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Characteristics of humic substances from municipal sewage sludge: a case study

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ABSTRACT

Recycling of sewage sludge is one of the most desirable solutions in waste management strategy. Mostly, sewage sludge is composted, used for biogas production, or simply used in agriculture as fertilizer (if it does not contain heavy metals (HM)). Sewage sludge can be also used as soil amendment to immobilize HM (stabilization strategy). The new trend is using sewage sludge as a source of humic substances (HS), which, after extraction, are considered to be effective washing agents for removal of HM from polluted soils (mobilization strategy). It should be emphasized that HS for soil washing can be recovered even from sewage sludge with elevated concentrations of HM that would make the sludge unsuitable for agricultural use and composting. However, the possibility of using HS in both aforementioned strategies of soil remediation requires knowledge about their detailed characteristics. In this study, the detailed characteristics of HS from 5 different municipal wastewater treatment plants are provided. It is shown that organic matter (OM) content in sewage sludges ranged from 70.2% to 84.2% and HS content ranged from 118.7 to 227.5 mg/g OM. In all sludges, the share of humic acids (HA) in HS ranged from 35.7% to 48.2%. In HA, stable HA predominated (>92%). $\Delta\log K$ values of 0.6–0.8 showed that HA were of B-type, indicating a medium degree of humification. These results provide useful information about HS introduced into the soil.

Keywords: Sewage sludge; Resources; Organic matter; Humic substances; Humic acids

1. Introduction

The amount of municipal sewage sludge is gradually increasing around the world. Due to its high content of organic compounds and high fertilizer value, sewage sludge has been used directly as soil fertilizer, composted, or used as a substrate for biogas production.

Sewage sludge may contain humus-like materials because, during municipal wastewater treatment, organic matter (OM) mineralization is accompanied or closely followed by humification, so sewage sludge is rich in intermediate products of decomposition, mostly 'raw' humus. Thus, sewage sludge may be a rich source of humic substances (HS), which after recovering may also be used in soil remediation.

It is known that HS substantially influence the mobility and bioavailability of heavy metals (HM) in soils because they are amphiphilic, with both hydrophobic and hydrophilic components, and their carboxyl and hydroxyl groups can form complexes with HM [1].Therefore, material rich in HS may be useful for remediation of soil contaminated with HM, via either stabilization (immobilization) or mobilization (soil washing/soil flushing). In the former strategy (stabilization), these materials may act as an organic amendment, which contributes to immobilization of HM. Sewage sludge considerably increases the cation exchange capacity of amended soil that affects HM behavior in soil [2,3]. In addition, sewage sludge application to contaminated soil can improve biomass production due to the formation of stable humate complexes with HM and decreased HM bioavailability [4]. Although immobilization process does not decrease the total HM concentration in soil, decreasing their mobility does substantially

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decrease environmental risk [5]. In the second strategy (soil washing/soil flushing), material rich in HS can be a source of HS, which may be used as a washing agent after extraction from sludge or other waste [6].

HS form complexes with HM as a result of ion exchange between H^+ and metal ions.

The hydroxyl, phenoxyl, and carboxyl groups in HS can form stable complexes and chelates with HM [7]. When considering the suitability of sewage sludge as a source of HS, it is important to assess not only HS content but also the relative amounts of the fractions of HS, i.e. the fulvic fraction (FF) and humic acids (HA). FF contains more functional groups than HA, including carboxylic groups (62%–88%) and hydroxyl groups (12%–37%), so FF could have a greater ability to complex metals than HA. Behavior of HM under the influence of HA can depend on the form of HA, i.e. labile humic acids (L-HA) or stable humic acids (S-HA). Complexes of HM with L-HA are more soluble and mobile in soil profile than complexes with S-HA [8]. Thus, determination of the forms of HA in organic materials rich in HS and designed to be used in soil remediation is very important.

The objective of this study was to determine the total concentration of HS and the concentrations of their fractions (FF and HA) in sewage sludge. L-HA and S-HA were characterized in terms of their elemental composition and spectral properties. These characteristics are important when sewage sludge is used as a source of HS in soil remediation and also provide useful information about exogenic substances being introduced into the soil when sewage sludge is used as soil amendment.

2. Materials and methods

2.1. Wastewater treatment plant location and characteristics

The sewage sludge originated from five municipal wastewater treatment plants (WWTPs) located in Poland. The WWTPs differed in capacity and the percentage of wastewater received from septic tanks: 60,000 m^3/d and <0.5% (WWTP 1), 1,500 m^3/d and 2% (WWTP 2), 1,200 m^3/d and <0.5% (WWTP 3), 750 m^3/d and <1% (WWTP 4), and 400 m^3/d and 8% (WWTP 5). All the WWTPs are mechanical-biological systems, and they all operated at low organic rates (0.08–0.2 g 5-day biochemical oxygen demand (BOD_5)/g mixed liquor suspended solids (MLSS·d)) and long sludge retention times (> 20 d).

All the WWTPs produce mixed sewage sludge: a dewatered mixture of primary and biological sludge after methane fermentation in WWTP 1 and a mixture of primary and biological sludge after thickening and dewatering without any further treatment in WWTPs 2–5.

2.2. Analytical methods

Sewage sludge samples were taken from the WWTPs five times at 1 month intervals. Sampling was carried out according to the Polish standard PN-EN ISO 5667-13:2004. Moisture, dry mass, OM, total N, and total P were analyzed according to Polish Standards (PN-EN 12176:2004; PN-EN 12880:2004; PN-EN 12879:2004; PN-EN 13342:2002; PN-EN ISO 14672:2006); total organic carbon (TOC) was measured using a Shimadzu Liquid TOC-VCSN analyzer.

2.2.1. HS extraction and fractionation

HS, HA, and the FF were extracted from sewage sludge by conventional procedures described by Boratyński and Wilk [9]. Before extracting the HS, the sludge was washed with distilled water to eliminate soluble non-HS, which can interact with HS [10]. Then, the sludge was defatted using a mixture of chloroform and methanol [11]. The FF content was calculated by subtracting the content of HA from that of HS. The detailed procedure of HS, FF, and HA extraction and the procedure of HA fractionation into L-HA and S-HA have been presented in previous studies [12–13].

Briefly, L-HA were extracted with 0.1M $Na_4P_2O_7$ at pH 7, and after separation of L-HA, S-HA were extracted with 0.1M NaOH at pH 12 [9]. In the procedure, 0.3 g of sewage sludge was shaken with 6 mL of 0.1M $Na_4P_2O_7$ for 1 h and centrifuged at 15,000 rpm for 15 min, and then the supernatant was transferred to a 50-mL volumetric flask. The procedure was repeated until a colorless supernatant was obtained. The extract in the 50-mL flask was filtered through a 0.45 µm filter, and then 0.1M $Na_4P_2O_7$ was added for a final volume of 50 mL.

Next, this extract was acidified to pH 1 with H_2SO_4, after which the precipitated L-HA were left to coagulate at 4°C for 24 h. Then, L-HA were separated from the FF by centrifugation at 15,000 rpm for 15 min and dissolution in 0.1M $Na_4P_2O_7$. S-HA were extracted from the sludge by repeating the above procedure with 0.1M NaOH. The concentrations of L-HA and S-HA were determined as TOC using a Shimadzu Liquid TOC-VCSN analyzer.

2.2.2. Analysis of the elemental composition of HA

The elemental composition of HA was determined according to the procedure of Alburquerque et al. [14]. L-HA and S-HA were successively washed by shaking twice with 0.1 M HCl and then once with distilled water for 15 min each time. After centrifugation, the supernatants were discarded and the purified HA was freeze-dried. The elemental composition (C, H, N, S) of HA was assayed with a Flash 2000 organic elemental analyzer (Thermo Scientific, Cambridge, UK). The percent content of oxygen was determined as the difference between the ash-free dry weight (100%) and the sum of the percent contents of C, H, N, and S. Based on the elemental composition of the HA, the atomic ratios (H/C, O/C, N/C, O/H) were calculated.

2.2.3. Spectral properties of HA

The absorbance of separated L-HA and S-HA at wavelengths of 280 nm (A280), 400 nm (A400), 465 nm (A465), and 665 nm (A665) was determined. Ultraviolet-visible spectra were performed with 0.02% solutions of HA in 0.1M $Na_4P_2O_7$ (L-HA) or 0.1M NaOH (S-HA). The spectra were determined with a Lambda 20 Perkin-Elmer Analyzer after fivefold dilution of HA. The following absorbance ratios were calculated: A2/4 – the ratio of absorbance at 280 nm to that at 465 nm, A2/6 – the ratio of absorbances at 280 and 665 nm, and A4/6 – the ratio of absorbances at 465 and 665 nm. Additionally, the coefficient $\Delta\log K = \log A400–\log A600$ was calculated for both kinds of HA.

3. Results and discussion

3.1. Basic physicochemical characteristics of sewage sludges

The physicochemical characteristics of the sewage sludges are presented in Table 1.

The moisture content of the sludges ranged from 83.17% (WWTP 1) to 91.3% (WWTP 4). The pH of all sludges was slightly alkaline. The lowest content of OM (70.2%) was found in the sludge from WWTP 1 (sewage after anaerobic digestion). The amount of OM in the sludge from the other WWTPs ranged from 84.2% (WWTP 5) to 81.6% (WWTP 3). The amount of total N in the sludges did not exceed 7.5%. The lowest percentage of total N (5.4%) was recorded in the sludge from the WWTP 5 and the highest (7.3%) in the sludge from WWTP 4. The content of P ranged from 2.4% (WWTP 5) to 4.3% (WWTP 1). Similar characteristics, i.e. OM (62.7%–72.0% d.m.), total N (5.2%–7.5% d.m.), and total P contents (2.9%–3.9% d.m.) were noted by Kazanowska and Szaciło [15] in sewage sludges from other WWTPs in Poland. Roman and Bernacka [16] have reported that total N concentration in primary sewage sludge can range from 2.0% to 7.0% d.m., while in excess sludge, it can vary from 3.0% to 10.0% d.m. According to other authors, however, the content of this element can vary more widely, from 1.6% d.m. [17] to 12.7% d.m. [18]. Similar variations in P content have been reported, ranging from 0.30% d.m. (14) to 6.04% d.m. [19]. In the present study, K concentration ranged from 0.35% (WWTP 5) to 0.62% (WWTP 1). According to Roman and Bernacka [16], K contents in primary and excess sludge range from 0.1% to 0.7% d.m. and from 0.1% to 0.8% d.m., respectively; however, other authors have shown that it can be higher and even exceed 1% d.m. [20,21].

In all the sewage sludges, the concentrations of HM were well below permissible limits for municipal sewage sludge in Poland (in mg/kg d.m.: 20 Cd, 1,000 Cu, 300 Ni, 750 Pb, 2,500 Zn) [22,23].

3.2. HS in sewage sludges

3.2.1. Concentrations of HS and their fractions

The sewage sludges from the WWTPs differed in HS content. The sludge from WWTP 1 had the highest concentration of HS (227.5 mg/g OM; 161.6 mg/g); in the other WWTPs, the HS concentrations were 1.6–1.9 times lower (Table 2). The higher concentration of HS in WWTP 1 may be connected with the fact that this sludge had been stabilized anaerobically, whereas in WWTPs 2–5, the sludge was a mixture of primary and biological sludge that had not been stabilized. The HS concentrations in sewage sludges in this study were much higher than those reported by Ayuso et al. [24], who found that the HS concentration in unstabilized sewage sludge was 75.7 mg/g. In contrast, Réveillé et al. [25] reported much higher concentrations of HS in sewage sludge (from 156.9 to 168.3 mg/g). However, these authors measured lower concentrations of HS when lipids were removed from the same sludges before HS extraction (138.2–145.2 mg/g). HS concentrations appear higher without lipid removal because the alkaline solution used to extract HS from fresh OM dissolves the structural components of vegetal residues and bacterial biomass and co-extracts non-HS such as lignin residues, lipids, etc. [25,26], and these substances coprecipitate with humic fractions [25,27].

Taken together, the data from these studies and from the present study indicate that the HS concentrations that are measured in sewage sludge depend on the degree to which the sludge was stabilized and on the pretreatment of the samples before HS extraction. Although these factors can make it difficult to compare results, it should be emphasized that, even though the samples were defatted in the present study, the HS concentrations were as high or even higher than that of compost from different kinds of waste or peat [24,28–29]. This indicates that sewage sludge is a rich source of HS.

Table 1
Physicochemical characteristics of sewage sludge from different WWTPs (n = 5, ± standard deviation)

Indicator	WWTP 1	WWTP 2	WWTP 3	WWTP 4	WWTP 5
Moisture, %	83.2 ± 2.4	86.7 ± 2.6	88.1 ± 2.1	91.3 ± 2.3	84.2 ± 1.9
pH	7.68 ± 0.21	7.64 ± 0.28	7.46 ± 0.18	7.89 ± 0.26	7.72 ± 0.21
Organic matter (OM), %	70.2 ± 3.4	83.8 ± 4.2	81.6 ± 4.1	83.4 ± 4.5	84.2 ± 3.9
N, %	5.9 ± 0.6	7.0 ± 0.8	6.9 ± 1.1	7.3 ± 0.5	5.4 ± 0.6
P, %	4.3 ± 0.3	4.1 ± 0.4	3.9 ± 0.7	3.9 ± 0.8	2.3 ± 0.3
K, %	0.6 ± 0.1	0.5 ± 0.15	0.4 ± 0.12	0.6 ± 0.1	0.3 ± 0.05

Table 2
Concentrations of HS and their fractions in sewage sludge from different WWTPs (n = 5, ± standard deviation)

WWTP	HS	HS	FF	HA	HA/FF	HA in HS	S-HA in HA	L-HA in HA
	mg/g	mg/g OM	mg/g OM	mg/g OM	–	%	%	%
1	161.6 ± 22.4	227.5 ± 18.1	135.5 ± 12.9	92.0 ± 9.8	0.68 ± 0.23	40.4 ± 2.3	96.4 ± 4.8	3.6 ± 1.3
2	119.8 ± 14.2	141.6 ± 15.5	74.6 ± 11.1	67.0 ± 12.3	0.90 ± 0.41	47.3 ± 3.2	95.8 ± 2.1	4.2 ± 0.4
3	96.1 ± 13.5	120.2 ± 14.3	77.3 ± 13.9	42.9 ± 7.5	0.55 ± 0.11	35.7 ± 0.7	92.3 ± 1.6	7.7 ± 0.5
4	122.9 ± 27.2	144.3 ± 23.2	77.8 ± 20.7	66.5 ± 14.3	0.85 ± 0.31	46.1 ± 5.1	95.9 ± 3.4	4.1 ± 1.2
5	93.9 ± 11.9	118.7 ± 15.2	61.5 ± 12.8	57.2 ± 8.9	0.93 ± 0.22	48.2 ± 3.6	92.8 ± 1.1	7.2 ± 0.5

In all sludges in the present study, FF constituted the largest share of HS; the share of HA in HS ranged from 35.7% (WWTP 3) to 48.2% (WWTP 5). The HA/FF ratio ranged from 0.55 (WWTP 3) to 0.93 (WWTP 5), which was within the range given by other authors for HA from sewage sludge (from 0.3 to 3.0) [30–32]. Iakimenko and Velichenko [33] and Ayuso et al. [24] also found that, in HS from sewage sludge, FF predominated, and carbon in HA constituted 7% and 21% of carbon in HS, respectively.

HA may be divided into L-HA and S-HA. L-HA are small- or medium-sized macromolecules with an aromatic character, which are weakly bound to mineral surfaces via cation bridges, while S-HA are larger macromolecules of aliphatic character [34]. This characterization has been confirmed for HA extracted from peat, where S-HA have a higher molecular weight (>50,000), while L-HA have lower molecular weight [35]. Thus, it can be concluded that L-HA have lower molecular weights than S-HA, irrespective of their origins. In the present study, S-HA predominated in the sewage sludges from the different WWTPs (more than 90% of HA, Table 2).

3.3. HA characteristics

HA from soil and from composts made from various wastes can be described and compared based on their elemental composition (C, H, N, O). To this end, Table 3 presents the elemental composition of the L-HA and S-HA in this study and in others.

In HA from all sewage sludges in the present study, C predominated (by weight). In S-HA, it comprised just above 50%, which is similar to C content in HA extracted from compost and soils. In L-HA, C content was slightly lower.

There was notable variation in the content of N and S in HA extracted from sewage sludge in this study and their contents in HA from different soils and composts from different kinds of waste. The content of N in the HA extracted from the sewage sludges ranged from 7.63% to 9.90%, which was higher than N content in HA from other sources (Table 3).

However, it should be emphasized that N content in HA differs noticeably even in HA from soils. For example, Steelink [41] found that N content ranged from 0.8% to 4.3%, but Garcia Gil et al. [40] found that its content was much higher (7.2%) (Table 3). In the present study, the S content in HA was relatively high, particularly in comparison with that in soil HA [40,41]. However, the S content in the present study was less than a third of that in compost from olive oil extraction residues [37].

The elemental composition of HA in soil amended with sewage sludge or with composted sewage sludge is quite similar to the composition of HA in sewage sludge, compost, or soil [42–44]. HA extracted from soil amendment with composted sewage sludge contained more C and N compared

Table 3
Elemental composition of humic acids (HA) form different sources (L-HA – labile humic acids; S-HA – stable humic acids)

Origin of HA	Elemental composition (% weight)					References
	C	H	N	S	O	
L-HA WWTP 1	47.93	6.20	9.90	2.18	33.79	this study
L-HA WWTP 2	47.95	6.57	9.37	2.15	33.97	
L-HA WWTP 3	47.72	6.31	8.53	2.23	35.22	
L-HA WWTP 4	49.76	6.90	9.13	2.30	31.91	
L-HA WWTP 5	49.56	7.63	6.63	2.20	33.98	
S-HA WWTP 1	50.44	6.99	7.58	2.23	32.76	
S-HA WWTP 2	51.40	7.36	9.47	2.20	29.57	
S-HA WWTP 3	50.27	6.95	8.41	2.30	32.07	
S-HA WWTP 4	53.07	7.54	8.91	2.16	28.31	
S-HA WWTP 5	50.65	7.00	7.63	2.14	32.58	
Sewage sludge compost	50.1	5.9	4.8	–	39.3	[36]
Olive oil extraction residues compost	58.5	6.34	5.43	7.04	22.72	[37]
Sorghum-tomato compost	52.8	4.7	3.1	<0.3	39.4	[38]
Urban waste compost	51.7	4.9	6.3	<0.3	37.1	
Urban waste vermicompost	50.2	4.9	5.9	0.6	38.4	
Chicken manure-soybean vermicompost	51.4	4.7	4.9	0.6	38.5	
Tannery sludge compost	42.5	4.7	2.5	–	50.3	[39]
Municipal waste compost	56.0	8.5	6.3	0.7	28.5	[40]
Soil	51.2	5.2	7.2	0.6	35.9	
Soil	53–58	3.2–6.2	0.8–4.3	0.1–1.5	32–38	[41]
Soil ameneded with sewage sludge	48.6–49.9	5.0–5.6	4.1–5.2	0.4–0.8	39.8–41.3	[42]
Soil ameneded with sewage sludge	53.3	5.45	5.6	0.88	34.3	[43]
Soil amended with composted sewage sludge	59.8	6.7	9	1.6	22.8	[44]

with HA extracted from soil, compost, or soil amended with sewage sludge (Table 3).

To sum up, the main differences in the elemental composition of the HA involve N and S. These differences depend on the origin of the HA and the process by which the OM is decomposed.

Changes in elemental composition are accompanied by changes in atomic ratios (H/C, N/C, O/C, O/H). These ratios provide information about the structure of the HA molecules in terms of the degree of condensation of the aromatic rings (H/C ratio) and the degree of HA maturity (N/C, O/C, O/H ratios, and internal oxidation ω) [45,46].

In soil HA, H/C values of ca. 0.3 are characteristic of compounds with highly condensed aromatic rings; values of about 0.7 indicate monocyclic aromatic hydrocarbons; values of 0.7–1.5 correspond to aromatic rings with aliphatic chains of up to 10 carbon atoms; values of 1.5–1.7 indicate alicyclic hydrocarbons; and values of about 2 are characteristic of paraffin [47].

The values of the H/C atomic ratio of HA extracted from sewage sludge in this study ranged from 1.55 to 1.85 (Table 4). They were higher than those of HA extracted from compost and some soils but similar to that of HA extracted from soil, as reported by Garcia Gil et al. [40]. This indicates that HA from sewage sludge had a lower degree of aromatization than HA from compost and most soils. In soil amended with sewage sludge or compost, HA can be more condensed than those in sewage sludge or compost alone (Table 4).

The OM humification process is connected with an increase in oxygen content and a decrease in hydrogen content, which changes the O/H and O/C atomic ratios. The values of the O/H and O/C ratios are an indicator of the degree of oxidation of HA [48,49], and the O/H value is also related to the degree of humification of HA molecules. The higher the O/H ratio, the higher the humification of HA molecules [48]. In the present study, the O/H ratio of L-HA and S-HA was lower than that of soil HA. This means that the HA from sewage sludge had a lower degree of humification than soil HA. In soil amended with sewage sludge, the degree of oxidation and humification of HA can be higher [42,43] than in soil amended with composted sewage sludge [44].

3.4. Spectral properties of HA

HA are a mixture of different molecules, with different degrees of humification expressed as Δlog *K* (the logarithm of the ratio of the absorbance of HA at 400 nm to that at 600 nm). Kumada [49] used Δlog *K* to categorize HA into three basic groups: A-type (Δlog *K* < 0.6), B-type (≥0.6 to <0.8), and *R*-type (0.8–1.1). A lower Δlog *K* value indicates a greater degree of humification. The usefulness of this indicator follows from the fact that the chemical characteristics of HA differ depending on the origin of the HA. In all sewage sludges in the present study, HA were of *B*-type.

As degree of HA humification may vary depending on HA origin, it is important to establish Δlog *K* especially for

Table 4
Atomic ratios in humic acids (HA) form different sources (L-HA – labile humic acids; S-HA – stable humic acids)

Origin of HA	H/C	N/C	O/H	O/C	References
L-HA WWTP 1	1.55	0.18	0.34	0.53	this study
L-HA WWTP 2	1.64	0.17	0.32	0.53	
L-HA WWTP 3	1.58	0.15	0.35	0.55	
L-HA WWTP 4	1.66	0.16	0.29	0.48	
L-HA WWTP 5	1.85	0.12	0.28	0.51	
S-HA WWTP 1	1.66	0.13	0.29	0.49	
S-HA WWTP 2	1.72	0.16	0.25	0.43	
S-HA WWTP 3	1.66	0.14	0.29	0.48	
S-HA WWTP 4	1.71	0.14	0.24	0.40	
S-HA WWTP 5	1.66	0.13	0.29	0.48	
Municipal waste compost	1.43	0.13	–	0.40	[40]
Olive oil extraction residues compost	1.28	0.079	–	0.34	[39]
Sorghum-tomato compost	1.07	0.05	–	–	[37]
Urban waste compost	1.14	0.104	–	–	
Urban waste vermicompost	1.17	0.10	–	–	
Chicken manure-soybean vermicompost	1.09	0.082	–	–	
Tannery sludge compost	1.33	0.050	–	0.89	[39]
Soil (chernozems)	1.35	0.111	0.40	0.54	[46]
Soil (haplic livisol)	1.18	0.076	0.45	0.53	
Soil (sandy loam)	1.67	0.087	–	0.50	[37]
Soil ameneded with sewage sludge	1.21–1.36	0.07–0.09	0.44–0.49	0.58–0.60	[42]
Soil ameneded with sewage sludge	1.22	0.09	0.39	0.48	[43]
Soil amended with composted sewage sludge	1.34	0.13	0.21	0.29	[44]

materials/wastes that are used very often as soil amendments, i.e. sewage sludge or compost. This indicator is, however, rarely given for sewage sludge alone. Roppongi et al. [50] reported that compost application to an alluvial upland soil caused an increase in the Δlog *K* value of HA and changed the type of HA from type *B* to type *R*. On the other hand, Rivero et al. [51] found that compost addition to soil did not significantly change the HA type during a 3-y study. Shindo et al. [52] showed that the humification degree of HA extracted from soils depends on the type of fertilizer applied. HA from soils fertilized with mineral fertilizers were characterized with a medium degree of humification (*B*-type; Δlog *K* 0.68), while soils fertilized with nutrients and compost had a low degree of humification (*R*-type; Δlog *K* > 0.8). Kwiatkowska and Maciejewska [53] also found that soil with or without amendment with different kinds OM (cow manure, compost) had a medium degree of humification (*B*-type; Δlog *K* = 0.654–0.690). Because the information in the literature is unclear, estimation of Δlog *K* in HA extracted from sewage sludge may allow estimation of the degree of maturity of HA introduced to soil.

The E4/E6 ratio is another indicator that gives important information about HA molecules and their origin. According to Chen et al. [54], the E4/E6 ratio (understood as optical densities or absorbances of dilute, aqueous humic, and fulvic acid solutions at 465 and 665 nm) is related to the degree of condensation of the aromatic carbon, carbon content, and molecular weight of HS. The values of the E4/E6 ratio obtained for HA ranged from 1.83 to 9.5 [54]. Campitelli and Ceppi [38] showed that the E4/E6 ratio for HA in soil (Entic Haplustol, Argentina) was 4.3, which was lower than that for HA in compost (5.32–6.18) and in vermicompost (8.34–8.77). Unsal and Ok [56] stated that in HA extracted from different wastes, the E4/E6 ratio ranged from 1.88 (raw tea waste) to 5.75 (spent mushroom compost); in most wastes, however, it was higher than 3.0 (3.16 for tobacco dust; 3.28 for composted grape marc; 4.52 for composted bark). According to these authors, HA from organic wastes generally have a lower degree of condensation and humification than HA from soil (E4/E6 ratio of 2.13). In the present study, the E4/E6 values ranged from 2.19 to 2.64 for L-HA and from 2.35 to 3.41 for S-HA (Table 5). Similar values were obtained by Polak et al. [55]. These authors showed that with HA extracted from sewage sludges before fermentation, the E4/6 values changed from 1.93 to 4.0 and slightly increased with HA from sewage sludge that had been fermented (2.35–4.64). This may be due to the reduction of the molecular weight of HA in sludge through the loss of their aliphatic compounds or the increase in their oxygen content during fermentation.

Table 5
Values of Δlog *K* and E4/6 for L-HA and S-HA extracted from sewage sludge from different WWTPs

HA	WWTP 1	WWTP 2	WWTP 3	WWTP 4	WWTP 5
		Δlog *K*			
L-HA	0.632	0.651	0.658	0.632	0.605
S-HA	0.800	0.618	0.659	0.724	0.754
		E4/E6			
L-HA	2.64	2.19	2.32	2.37	2.44
S-HA	2.35	3.18	2.60	3.41	2.75

4. Conclusions

It was shown that all the investigated sewage sludges are rich sources of both nutrients and HS. In HS from all sludges, FF prevailed, and the share of HA in HS ranged from 35.7% to 48.2%. In the HA extracted from all the sludges, S-HA predominated (>92%). Δlog *K* values of 0.6–0.8 showed that HA from all the sludges were of *B*-type, indicating a medium degree of humification. This clearly indicates that the sludges from all the investigated WWTPs are similar, taking into account HS characterization. These results show that sewage sludge can be considered a resource, e.g. a soil conditioner or a source of HS, which are useful for soil remediation (soil washing/soil flushing).

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