as well as SS1 and SS2 did not differ from each other in CL amounts. The lack of significant difference was also observed in the case of CHSs and CFAs (for SS2 and SS3), CHAs (for SS1, SS2, and SS4), and TOC, CWEOC, HWEOC, and WEOC (for SS1 and SS2) (Table 5). Analyzing the quantitative changes of the tested parameters in the sewage sludge collected in 2019, the same trends as demonstrated above one can note. Again for SS3, the highest values of all parameters besides CL were obtained, and the lowest amounts were characteristic of SS1. However, the values of individual parameters in 2018 and 2019 differed. For CL there was a temporary increase in the value of this parameter for SS4 (increment was significant on the level of $\alpha = 0.1$, Table 3). For the rest of the analyzed SS, the values of CL were at the same level and did not differ significantly. A similar increase was found for CHSs and CFAs, with the pronounced change for SS3 (1.5 and 2.0 times respectively). In the case of these both parameters, the increase from 2018 to 2019 for SS3 was highly significant, $\alpha = 0.001$ (Table 3). The data presented for the values of TOC, WEOC, CWEOC confirm their increment. In the case of the latter parameter, SS2, SS3, and SS4 displayed increases by 2, 1.5, and 2 times, respectively, and it was highly significant, $\alpha = 0.001$ (Table 3). The amounts of CHAs generally decreased in years of study. The decrease was confirmed statistically for SS1 ($\alpha = 0.05$), while for SS2 and SS3 the decrease in CHAs was not significant (Table 3). SS4 was an exception because an increase in the value of this parameter was noted what was significant at α=0.1 (Table 3). The reduction of HWEOC amounts in sewage sludge in 2019 compared to 2018 should be also mentioned and this tendency was proved statistically at the level of $\alpha = 0.001$ (Table 3).

From a series of correlation analyses, it appears that the overwhelming majority of pairs of parameters behave differently in 2018 and 2019. However, within each sewage sludge pairs of parameters can be distinguished, which behave similarly in the years of research in terms of mutual influences. Those are:

- for SS1, pair HWEOC and CHAs, (correlation for 2018 $r = 0.31$, for 2019 $r = 0.95$, for both years together correlation $r = 0.91$);
- for SS2: WEOC and CFAs (correlation for 2018 $r = 0.46$, for 2019 $r = 0.94$, for both years together $r = 0.93$);
- for SS3: TOC and CHSs (correlation for 2018 $r = 0.75$, for 2019 $r = 0.86$, for both years together correlation $r = 0.86$);
- for SS4: HWEOC and CFAs (correlation for 2018 = –0.71, for 2019 = –0.38, for both years together correlation $r = -0.69$ together).

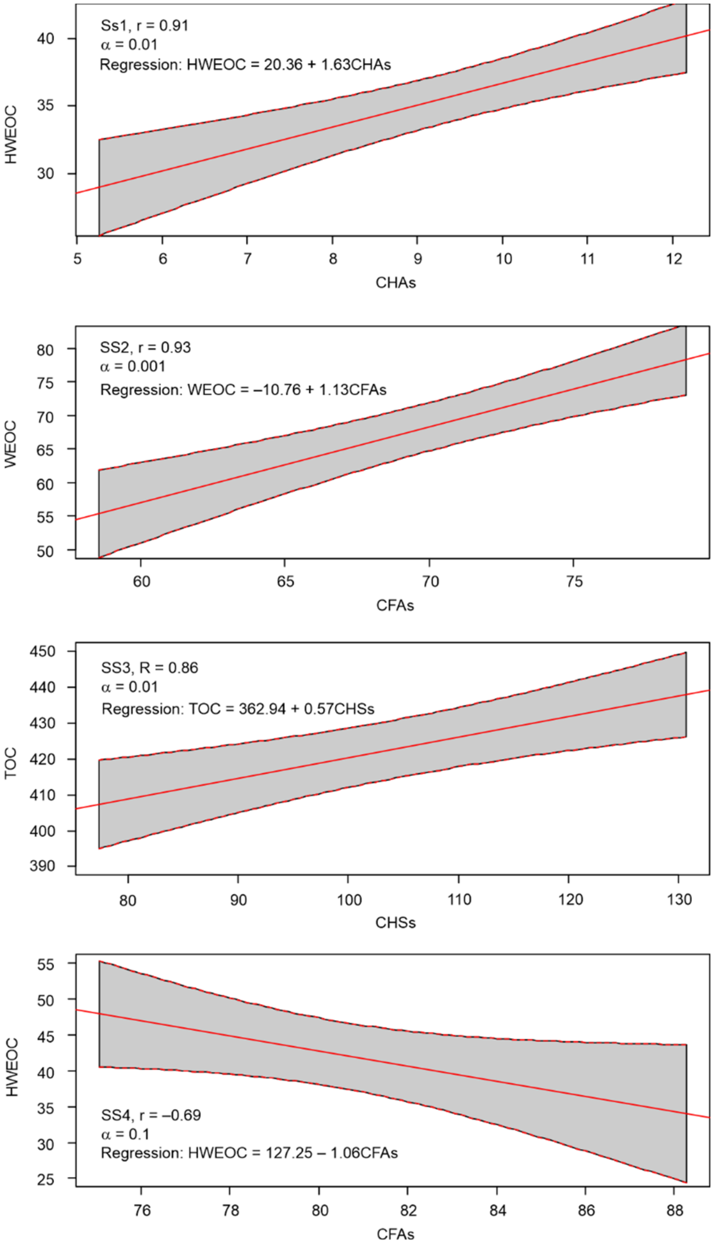

Fig. 2. Regression equations, confidence curves,
and linear correlation coefficients for selected pairs of parameters

This can be regarded as a positive conclusion: each sewage sludge is different and is characterized by a different pair of parameters. A regression line was determined for each of the pairs discussed above (regression model). Estimates of regression parameters are presented in Table 6.

Table 6

Estimates of linear regression parameter estimators (regression model) for pairs

Sludge	y	x	β_0	β_1
SS1	HWEOC	CHAs	20.36	1.63^b
SS2	WEOC	CFAs	–10.76	1.13^a
SS3	TOC	CHSs	362.94	0.57^b
SS4	HWEOC	CFAs	127.25	-1.06^c

Superscripts denote the following levels of significance: a – $\alpha = 0.001$, b – $\alpha = 0.01$ c – $\alpha = 0.1$.

The values in Table 6 show that the regression between HWEOC and CHAs (SS1) is highly significant ($\alpha = 0.01$), between WEOC and CFAs (SS2) is very highly significant ($\alpha = 0.001$), between TOC and CHSs (SS3) is highly significant ($\alpha = 0.01$), and between HWEOC and CFAs (SS4) is not significant ($\alpha = 0.1$). Besides, based on simple regressions, it is possible to predict average changes in y depending on changes in x. If in the SS1 CHAs content increases by 1 unit (1 $\mathrm{g{\cdot}kg^{-1}}$), the HWEOC content will increase by 1.63 units (1.63 $\mathrm{g{\cdot}kg^{-1}}$) on average. If in the SS2 CFAs content increases by 1 unit, the WEOC content will increase by 1.13 units on average. If in the SS3 CHSs content increases by 1 unit, the TOC content will increase by 0.57 units on average. If in the SS4 CFAs content increases by 1 unit, the HWEOC content will decrease by 1.06 units on average. The above results allow us to predict how the change in one parameter will change the other (for a specific sludge and a specific pair of parameters). Besides, a 95% confidence curve was determined. This is an amazing convenience for researchers conducting future experiments. Based on confidence intervals, it will be possible to determine the range of other values to be expected (Fig. 2). For example, when the CHAs value in the SS1 sewage sludge is 8 $\mathrm{g{\cdot}kg^{-1}}$, we can expect with 95% confidence that the HWEOC values will be in the range from 31.28 $\mathrm{g{\cdot}kg^{-1}}$ to 35.5 $\mathrm{g{\cdot}kg^{-1}}$, regardless of the year of testing. Similarly, with 95% certainty, ranges of values for other pairs and established sediments can be predicted (Fig. 2).

4. DISCUSSION

Sewage sludge is noxious waste and due to this fact, it must be subject to restrictive analysis for sanitary and chemical pollution. In Poland, in the case of natural SS application (for agriculture, horticulture, forestry, or land reclamation), this waste must meet some regulations specifying criteria for heavy metals and amounts of pathogenic microorganisms, while specific soil conditions also must be accomplished [21]. The amounts of organic matter and TOC, pH, as well as macro- and micronutrient content, are also routinely determined. This type of evaluation is required when SS is applied in the natural environment (agriculture, reclamation). However, apart from the standard assessment of OM and TOC contents, detailed studies of sewage sludge humus compounds are rarely carried out. Statistical analysis showed significant differences for most parameter values between sewage sludge and years of studies. Moreover, generally analyzed humic parameters increased in their values in 2019 concerning those in 2018 (with the only exception in the case of CHAs and HWEOC amounts). Nevertheless, in 2018 there were no differences between SS1 and SS2 originating from big WWTPs or small ones (SS3 and SS4). The lack of significant differences was shown for CL, CHAs, TOC, CWEOC, and HWEOC amounts. In 2019, SS1 and SS2 differed statistically in the contents of CHSs, CFAs, TOC, and WEOC. On the other hand, SS3 and SS4 did not differ in terms of CHAs, TOC, and HWEOC amounts obtained in 2019.

Due to this fact it might be tentatively concluded that the size of WWTPs influences the quality of SS. Even though all installations treated wastewater in the same technology, the different quantity and composition of wastewaters depending on the served agglomeration were probably factors determining the observed changes. This integrally relates to the WWTP efficiency, which was better for the smaller ones, because SS3 and SS4 were characterized by higher levels of all tested parameters compared to SS1 and SS2. Large WWTPs are usually burdened with an excessive load of biogenic compounds coming from sludge from non-drainage tanks (such a situation was observed in the case of the analyzed installations). The high costs of emptying non-drainage tanks induce users to significantly reduce the amount of water used and excessively long intervals between emptying tanks are noted. As a result, significant increments of biogenic pollutant concentration and advanced fermentation processes (rotten stage of sludge) are observed. This leads to the composition of such wastewaters being similar to sludge with very high hydration and emission of an unpleasant smell (e.g., hydrogen sulfide) and black and gray color [22]. Therefore the addition of sludge from non-drainage tanks to the wastewater network at the WWTPs can slightly and periodically reduce the efficacy of sludge purification, resulting in lower amounts of biogenic elements in sewage sludge.

Taking into account the fact of enhancing soil organic matter with sewage sludge application, the comprehensive analysis of their organic matter composition is essential. In the present work, WEOC was analyzed and it cannot be fully identified with water-extractable organic matter (WEOM), which according to Convasce et al. [23], represents mobile and readily soluble fraction of organic matter. Nevertheless, both these parameters (WEOM and WEOC) are closely interdependent, so the interpretation of obtained data may be similar. The WEOC contents regardless of the year ranged from

57.93 $g\cdot kg^{-1}$ (SS1) to 104.58 $g\cdot kg^{-1}$ (SS3) (Table 5). Moreover, these figures are comparable to CHSs data (59.47 $g\cdot kg^{-1}$for SS1 – 129.31 $g\cdot kg^{-1}$ for SS3) and an increase both in CHSs and WEOC amounts was found in 2019. As a result of these similarities, percentage shares of CHSs in TOC contents as well as WEOC amounts in TOC contents were comparable and ranged from 18.0% (SS1 in 2018) to 29.6% (SS3 in 2019) for CHSs and from 18.2% (SS1 in 2019) to 23.9% (SS3 in 2019) for WEOC. Calculation of CWEOC and HWEOC percentage shares in WEOC showed that regardless of individual SS higher values were obtained for HWEOC (55.5% for SS3 to 66.2% for SS2) in 2018. On the other hand, in 2019 the predominant share of CWEOC was found (45.9% for SS1, 67.7% for SS4) .

Many authors [18, 24, 25] have emphasized the importance of HWEOC transformations. The cited authors considered hot water extracted organic carbon as the most sensitive indicator reflecting changes in organic matter caused by different soil management practices between sites and within an ecosystem. According to Ghani et al. [18], HWEOC is a component of the labile soil organic matter and is a sensitive measure of subtle changes within the ecosystem. Of course, it cannot be ruled out that the quantitative changes in HWEOC observed in soil conditions will similarly inform about the changes in SS organic matter, but the obtained outcomes confirm the relationships between HWEOC as well as CFAs and CHAs amounts (Table 6). This is also evidenced by the simultaneous decrease in HAs and HWEOC (Table 5) observed in the years of research, which may be interpreted as some deterioration in the humic properties of SS, especially those with a more complex structure. The smaller amounts of HAs in 2019 compared to those in 2018 may be the result of more intensive microbiological processes in activated sludge. Such a possibility is indicated by Filip et al. [26], who in their study confirmed that HAs from sewage sludge can be readily utilized by a mixed microbial community under aerobic conditions (aerobic conditions are required during the wastewater treatment) as a supplementary source of nutrients, especially at a deficit of C and N.

The noticeable similarity between HSs and WEOC amounts in SS is not surprising when considering the HSs composition of FAs and HAs. Fulvic acids are compounds weakly polymerized and relatively easily subject to chemical and microbiological changes, which results in their considerable solubility and mobility. In turn, HAs are generally recognized as being non-degradable or sparsely degradable compounds with a strongly polymerized structure. These assumptions are partly confirmed by $Q_{4/6}$ values (Table 2) calculated for both CHSs and CHAs of sewage sludge. The figures indicate a strongly polymerized structure of these compounds and a larger molecular weight [14]. However, as indicated by the obtained data, regardless of the sewage sludge or year of study, the percentage shares of CFAs contents in CHSs was dominant, amounted from 77.1% (SS3) to 89.4% (SS2), and was higher in 2019. Sewage sludge, regardless of the WWTP size, was characterized by low CHAs contents (from 7.25 to 18.50 $g\cdot kg^{-1}$), which constituted their percentage share from 10.6% (SS1) to 22.9% (SS3) of CHS amounts.

The given results are consistent with the earlier researches conducted by Iakimienko and Velichenko [27], where the predominant fulvic acid fraction of sewage sludge was reported. Moreover, the cited authors underlined a low CHAs:CFAs ratio, similarly as in the presented study (Table 2).

Among the analyzed parameters, the lowest values were determined for CL (from 3.52 to 8.04 $g\cdot kg^{-1}$) (Table 5). Despite the 2-fold difference between the figures, the percentage share of CL amounts in TOC contents was comparable in SS regardless of the experimental factors and ranged from 1% (SS1) to 1.9% (SS4). In the light of statistical results (Table 3), the labile carbon was the most stable parameter (constant values within years of the study), apart from HAs and TOC. The amounts of CL were highly significant for SS1 – SS3 and less significant for SS4. Obtained findings regarding CL amounts may be an incentive for further and more detailed research connected with the application of CL as a potential indicator of SS quality. Also, more detailed studies should be carried out for CFAs and CHAs, because as it was proved by statistical analysis (Table 6), these parameters were closely related to HWEOC and WEOC. Assessing only the content of CFAs and CHAs one can predict the amounts of WHEOC and WEOC without additional laboratory work. In the obligatory routine laboratory work, low-cost, quick, and reliable methods of SS analysis are required, so more precise and broader studies related to the parameters indicated in this paper should be taken under consideration and such knowledge should be developed. Such a fast and simple chemical analysis will help to valorize SS, especially when this waste is proposed for applications in the natural environment. The amounts of readily and sparsely soluble humic compounds are closely connected with the rate of SS transformation in soil and its potential influence on soil fertility.

5. CONCLUSION

Despite the use of the same purifying technology, the amount of wastewaters reaching WWTPs as well as the effectiveness of the treatment process significantly influenced the quality and quantity of the analyzed parameters. Sewage sludge originating from small WWTPs had higher values of the parameters in comparison with those determined for SS representing big WWTPs. Considering a large amount of organic matter and total organic carbon in SS, its agricultural or reclamation use is justified. In this aspect, special attention should be focused on the dominance of FAs in humic substances and WEOC amounts (quantitatively comparable to the HS amount), compounds that can actively shape the carbon pools in soil and soil microbiologic activity. The probability of rapid transformation of these compounds in the soil is connected with their lability and significance both for the creation of a labile pool of carbon and fulfilling the basic environmental functions. This is since both water dissolved carbon compounds and the less complex structure of FAs are the main energy sources for soil microorganisms and a primary source of mineralisable N, P, and S compounds. The statistical analyses carried out indicate the significance of such parameters as CL, FAs, and HAs in SS valorization particularly in the aspect of their application in the natural environment.

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