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AGRICULTURAL USE OF WASTEWATER SLUDGE FROM VARIOUS SOURCES WITH SPECIAL EMPHASIS ON TOTAL AND DTPA-EXTRACTABLE HEAVY METAL CONTENT

This study was conducted to evaluate wastewater sludge from various sources for agricultural utilization. The results showed that sludge from municipal and food industrial wastewater treatment plants (WWTPs) have high fertilizing value with respect to nutrients and organic matter levels. When the sludge samples were evaluated for their total heavy metal contents, the Pb, Cd and Cu concentrations in all of the sludge samples were found to be below the limit specified by Turkish regulations. However, the Cr, Ni and Zn contents of domestic type, organized industrial zone, food industry sludge samples exceeded these thresholds. Other sludges were found to be suitable for agricultural usage in terms of plant nutrient and heavy metal content. The analysis of the sludge samples from twelve different WWTP's showed that the agricultural properties and the total and bioavailable (DTPA-extractable) heavy metal fraction varies depending on the sludge samples. Therefore discussed sludges should be evaluated separately for the agricultural utilization potential in terms of soil pollution

1. INTRODUCTION

The application of wastewater treatment sludge to agricultural land has become a common practice over the past several decades. It is estimated that 30–40% of the total sludge production in EU and US countries are recycled for agricultural use; but down to 5–10% being used in Turkey. In Turkey, more than 10 million tons of sewage sludge are produced annually [1]. The agronomic and hence fertilizing value of wastewater sludge depends on its plant nutrient elements such as nitrogen, phosphorus and potassium, calcium, magnesium and iron [2] and organic matter content. However, some

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other factors should be considered by evaluating the suitability of sludge for agricultural use. The most important points are the potential for usage (i) nitrate or phosphate contamination of water, (ii) environmental damage caused by the release of toxic metals (heavy metals) and (iii) the transfer of pathogens [3]. Therefore, the safe use of wastewater sludge in agriculture should be the primary goal. Hence, sludge should be analyzed for toxic or hazardous contaminants before application, and if any contaminants exceed the standards prescribed by respective regulations, the direct usage on agricultural land must be restricted or prohibited.

The regulations currently in place were designed to limit the application of wastewater sludge to agricultural land by means of the European Directive 86/278/EEC but also by 40 CFR Part 503 in the US and Turkey. The aim of these directives is to prevent harmful effects on soil, vegetation, animals and humans.

In accordance with current legislation, total heavy metal content should be determined in sludge samples. However, the determination of total metal content does not guarantee that the concentration of each metal is harmless to the environment or to humans. Measuring the extractable concentration of the metals provides besides information about the general degree of contamination also an assessment of metal's mobility in sludge and sludge-amended soil [4]. In this context is the single (DTPA, EDTA, $CaCl_2$, NH_4Cl, etc.) or sequential chemical extraction (SCE) a commonly used experimental approach [5]. Studies are still continuing this issue. Diethylene triamine pentaacetic acid (DTPA) is most frequently used for extraction because it is considered indicative for the amount of metals potentially available for crops or natural vegetation [6]. In addition, heavy metals at elevated concentration affect soil microbial population and their associated activities which may directly influence the soil fertility [7]. Therefore, it seems reasonable to relate the bioavailable metal concentration in sludge to regulatory thresholds prior to its application on the field.

The main objectives of the present study were to: investigate municipal, municipal-industrial and food industrial wastewater sludge for its agronomic value as fertilizer, determine the total and bioavailable heavy metal concentrations, and compare these concentrations with the limits set by Turkish, US and EU regulations.

2. EXPERIMENTAL

The sludge was collected monthly from twelve different wastewater treatment plants (WWTP's) in Bursa from May 2009 to April 2010. The collected samples were dried under greenhouse conditions (temperature over 20 °C during the drying period with air conditioner) for three months to achieve sufficient disinfection and meet the class B or conventional sludge standards referred to in European Directive 86/278/EEC and 40 CFR Part 503 regulations. Detailed information about the WWTP's is presented in Table 1.

Table 1

Characteristics of the sludge treatment plants in Bursa

Wastewater treatment plant	Source of wastewater and industrial activity	Sludge produced [t dm/year]
Buski 1 (BD)	domestic type (the city's east side)	6500
Buski 2 (BB)	domestic type (the city's west side)	5500
Yenice (Y)	domestic type	360
Tat (T)	food (tomato paste)	110
Penguen (P)	food (canned food)	60
Natura (N)	food (ice cream)	60
Mauri (M)	food (bread yeast)	70
BTSO (B)	organized industrial zone	1250
Nilüfer (F)	supply water for industry	150
İnegöl (L)	mixture of industry and domestic type	1350
Nestle (S)	milk products (chocolate, coffee, etc.)	70
Sütaş (A)	milk products (cheese, yogurt, etc.)	120

The wastewater sludge samples were analyzed for basic physicochemical properties using standard procedures: pH and electrical conductivity (EC) were determined by using a pH-meter (WTW pH 320) and EC-meter (WTW LF 320) according to the sludge extract at a sludge/deionized water ratio of 1:5 (v/v). The organic matter content was determined by the loss on ignition at 550 °C and organic carbon (OC) was analyzed by the Walkley-Black method. Total N was determined using a Buchi K-437/K-350 digestion/distillation unit according to the Kjeldahl method. Ammonium-N concentrations were determined using the indophenol blue method. Total P was determined by the vanadomolybdophosphoric method and available P was determined by the molybdenum blue method. The cation concentrations (Na, K, Ca and Mg), samples were determined by the flame emission method using a Eppendorf Elex 6361 model flame photometer.

The concentration of metals (Cd, Cr, Ni, Pb, Fe, Cu, Zn, and Mn) was determined after the microwave assisted digestion with HNO_3. Metals were analyzed in the extracts using ICP OES (Perkin Elmer OPTIMA 2100 DV). The DTPA-extractable fraction was obtained by mechanically shaking 4 g of dried sample for 2 h in 40 cm^3 of 0.05 M DTPA, 0.01 M $CaCl_2$ and 0.1 M TEA (triethanolamine) buffered solution at a pH of 7.3, and the metal concentrations were determined by the inductively coupled plasma optical emission spectroscopy method (Perkin Elmer Optima 2100 DV spectrometer).

All obtained data (agricultural value and heavy metal content of wastewater sludges) were subjected to statistical analysis. Mean values were statistically compared by using the least significant differences (LSD) multiple range tests ($p < 0.01$) using the software TARIST.

3. RESULTS AND DISCUSSION

3.1. AGRICULTURAL PROPERTIES OF WASTEWATER SLUDGE

As shown in Table 2, the studied wastewater sludge samples are characterized by varying chemical compositions. The pH, EC, organic matter, organic carbon, C/N ratio, nitrogen and phosphorus contents are generally accepted as the primary features of sludge that reflect its value as a fertilizer.

The mean pH of the wastewater sludge samples ranged from 5.37 to 10.72, while the variability over the study course was limited. Only the samples from the anaerobic food industry (M) showed significant seasonal fluctuations in pH (9.82–10.72), most likely reflecting the variety in the production process (e.g. bread yeast production). One of the most influential parameters controlling the solubility of metals is pH [8]. pH of sewage sludge can affect crop production by altering pH of the soil and influencing the plant uptake of metals. Low pH sludge (lower than approximately 6.5) promotes leaching of heavy metals, while high pH sludge (higher than 11.0) kills many bacteria and, in conjunction with soils of neutral or high alkalinity can inhibit movement of heavy metals through soils. Therefore, the solubility of heavy metals increased with decreasing pH, the agricultural utilization of sludge is not commonly carried out in acidic soil (pH < (6.0–6.5)) [9].

Another important limitation in the agricultural use of wastewater sludge are EC levels [10] which varied between 1.10 and 105.6 $mS\cdot cm^{-1}$ in the present study. Only two sludge samples originating from the food industry (food industry – sample S and bread yeast – sample M) reached extremely high values (10.0–28.0 and 23.4–105.6 $mS\cdot cm^{-1}$, respectively) during the investigation period. Anthropogenic sources of soil salts include salts present in irrigation waters, and animal wastes (manures and wash waters), chemical fertilizers, and applied sewage sludges [11]. Some of sludge show relatively low EC values (<4.0 $mS\cdot cm^{-1}$) indicating that its direct use in agriculture, in moderate amounts, would not imply a risk of soil salinization. Nevertheless, existing salinity levels and amount of salt contained in wastewater sludges should be closely monitored to prevent salinity problems in soils especially in arid climates.

The organic matter content of the investigated sludge samples was between 24.3 and 78.1%. Municipal sludge samples (samples BB, BD and Y) showed the highest values (60.0–78.1%) when compared to the other sludge samples statistically (Table 2). The application of sludge samples rich in organic matter can improve the physical, chemical and biological properties of soil [12]. The range of the C/N ratio of the sludge samples was 5.37–20.2. C/N ratio of sludge is an important factor affecting the use of sludge as a fertilizer or soil conditioner. Sludge mineralization rate is also closely related to C/N ratio. The higher the C/N ratio, the lower the N mineralization rate is. In some cases, the mineralization process was more influenced by soil type than by rate and type of sludge applied [13].

Table 2

Agronomical characteristics of investigated wastewater sludge

Parameter	Value	BB	BD	Y	L	B	F	S	A	P	N	T	M	LSDa
pH 1:5 ratio	min	5.37	5.45	6.18	6.02	6.32	6.94	6.30	7.31	5.56	5.56	6.28	9.82	0.499
	max	6.14	6.14	6.40	6.84	6.48	7.47	7.56	8.54	6.77	7.73	7.08	10.72	
	mean	5.83	5.76	6.29	6.80	6.44	7.28	6.96	7.80	6.11	6.62	6.54	10.33	
EC, mS·cm^{-1}	min	3.63	4.33	3.83	2.51	1.35	1.98	10.02	4.28	3.05	1.10	4.91	23.4	12.74
	max	5.92	8.09	5.41	3.90	6.30	5.77	28.0	8.95	6.08	3.49	7.27	105.6	
	mean	4.98	5.57	4.36	2.63	3.99	3.21	20.70	5.19	4.65	2.42	6.09	61.34	
OM, wt. %	min	62.8	61.5	60.0	53.5	47.6	24.4	73.3	62.0	52.8	47.8	24.3	27.5	10.12
	max	70.1	76.3	72.8	57.6	71.0	54.4	85.8	70.9	66.7	78.1	51.8	32.8	
	mean	68.0	71.0	66.6	55.6	64.4	43.1	77.1	67.9	59.2	72.9	39.5	29.7	
Org, C, wt. %	min	36.4	35.7	34.8	31.1	27.6	14.2	42.5	36.0	30.6	27.7	12.2	15.9	5.575
	max	41.0	44.3	42.3	33.4	41.2	31.5	49.8	41.1	38.7	45.3	25.9	19.0	
	mean	39.5	41.2	38.6	32.2	37.3	25.0	44.7	39.4	34.3	42.3	19.8	17.2	
C:N ratio	min	5.60	5.37	5.41	7.05	6.55	7.76	5.20	5.55	6.75	12.9	5.81	6.61	1.135
	max	6.99	6.78	6.56	7.62	11.6	9.35	8.94	6.68	13.43	20.2	7.05	10.1	
	mean	6.34	6.10	5.97	7.33	9.87	8.60	7.34	6.08	9.63	16.05	6.41	7.60	
N, wt. %	min	5.69	5.88	5.47	4.19	3.21	1.53	5.46	5.87	2.48	2.10	1.83	1.60	0.950
	max	6.99	7.74	7.51	4.62	4.73	3.95	9.20	6.96	4.92	3.09	4.46	2.74	
	mean	6.24	6.80	6.50	4.40	3.83	2.95	6.09	6.49	3.67	2.66	3.12	2.30	
NH_4-N, mg·kg^{-1}	min	185	181	48.1	103	trace	51.8	11.1	29.6	137	37.0	88.8	trace	303.3
	max	518	765	523	244	222	288	651	163	945	333	1297		
	mean	331	399	228	154	37.6	137	114	90.1	273	129	453		
P, wt. %	min	1.83	1.94	0.80	1.14	1.12	0.52	1.53	3.20	0.30	0.36	0.47	0.50	0.407
	max	2.63	3.10	1.24	1.51	2.57	2.01	2.03	3.89	0.80	0.82	0.96	1.42	
	mean	2.23	2.30	1.09	1.36	1.96	1.44	1.87	3.60	0.46	0.55	0.72	1.06	
Available P, wt. %	min	0.128	0.109	0.032	0.023	0.003	0.002	0.126	0.021	0.008	0.001	0.013	0.024	0.515
	max	0.296	0.318	0.067	0.038	0.014	0.014	0.280	0.052	0.019	0.007	0.027	0.066	
	mean	0.223	0.241	0.053	0.027	0.007	0.006	0.177	0.035	0.013	0.004	0.021	0.044	

Table 2

Agronomical characteristics of investigated wastewater sludge

Parameter	Value	BB	BD	Y	L	B	F	S	A	P	N	T	M	LSDa
K, w/w	min	0.68	0.58	0.36	0.37	0.04	0.08	1.22	0.12	0.19	0.01	0.26	1.19	0.364
	max	0.81	0.91	0.93	0.47	0.11	0.28	2.93	0.22	0.49	0.04	0.41	13.2	
	mean	0.71	0.81	0.71	0.42	0.07	0.17	2.01	0.17	0.34	0.02	0.33	4.60	
Ca, w/w	min	2.52	1.48	4.35	2.98	2.28	0.13	0.92	3.38	1.68	1.13	0.94	7.93	0.386
	max	3.40	2.98	8.81	4.24	3.66	1.85	1.53	4.68	10.26	3.16	2.98	22.3	
	mean	2.99	2.16	6.72	3.34	2.79	0.58	1.38	3.86	6.26	1.97	1.81	17.2	
Mg, w/w	min	0.96	0.80	0.46	0.70	0.41	0.50	0.66	0.43	0.50	0.03	1.09	0.69	0.151
	max	1.21	0.98	0.60	0.87	0.55	1.29	1.02	0.91	0.91	0.20	1.78	0.91	
	mean	1.05	0.89	0.55	0.77	0.48	0.83	0.82	0.58	0.65	0.08	1.41	0.77	
Na, w/w	min	0.11	0.09	0.14	0.29	0.26	0.08	1.22	0.48	0.21	0.30	0.15	2.14	0.183
	max	0.21	0.15	0.19	0.36	0.37	0,32	2.93	1.56	0.44	1.23	0.44	9.07	
	mean	0.15	0.12	0.17	0.33	0.30	0.21	1.96	0.81	0.30	0.52	0.26	4.13	

[a]LSD – results of least significant differences multiple range tests ($p < 0.01$).

Organic residues with low C/N ratios show more N mineralization than those with high C/N ratios, with the latter mostly causing N immobilization during decomposition [14]. The balance between nitrogen mineralization and immobilization is strongly influenced by the C/N ratio of the decomposing organic matter [15]. Organic matter with the C/N ratio greater than 30:1 does not contain enough nitrogen to support microbial growth, and microbes must scavenge additional nitrogen from the soil. Since soil microbes are considered stronger competitors for nutrients than plants, much of the available nitrogen pool will be immobilized by soil microbes and be unavailable to plants [16].

The results (Table 2) show that different amounts of N (1.60–9.20%), P (0.30–3.89%), K (0.04–13.16%), Ca (0.13–22.28%), Mg (0.03–1.68%) and Na (0.08–9.17%) were found in the sludge samples from Bursa Plain. Nutrient values of sludge vary with sources of wastewater and wastewater treatment processes. Similarly, the sludge samples contained different amounts of bioavailable nitrogen and phosphorus. The NH_4-N content in the wastewater sludge of domestic origin (BB (mean 331 $mg \cdot kg^{-1}$ and 0.53% of the total N), BD (mean 339 $mg \cdot kg^{-1}$ and 0.58% of the total N) and T (mean 453 $mg \cdot kg^{-1}$ and 1.45% of the total N)) was higher than that from other wastewater treatment plants, and the anaerobic food industry sludge (sample M) had the lowest NH_4-N content. This difference is related to the treatment system. Nutrient composition of sludges is significantly altered by stabilization processes. The rate of nutrient release (or mineralization) is also affected by the processes. Mineralization of N from aerobically digested sludges was reported to be significantly higher than that from anaerobically digested sludges [13].

The available P content of the sludge varied from 0.001 to 0.318%. Generally, the available P levels in the BB, BD (domestic origin) and S (food industry) sludge samples were higher than the other wastewater treatment plants statistically (Table 2). The differences in P and N contents in the sludge depend on the treatment efficiency and the sources of wastewater for the individual treatment plant [6]. The mean N content in the municipal sludge samples was higher than the corresponding values in the other sludge samples. Sludge N and P contents are accepted as important factors in the determination of the sludge application rate. According to the guidelines, the total amount of N in wastewater sludge that can become plant available is approximately 30% in the first year of application, 15% in the second year and 5% in the third year. Typical N mineralization rates for the first year range from 0 to 60% of the organic N. Decomposition is not complete in the first year. It continues during the next few years at progressively slower rates. Some of the N is retained in stable organic matter (such as humus), which continues to mineralize very slowly. As much as half of the organic N in some sludges may remain stable for decades [17].

According to relevant legislation, the maximum annual sludge application rates were calculated using the N content of the sludge. In principle, sludge is applied to soil to provide amounts of N equal to recommended inorganic N fertilizer rates [18]. Although maximum nutrient application rates in federal sludges regulations are not well defined, the 503 Rule stipulates that agronomic rates cannot be exceeded. To protect groundwater or surface water quality, nitrogen is regulated through an agronomic rate approach, requiring an estimate of crop N need and sludges N availability. Sludge P applications are not regulated by the US EPA, but increasing numbers of states are introducing regulations, because of concerns about the effects of repeated manure or sludge applications on soil P and risk of P loss to surface water.

3.2. TOTAL HEAVY METAL CONTENTS OF SLUDGE SAMPLES AND COMPARISON WITH THE ENVIRONMENTAL STANDARDS

A comparison of the measured heavy metal content with USEPA, EU and Turkish permissible limits for wastewater sludge is given Table 3. Turkish legislation prohibits the agricultural use of wastewater sludge that exceeds the maximum allowed values for total concentrations of heavy metals [19]. It is worth noting that those national values are all below the limit prescribed by the EU (86/278/*EEC*) and US EPA (40 CFR 503), with the exception of Cr (Table 3).

Zn and Fe were found to be widespread in all analyzed wastewater sludge samples from Bursa WWTP's. Cd concentrations in all sludge samples were lowest during the investigation period. As seen in Table 3, the total metal concentrations (in $mg\cdot kg^{-1}$) were in the ranges: 0.89–239.9 for Pb, 0.18–4.47 for Cd, 3.90–1958 for Cr, 9.69–1448 for Ni, 15.29–5577 for Cu, 61.61–28210 for Zn, 0.071–11.54 9 (wt. %) for Fe and 46.59–2258 for Mn. The concentrations of Cr (maximal 1958 $mg\cdot kg^{-1}$), Ni (maximal 1448 $mg\cdot kg^{-1}$) and Zn (12 610–28 210) in the BTSO sludge (from the organized industrial zone) and the concentrations of Cr (maximal 1358 $mg\cdot kg^{-1}$) and Ni (351.4–918.1 $mg\cdot kg^{-1}$) in the sludge from Y municipality (domestic + industrial) were found to exceed the limit set by Turkish sludge legislation. In addition, the Cr content in the BB and BD wastewater sludge (domestic type) samples were found to be above the limit set by the US EPA.

The results indicated that heavy metal content in the wastewater sludge samples from the food industry treatment plants (F, S, P, T and M) are below the regulatory threshold during the one-year investigation period. First of all, this sludge may be considered in terms of application to the soil. The total concentrations of heavy metals in sludges strongly varied depending on the sources which were related to different industries discharging effluents in the sewerage system [12].

3.3. DTPA-EXTRACTABLE HEAVY METAL CONTENT OF THE SLUDGE SAMPLES

The percentages of DTPA-extracted elements in the total contents of these elements are given in Table 4.

Table 3

Total heavy metal levels in selected wastewater sludges in comparisons with regulatory threshold levels

Treatment plant	Value	Pb	Cd	Cr	Ni	Cu	Zn	Fe	Mn
BB	min–max mean	23.72–41.45 29.21	0.92–1.20 1.04	153.8–545.5 254.0	48.21–95.80 58.47	160.2–254.4 209.6	1497–3898 2374	0.82–1.28 0.99	158.8–328.3 215.9
BD	min–max mean	24.64–34.63 30.99	1.12–1.70 1.25	226.5–352.4 286.2	75.31–146.8 93.03	108.7–161.6 131.7	612.9–1078.0 746.9	0.58–0.11 0.84	162.9–283.4 224.4
Y	min–max mean	17.02–27.73 19.66	0.75–0.88 0.79	710.7–1358 1014.7	351.4–918.1 767.1	62.99–84.14 80.14	387.2–786.7 495.1	0.74–1.15 0.93	95.26–139.0 115.4
L	min–max mean	22.92–26.75 25.00	3.56–4.47 3.99	138.0–156.1 144.0	60.17–69.34 64.67	189.9–224.8 208.8	150.2–260.4 179.9	2.20–2.52 2.42	202.4–249.1 223.3
B	min–max mean	101.9–239.9 154.2	1.19–1.50 1.31	1005–1958 1479	273.1–1448 670.1	363.5–557.7 455.6	12610–28210 19554	4.40–6.73 5.09	765.2–2258 1264
F	min–max mean	9.28–22.75 15.08	1.45–3.22 2.22	163.2–294.6 238.2	96.5–147.1 111.9	83.22–141.8 118.0	342.6–1186 789.2	0.89–3.63 1.85	353.8–729.7 543.7
S	min–max mean	8.63–39.49 22.69	0.55–0.61 0.58	20.29–32.48 28.21	14.67–20.09 18.06	60.70–88.02 74.87	151.2–264.8 214.1	0.31–0.44 0.36	46.59–61.76 54.27
A	min–max mean	14.08–57.32 31.01	0.37–1.11 0.65	32.17–53.81 40.91	15.85–27.19 19.87	27.03–72.72 31.66	3353–10300 6415	2.38–9.28 5.12	188.7–399.3 285.8
P	min–max mean	7.01–13.96 9.94	0.46–0.85 0.54	27.91–73.08 42.22	24.31–71.32 38.47	39.75–80.57 55.84	167.6–432.1 221.6	0.98–2.44 1.59	134.3–268.2 177.6
N	min–max mean	53.28–83.78 72.34	0.18–0.57 0.41	35.56–67.03 47.31	17.53–58.84 28.04	40.83–64.53 52.71	7051–18760 13087	7.24–11.54 9.82	141.1–374.6 272.2
T	min–max mean	11.37–24.63 15.83	2.43–4.81 3.65	48.22–90.18 65.45	65.58–119.5 88.64	52.21–75.15 60.27	228.0–396.3 320.3	1.76–3.05 2.34	420.0–1651 1006
M	min–max mean	0.89–2.41 2.01	0.74–0.89 0.77	3.90–10.50 7.23	9.69–14.46 12.50	15.29–39.58 29.81	61.61–178.2 120.3	0.071–0.224 0.165	272.7–894.6 658.1
40 CFR Part 503		840	85	300	720	4300	7500		
86/278/EEC		1200	40		400	1750	4000		
[19]		750	10	1000	300	1000	2500		
LSD		25.55	0.577	190.6	146.9	41.07	4174.0	1.090	293.1

[a]The concentrations of the elements in $mg \cdot kg^{-1}$, except for Fe content given in w/w.

Table 4

Concentrations of DTPA extractable of heavy metals and their proportion in the total element concentration of the investigated wastewater sludge[a]

Treatment plant		Value	Pb	Cd	Cr	Ni	Cu	Zn	Fe	Mn
BB	DTPA	min–max	3.00a–4.49	0.157–0.229	0.844–1.594	7.779–22.17	19.27–50.55	429.7–1222	66.51–235.8	25.09–65.99
		mean	3.90	0.206	1.081	10.79	35.36	838.4	170.5	48.43
	% of total	min–max	8.83–15.7	13.6–24.9	0.29–0.64	15.7–23.1	8.43–23.0	15.7–45.4	0.83–2.53	12.8–31.2
		mean	13.58	19.86	0.46	18.35	17.04	36.25	1.714	23.38
BD	DTPA	min–max	3.93–6.19	0.133–0.379	1.530–3.121	30.94–60.01	32.63–60.02	186.4–481.6	92.09–203.5	40.40–76.37
		mean	5.11	0.330	2.08	36.82	45.90	347.3	131.1	59.09
	% of total	min–max	12.4–20.8	18.5–33.6	0.45–1.00	34.9–43.0	22.6–40.4	30.4–56.1	0.90–2.45	18.1–35.3
		mean	16.53	26.61	0.724	39.61	34.89	46.78	1.578	26.18
Y	DTPA	min–max	2.29–3.94	0.079–0.162	2.834–7.165	276.5–721.6	14.40–27.40	54.54–216.7	85.62–272.3	19.60–32.65
		mean	3.14	0.125	4.18	439.0	18.51	139.1	174.5	27.90
	% of total	min–max	11.2–19.6	9.00–21.5	0.29–0.43	49.4–62.7	18.7–33.9	14.1–36.0	0.74–2.71	15.3–34.3
		mean	16.13	15.88	0.434	57.35	23.13	27.78	1.925	24.41
L	DTPA	min–max	3.16–4.65	0.316–0.447	0.275–0.605	3.741–5.692	25.60–37.74	53.91–79.73	123.9–373.0	19.43–36.18
		mean	4.09	0.416	0.443	4.433	31.18	69.95	262.2	26.23
	% of total	min–max	12.2–18.3	8.88–11.9	0.20–0.44	5.73–8.37	11.8–18.2	20.7–46.3	0.56–1.49	9.09–14.5
		mean	16.37	10.42	0.309	6.85	14.90	39.62	1.081	11.68
B	DTPA	min–max	2.00–7.22	0.002–0.010	0.394–0.829	74.59–381.4	0.381–3.265	379.7–1299	446.2–940.1	104.3–539.9
		mean	3.33	0.008	0.546	173.4	1.508	952.3	695.6	232.9
	% of total	min–max	1.39–3.01	0.14–1.60	0.03–0.05	22.0–30.4	0.10–0.46	3.01–6.44	1.01–1.71	11.5–23.9
		mean	2.13	0.575	0.037	26.69	0.319	5.61	1.358	18.12
F	DTPA	min–max	1.12–4.01	0.050–0.230	0.060–0.850	0.770–25.50	8.490–47.23	9.60–368.3	51.52–174.9	13.49–87.73
		mean	2.14	0.118	0.412	12.12	22.37	144.0	105.6	45.08
	% of total	min–max	6.42–25.2	1.89–16.1	0.04–0.31	0.80–22.7	9.30–33.3	1.45–31.1	0.14–1.27	1.86–16.3
		mean	13.82	5.74	0.162	10.65	18.15	15.99	0.694	8.369
S	DTPA	min–max	1.73–2.69	0.174–0.259	0.179–0.336	1.582–2.344	19.54–43.98	92.16–137.0	115.6–187.6	11.38–22.62
		mean	2.27	0.210	0.269	2.188	37.48	124.7	146.4	16.89
	% of total	min–max	4.99–23.1	29.4–45.4	0.58–1.36	10.1–16.0	49.6–50.3	48.8–71.3	2.79–5.39	26.4–41.6
		mean	15.88	36.37	0.993	12.36	50.04	59.75	4.215	31.15

Table 4

Concentrations of DTPA extractable of heavy metals and their proportion in the total element concentration of the investigated wastewater sludge[a]

A	DTPA	min–max mean	2.51–4.11 3.27	0.020–0.080 0.040	0.079–0.134 0.106	4.919–10.46 7.273	0.207–0.832 0.440	538.3–1143 646.4	606.1–979.3 818.7	23.72–69.32 42.60
	% of total	min–max mean	6.83–15.3 11.00	2.63–9.73 6.16	0.18–0.32 0.26	23.8–45.9 36.97	0.48–2.74 1.398	8.07–15.5 10.25	0.91–3.84 1.703	11.6–25.1 14.70
P	DTPA	min–max mean	1.81–2.94 2.38	0.054–0.194 0.106	0.071–0.299 0.218	5.810–9.830 7.164	13.22–27.61 20.03	49.49–163.3 76.02	218.1–519.7 356.3	7.420–40.66 22.00
	% of total	min–max mean	15.6–31.0 23.97	11.5–24.8 19.32	0.10–1.07 0.583	12.8–23.9 19.60	24.2–44.9 36.22	17.2–52.2 35.41	1.20–3.39 2.305	6.10–21.4 12.31
N	DTPA	min–max mean	0.23–2.29 0.74	trace–0.008 0.003	0.036–0.178 0.079	2.298–22.19 6.041	0.152–4.157 1.321	647.3–1799 1280	214.7–984.6 462.9	10.99–75.39 42.84
	% of total	min–max mean	0.35–2.88 1.05	0.34–1.91 0.873	0.06–0.46 0.166	9.83–33.9 20.11	0.25–9.70 2.453	4.80–21.3 9.81	0.22–0.89 0.469	7.79–23.5 16.05
T	DTPA	min–max mean	2.35–3.74 2.99	0.319–0.462 0.392	0.160–0.201 0.172	9.721–14.38 12.33	14.39–28.54 21.02	87.05–186.3 141.6	269.9–558.5 428.6	99.90–299.9 199.6
	% of total	min–max mean	15.2–25.2 19.11	8.28–15.0 11.18	0.20–0.42 0.275	11.9–17.3 14.11	31.8–42.5 34.78	32.5–54.9 44.34	1.21–3.16 1.881	14.1–28.8 20.65
M	DTPA	min–max mean	0.24–1.34 0.63	0.313–0.616 0.392	0.567–1.399 0.959	6.254–8.338 7.256	10.41–22.47 18.00	30.79–62.81 45.85	172.0–505.7 404.1	13.85–32.95 23.77
	% of total	min–max mean	7.68–71.6 30.07	37.1–79.6 55.42	5.84–32.8 13.68	47.8–66.0 58.08	51.0–70.1 60.64	29.7–50.0 38.26	16.8–30.1 24.81	2.12–4.75 3.91
LSD	DTPA	min–max mean	1.096	0.061	0.426	74.33	11.06	251.5	173.7	63.72
	% of total	min–max mean	11.64	7.465	2.447	8.220	7.131	13.06	1.961	8.090

[a]The concentrations of the elements in $mg \cdot kg^{-1}$, ˙except for Fe content given in w/w.

The DTPA-extractable Pb content of the investigated wastewater sludge samples varied from 0.231 mg·kg^{-1} (N – food industry) to 7.220 mg·kg^{-1} (B – organized industrial zone). Cd and Cr concentrations were 0.002–0.616 mg·kg^{-1} and 0.036–7.165 mg·kg^{-1}, respectively. The highest DTPA-extractable Ni concentration was recorded as 721.6 mg·kg^{-1} (Y – municipal sludge), whereas the lowest value of 0.770 mg·kg^{-1} was measured in the F water supply sludge. The DTPA-extractable concentrations were 0.152–60.02 mg·kg^{-1} for Cu and 9.60 to1799.0 mg·kg^{-1} for Zn. In addition, the DTPA extractable Fe and Mn contents varied from 51.52 to 984.6 mg·kg^{-1} and from 7.420 to 539.9 mg·kg^{-1}, respectively.

Determination of total metal levels does not guarantee that the concentration of each metal is harmless for the environment or for humans but instead gives an overall picture of the level of pollution in the sludge sample studied. In contrast, the metal extractable forms cannot only inform about the general degree of contamination but can also provide an assessment of the mobility of these elements in sludge and sludge-amended soil, and may help to predict the release of metals in soil solution [4]. The DTPA-extractable fractions of heavy metals in the wastewater sludge samples were lower compared to the total content of these elements. This fraction reflected the bioavailable amounts of heavy metals present in the investigated sludge samples [20]. Although the concentrations of DTPA-extractable of heavy metals in wastewater sludge may show wide variation, zinc, copper and nickel are usually found at higher concentrations than other metals [2]. The quantity of metals extracted with DTPA diminished in the following order: Zn > Ni > Cu > Cd > Mn > Pb > Fe > Cr. The percentages of DTPA-extracted heavy metals in their total contents were also quite variable and no specific trend for the individual heavy metals was observed (Table 4). In the sludge samples 0.14–33.6% of Cd was in the DTPA-extractable fraction except for the S and M sludge samples. The DTPA-extractable Cd concentrations in those sludge samples were lower than 0.616 mg·kg^{-1}, whereas relatively higher percentage values (45.4–79.6% in the S and M samples, respectively) were found.

The percentages of Pb, Cr and Mn in the sludge that were bound to the extractable fraction were 0.35–22.1, 0.03–32.8 and 1.71–35.3%, respectively. Generally, Ni, Cu and Zn were the most mobile elements in the sludge [5, 21]. The predominant portion (61%–93%) of Zn was in the exchangeable and reducible fractions, indicating the high potential mobility and bioavailability of Zn [22]. Considering the high content of Zn and its high potential mobility in the environment, it could be concluded that these types of sludge should not be directly applied to agricultural fields without further treatment. Phytotoxicity could be caused by the high Zn bioavailability [6]. The amounts of plant-available (DTPA-extractable) Ni, Cu and Zn in the investigated sludge samples were 5.73–62.7%, 8.43–70.1% and 3.01–71.3%, respectively. Fe was observed to be the least extractable metal in all sludge samples except for the M sludge. The mobility of heavy metals, their bioavailability and related ecotoxicity to plants, depend strongly on their specific chemical forms or ways of binding. Consequently, these are the parameters that have to be determined, rather than the total element contents, in order to assess toxic effects and to study geochemical pathways [23–25].

4. CONCLUSION

Wastewater sludge from domestic and food industrial WWTP's appeared to have higher fertilizing value with respect to plant nutrients and organic matter levels. The chemical compositions of sludges are an important issue in developing recommendations for the rates of sludge application on agricultural soil and reducing the risks of pollution soil. Otherwise, uncontrolled sludge application may have a potentially toxic impact on soil, especially when sludges contain high contents of available plant nutrient elements (N and P etc.) and heavy metals.

However, the heavy metal content of some wastewater sludge from domestic sources exceeded the values permitted by the national and international standards. The results also indicated that the ratios of DTPA-extractable/available/mobile fractions were changed due to sludge origin. For example, Ni and Cu, found in domestic and food industry sludge, indicates high metal availability and this might cause toxicity to plant growth. Therefore, sludge application should be controlled to avoid potential Zn, Ni and Cu toxicity to soil.

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