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Fractionation of potentially toxic and essential elements in sewage sludge from wastewater treatment plants

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The application of sewage sludge in agriculture is controlled regarding the total concentrations of the potentially toxic elements (PTEs) Cd, Cu, Ni, Pb, Zn, Hg, Cr and As. Additionally, the essential elements K, Ca, Mg and P are included without concentration thresholds. Their bioavailability, however, depends on their speciation. In the present work, single extraction with deionized water and BCR sequential extraction were applied for two types of sewage sludge and two certified reference materials CRM 029 and ERM-CC144. The concentrations of the controlled elements and of Na, Mn, Fe, B, and Mo in the obtained fractions were determined by ICP-MS. The results showed water solubility between 0.04% and 11.5% for the PTEs and varying degrees between 0.03% to 60% for the essential elements. The BCR fractionation indicated a high degree of bioavailability for the essential elements being concentrated in the exchangeable or oxide fractions. A high tendency to form organic complexes was found for P and Mo, which indicated their low bioavailability for plants. The fractionation of PTEs showed low sum extraction for Pb and Hg and immobilization in organic complexes of Cu and Cr. A risk of soil and plant pollution exists for Zn, As, Cd and Ni. Zn and As dominated in the exchangeable and oxide fractions, Cd - in the oxide fraction, while for Ni the dominant fraction varied between the samples.

INTRODUCTION

The current approaches to management of sewage sludge include recycling into construction materials [1], landfilling, incineration, composting, reclamation of unused land, and the highest share in the European Union (EU), including Bulgaria, is their use as fertilizer in agriculture [2-4]. According to Bulgarian [5] and European [6] legislations, strict limit values for a number of toxic pollutants, including the potentially toxic elements (PTEs) Cd, Cu, Ni, Pb, Zn, Hg, Cr and As, both in sludges and soils have been set.

The determination of the total concentrations of chemical elements provides general information about the content of potentially toxic and essential elements and, accordingly, on the level of contamination or the positive effects when used in agriculture [7-10]. An opportunity to provide an assessment of the mobility of the elements in the sewage sludge, the degree of their release into the soil solution and their bioavailability to plants is given by the fractionation of the sewage sludge [11-13]. In recent years, fractionation studies have been of great interest and a lot of literature data have been published, mainly for PTEs, e.g. [12-16]. The extraction procedures vary in the different studies in terms of the procedure used, or the use of the same extractant for a particular phase but under different experimental conditions [11]. For example, the determination of the exchangeable fraction is usually done using 0.11M CH_3COOH for 16 h at room temperature [15-19] according to the BCR procedure, as well as at extraction times of 4 h [20] and 7 min [13]; using 0.5M KNO_3 for 16 h [21] and 17 h [22]; using 0.5M $MgCl_2$ at pH 7.0 for 1 h [23] or 1M $MgCl_2$ at pH 7.0 for 1 h [24, 25]. Furthermore, the distribution of the metal ions in the different chemical fractions depends on the solid matrix composition, its physico-chemical properties, the stabilization process of the sewage sludge [13, 17, 22] and on the nature of the metal itself [21]. All this makes it difficult to compare the data obtained in different studies, as well as to predict the element distribution and mobility according to their total concentrations. However, according to published data, several trends in the distribution of elements emerge. In general, an appreciable part of Cu in sewage sludge is mainly associated with organic matter [13, 17, 21-23], carbonate [17, 22] and silicate phases [17, 22, 26]; Ni is bound to the residual [13, 17, 26], exchangeable [17, 27] and carbonate phases [17, 21, 22]; Cd is bound to the exchangeable phases [27], residual matrix [13, 28], carbonate [21, 22] and organic phase [17]; Pb is

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bound to the residual matrix [13, 17, 26], organic matter [17, 23] and carbonates [21, 22]; Zn is bound to carbonate [21, 22], exchangeable [27], and reducible phases [17, 23, 26], organic and residual fractions [23]; Cr is bound to organic [17, 23] and residual fractions [17, 21, 26, 28]; Fe is bound to the residual fraction [17, 26], or distributed among oxide, organic and residual fractions [23]. The data on the impact of sludge stabilization on the metal distribution are also not unambiguous. It was found that the stabilization treatment undergone by the sludges strongly influenced the heavy metal distribution and the phases to which they were associated [17, 26]. Other studies have found that the sewage sludge processing has no significant effect on the prevailing metal fraction [21, 22]. Despite the variations depending on the sample and element, the literature data indicate that PTEs non-specifically adsorbed in the most mobile and bioavailable exchangeable fraction, represent a small portion of the total amount of metals found in the sewage sludge. Most of them are associated with silicates, as well as sulfides and organic matter, which are practically inaccessible to plants under natural conditions [12, 13].

The objective of the present study was to assess the water solubility and the fractionation of the regulated PTEs (Cd, Cu, Ni, Pb, Zn, Hg, Cr and As) and the essential elements Na, K, Ca, Mg, P, Mn, Fe, B, and Mo, according to the BCR extraction procedure in two types of sewage sludge – municipal and industrial and two sewage sludge certified reference materials (CRMs) CRM 029 and ERM-CC144. The obtained data revealed the fractionation, mobility and bioavailability of both potentially toxic and essential elements in sewage sludge samples.

EXPERIMENTAL

Sewage sludge samples and certified reference materials

A sewage sludge sample from an urban wastewater treatment plant (Sewage sludge 1, SS1) and another from a mixed flow of domestic, fecal and industrial water treatment (Sewage sludge 2, SS2) were analyzed. Both samples were taken from sludge drying fields after biological treatment. The extraction procedures were also applied to CRM 029 (Trace Metals—Sewage Sludge 2—Sigma-Aldrich, Laramie, WY 82070, USA) and ERM-CC144 (Sewage Sludge—elements, European Commission—Joint Research Centre Directorate F—Health, Consumers and Reference Materials, Geel, Belgium).

The CRM BCR-701 (lake sediment, trace elements, European Commission – Joint Research Centre Directorate F – Health, Consumers and Reference Materials, Retieseweg 111, B - 2440 Geel, Belgium) with certified values for Cd, Cr, Cu, Ni, Pa and Zn in Fractions 1, 2 and 3 of the BCR extraction scheme was analyzed to assess the accuracy of the results.

Sample preparation

Extraction of 1 g of sewage sludge sample or CRMs with 20 mL of deionized water was performed by shaking for 16 h on a rotator, followed by centrifugation at 3600 rpm for 15 min and decantation.

The BCR sequential extraction procedure [29] defines the metal content as exchangeable (Fraction 1), Fe/Mn-oxides (reducible, Fraction 2) and organic and sulfide (oxidizable, Fraction 3) fractions.

The determination of the total concentrations of the investigated elements was carried out after acid digestion of the sewage sludge samples and CRMs. The detailed procedure of the microwave digestion is presented in [30]. The sludge pH was measured on sludge extract at a sludge/deionized water ratio of 1:10 (w/v). The total organic carbon (TOC) content was determined by the loss on ignition at 200°C (total inorganic carbon) and 900°C (total carbon).

Instrumentation

Metal determination in the extracts and digests was carried out using inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer SCIEX Elan DRC-e) with a cross-flow nebulizer. The calibration standards, experimental conditions and the determined isotopes are described in [10]. A mechanical rotator (MX-RL-E), a centrifuge (Rotofix 32 A Hettich, Germany), and a pH meter (Sartorius PT-15) were used throughout the extraction experiments. For microwave digestion of the samples, the Microwave Reaction System (Anton Paar, Multiwave 3000) was used.

RESULTS AND DISCUSSION

Total concentrations of the elements

The concentrations measured in each fraction, the sum concentration in the three BCR fractions (Fr.1+Fr.2+Fr.3), and the total concentrations are presented in Table 1 for the essential elements and in Table 2 for the PTEs. The results are an average of three replicates, characterized by the respective standard deviations. For the CRMs ERM-CC144 and CRM 029 the experimental results for the total concentrations, as well as the certified/indicative values (in brackets) are presented.

Table 1. Concentrations (mg/kg) of the essential elements in the studied fractions. Reported values are means ± standard deviation.

	Distilled water extract	Fraction 1	Fraction 2	Fraction 3	Sum BCR	Total concentration: Experimental value (Certified value)
Sewage sludge 1 (pH 4.83, TOC 44.0%)						
Na	427±21	688±32	69±3	55±3	812	5124±105
K	621±30	1365±61	578±26	189±9	2132	10251±230
Ca	3873±190	9140±450	6195±305	564±26	15899	16029±610
Mg	1098±55	2211±108	646±31	429±21	3286	4845±208
Mn	17.6±0.7	111±4	71±3	11.0±0.5	193	194±6
P	1273±61	3583±176	4775±236	3085±150	11443	21564±650
Fe	63±3	135±6	5869±290	1047±51	7051	26804±1210
B	0.089±0.005	0.19±0.01	0.22±0.01	0.29±0.02	0.70	0.82±0.03
Mo	0.082±0.004	0.030±0.002	0.10±0.01	3.35±0.07	3.48	3.5±0.2
ERM-CC144 (pH 6.40, TOC 33.1%)						
Na	361±17	627±31	160±7	63±3	850	1780±73 (1800)
K	533±23	920±46	457±23	112±5	1489	2920±140 (2900)
Ca	2953±144	19777±980	9192±440	1566±72	30535	30885±896 (31000)
Mg	335±15	1110±54	863±43	290±15	2263	3780±163 (3800)
Mn	5.61±0.21	159±7	166±8	22±1	346.9	348±16 (352±14)
P	258±12	372±16	1168±56	3363±168	4903	16680±584 (16600)
Fe	100±5	841±41	8795±410	2710±132	12346	32875±887 (32900±1600)
B	17.7±0.7	20.5±0.9	10.1±0.5	3.51±0.17	34.04	54.1±0.9
Mo	1.62±0.08	0.72±0.04	0.15±0.01	4.04±0.08	4.91	12.7±0.6
CRM 029 (pH 6.60, TOC 28.2%)						
Na	2248±110	3318±161	225±11	33±2	3576	3860±158 (3773±275)
K	1438±70	2218±110	577±26	56±3	2851	5110±245 (4918±975)
Ca	2506±123	22638±1129	13313±661	1083±52	37034	37986±1140 (38016±2800)
Mg	1430±70	7209±350	2438±120	886±44	10533	12073±520 (11858±266)
Mn	3.53±0.09	81±4	167±8	13.6±0.6	262	259±13 (264±10)
P	475±21	2688±131	3395±163	3804±190	9887	20987±734 (21100±2600)
Fe	52±3	185±9	3435±170	1046±52	4666	20126±543 (20199±1343)
B	116±5	152±4	27.0±0.8	8.1±0.3	187	601±27 (606±49)
Mo	72±3	5.0±0.2	1.57±0.08	142±6	149	152±7 (155±4)
Sewage sludge 2 (pH 7.58, TOC 52.3%)						
Na	2067±103	2475±121	157±7	43±2	2675	4068±102
K	1199±57	1722±84	444±22	78±4	2244	3418±165
Ca	792±40	29635±1480	10542±525	1137±56	41314	41649±1180
Mg	223±10	1923±98	539±26	164±8	2626	3587±108
Mn	2.90±0.06	814±23	2255±112	186±9	3255	3316±329
P	51±2	74±3	61±3	317±14	452	32806±1300
Fe	74±3	128±6	44355±2200	11245±560	55728	238603±10900
B	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Mo	2.35±0.07	0.010±0.001	0.056±0.003	1.67±0.07	1.74	13.2±0.2

[a] result obtained in [30]

Table 2. Concentrations [mg/kg] of PTEs in the studied fractions. Reported values are means ± standard deviation.

	Distilled water extract	Fraction 1	Fraction 2	Fraction 3	Sum BCR	Total concentration: Experimental value (Certified value)
Sewage sludge 1						
Ni	1.23±0.05	5.02±0.20	10.7±0.4	9.56±0.4	25.3	29±1
Zn	46.9±0.8	543±10	488±9	32.4±0.6	1063	1108±60
Cd	0.069±0.004	0.52±0.02	1.32±0.03	0.15±0.01	1.99	2.0±0.1
Cu	1.34±0.05	4.05±0.12	16.8±0.16	204±8	225	229±7
Pb	0.040±0.002	0.15±0.01	5.30±0.01	0.86±0.04	6.31	32±1
Cr	0.12±0.01	1.00±0.05	3.36±0.05	61±3	65.0	88±4
As	0.35±0.02	0.83±0.05	3.58±0.04	2.51±0.12	6.92	15±1
Hg	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
ERM-CC144						
Ni	4.75±0.15	8.10±0.08	9.90±0.09	16.6±0.2	34.6	92±6 (91±7)
Zn	14.9±0.3	405±8	354±7	215±4	974	985±33 (980±40)
Cd	0.14±0.07	2.45±0.09	9.07±0.5	0.87±0.04	12.4	14.7±0.9 (14.5±1.4)
Cu	29.1±0.9	25.2±0.7	11.0±0.4	316±11	352	351±12 (348±18)
Pb	0.074±0.004	0.40±0.02	1.99±0.08	2.03±0.08	4.42	159±6 (157±9)
Cr	0.84±0.03	1.74±0.09	1.34±0.07	42±2	45.1	167±8 (168±14)
As	0.90±0.05	1.71±0.08	3.40±0.20	2.56±0.09	7.67	7.8±0.4 (7.7±0.7)
Hg	0.024±0.002	0.030±0.002	0.010±0.001	0.009±0.001	0.05	6.1±0.3 (5.9±0.6)
CRM 029						
Ni	7.97±0.11	30.4±0.7	36±1	10.8±0.4	77.4	127±4
Zn	8.83±0.12	5.90±0.08	1015±20	44.4±0.8	1065	1080±20
Cd	0.73±0.04	21.8±0.6	73±3	2.93±0.07	98.0	122±7
Cu	15.5±0.3	24.3±0.7	17.6±0.7	689±23	731	736±33
Pb	0.22±0.01	0.33±0.02	2.15±0.08	2.06±0.05	4.54	119±5
Cr	1.54±0.07	8.31±0.4	23.5±0.9	308±14	340	353±12
As	10.6±0.6	77±3	48±2	72±4	197	256±9
Hg	0.29±0.02	0.17±0.01	0.060±0.004	0.93±0.06	1.16	18.7±0.8
Sewage sludge 2						
Ni	8.61±0.13	26.5±0.8	63±2	18.7±0.7	108	108±3
Zn	1.82±0.04	31.3±0.6	578±12	27.0±0.5	634	670±30
Cd	0.010±0.001	0.045±0.002	0.38±0.02	0.036±0.002	0.42	0.57±0.02
Cu	36.4±0.8	8.68±0.3	77±3	415±16	500	504±12
Pb	0.0038±0.0002	0.015±0.002	0.063±0.003	0.19±0.01	0.27	9.6±0.4
Cr	0.12±0.01	0.91±0.05	5.08±0.15	170±8	176	185±11
As	0.79±0.05	0.40±0.02	4.05±0.12	0.17±0.01	4.62	12±1
Hg	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002

The data for the total concentrations show that Fe, P, Ca, K, Na, Mg and Mn are the macroelements in all the samples. The order of decreasing concentrations is: Sewage sludge 1: Fe>P>Ca>K>Na>Mg>Mn; ERM-CC144: Fe>Ca>P>Mg>K>Na>Mn; CRM 029: Ca>P>Fe>Mg>K>Na>Mn; Sewage sludge 2: Fe>Ca>P>Na>Mg>K>Mn.

The analyzed samples and CRMs are of different types – domestic (SS1, CC144 and CRM 029) and industrial (SS2) sewage sludge. The data in Table 1 show that the total concentrations range from 1800 to 5124 mg/kg for Na, 2900-10251 mg/kg for K, 16029-41649 mg/kg for Ca, 3587-11858 for Mg, and 16600-32806 mg/kg for P. Wider concentration ranges were established for Fe (20199-238603 mg/kg), and Mn (194-3316 mg/kg), being in one order higher concentrations in Sewage sludge 2. With regard to the PTEs, wide concentration ranges were found for Mo (3.5-155 mg/kg), B (<0.002-606 mg/kg), Cd (0.57-122 mg/kg), Pb (9.6-157 mg/kg), As (7.7-256 mg/kg), and Hg (<0.002 to 18.7 mg/kg), the maximum concentrations were determined in the domestic sludge CRM 029. The rest of the microelements show narrower concentration ranges, e.g., 670-1108 mg/kg for Zn, 229-736 mg/kg for Cu, 88-353 mg/kg for Cr, and 29-127 mg/kg for Ni. The concentrations of B, Cd, Pb are much lower in the examined Bulgarian samples than in the analyzed CRM; Hg is below the LOD. Although the concentration intervals varied to a different extent for the individual elements, the application of ANOVA showed statistically significant differences between the samples for all elements.

Water solubility

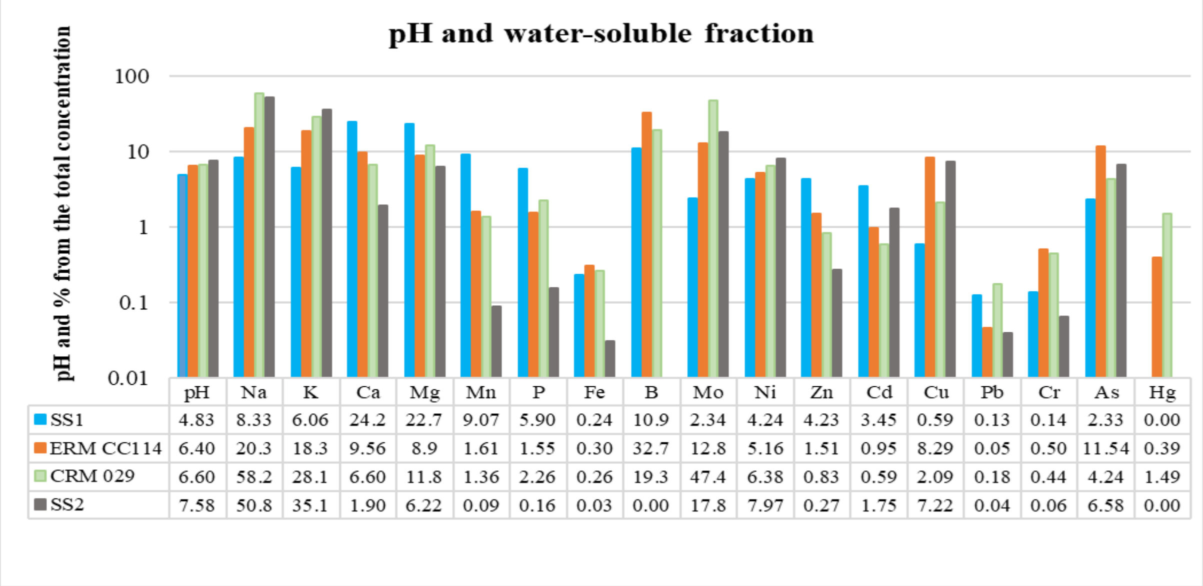
The water-soluble fractions of the studied elements, expressed as a percentage of the total concentrations, are presented in Fig. 1.

The results show a linear relationship between the increase in sample pH and the water solubility of K and an inverse relationship for Ca and Mg. The solubility of Na also increased from sample pH 4.83 (SS1) to sample pH 6.60 (CRM 029) and decreased slightly at sample pH 7.58 (SS2). An increase in the solubility of K in the direction from very acidic to alkaline sample pH was also found in [31] for soil samples. Despite the low percentages, a tendency for decrease of water solubility with sample pH increase was found for Mn, and P. Low solubility with maximum of 0.3% in ERM-CC144 was found for Fe. The solubility of Mo and B varies widely and is between 2.3% and 47% for Mo and in the range from 11% to 33% for B. A low degree of water solubility, was found for the PTEs. The data show no dependence of their solubility on the acidity of the samples, with the exception of a slight increase for Ni, resp. decrease for Zn on increasing sample pH. The presented results indicate low mobility in water for the PTEs, irrespective of their total concentrations. The lowest solubility was established for Pb (0.04%) and Cr (0.06%) and the highest for As (11.5%). These data indicate that there is no potential ecological threat when the sewage sludge samples are leached with water under natural conditions. With the decrease in the pH of the water, however, for example in the case of acid rain, an increase in the extraction efficiency is expected. The effect of pH on the heavy metal extraction with nitric and hydrochloric acid on the degree of extraction of Ni, Cu, Zn, Cr, and Pb in the pH range from 1 to 4 was studied in [32]. Although there was a wide variation of the extraction efficiency for the metals within the studied pH interval, for all elements an increase in the degree of extraction with decreasing pH was found.

BCR extraction scheme

The accuracy of the obtained results was assessed by analysis of the CRM BCR-701, for which certified values for the concentrations of Cd, Cr, Cu, Ni, Pb and Zn in Fraction 1, Fraction 2 and Fraction 3 of the BCR sequential extraction procedure are available. A comparison of the experimental and certified values is presented in Table 3. The experimental and the certified values agree well within uncertainty limits.

The results of the BCR extraction scheme of the sewage sludge samples and CRMs, expressed as a percentage of the total concentrations, are presented in Fig. 2.



	pH	Na	K	Ca	Mg	Mn	P	Fe	B	Mo	Ni	Zn	Cd	Cu	Pb	Cr	As	Hg
SS1	4.83	8.33	6.06	24.2	22.7	9.07	5.90	0.24	10.9	2.34	4.24	4.23	3.45	0.59	0.13	0.14	2.33	0.00
ERM CC114	6.40	20.3	18.3	9.56	8.9	1.61	1.55	0.30	32.7	12.8	5.16	1.51	0.95	8.29	0.05	0.50	11.54	0.39
CRM 029	6.60	58.2	28.1	6.60	11.8	1.36	2.26	0.26	19.3	47.4	6.38	0.83	0.59	2.09	0.18	0.44	4.24	1.49
SS2	7.58	50.8	35.1	1.90	6.22	0.09	0.16	0.03	0.00	17.8	7.97	0.27	1.75	7.22	0.04	0.06	6.58	0.00

Figure 1. Water-soluble fractions of essential and PTEs. BCR extraction scheme

Table 3. Experimental and certified concentrations of Cd, Cr, Cu, Ni, Pb and Zn in CRM BCR – 701, obtained by the BCR extraction procedure.

	Fraction 1		Fraction 2		Fraction 3	
	Determined	Certified	Determined	Certified	Determined	Certified
Cd	7.70±0.50	7.3±0.4	3.81±0.34	3.77±0.28	0.30±0.07	0.27±0.06
Cr	2.41±0.15	2.26±0.16	47.0±3.0	45.7±2.0	146±6	143±7
Cu	50.4±2.5	49.3±1.7	128±5	124±3	54±5	55±4
Ni	16.4±0.9	15.4±0.9	29.0±2.0	26.6±1.3	14.8±0.9	15.3±0.9
Pb	3.29±0.35	3.18±0.21	123±5	126±3	10.5±1.4	9.3±2.0
Zn	209±8	205±6	116±6	114±5	45.4±2.3	46±4

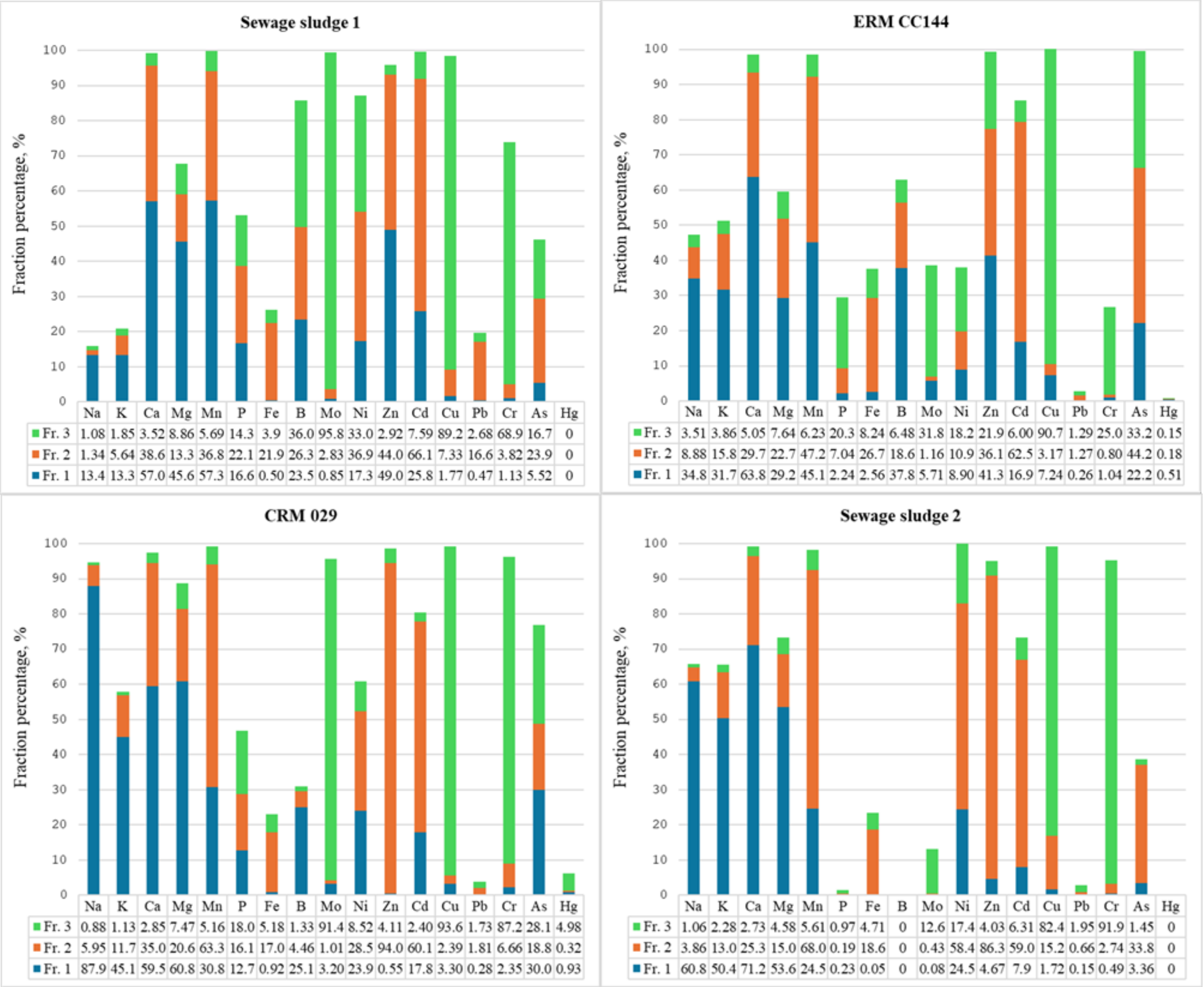


Figure 2. Percentage of essential and PTEs in the sludge samples.

The results show an increase of the sum BCR extraction percentage (Fr.1+Fr.2+Fr.3) for Na with increasing pH of the samples from 4.83 (SS1) to 6.60 (ERM-CC144) and a decrease at 7.58 (SS2), which is fully consistent with the data of the water extraction. High mobility and linear increase of the sum extraction with increasing sample pH was also found for K. A trend of increasing the available fraction of K with increasing pH was established for soil samples [31]. The decrease in the concentration of mobile K forms at low pH could be explained by competition with high concentrations of H^+ and other soluble ions (Al, Ca). Increasing the pH leads to the formation of insoluble calcium phosphate species and aluminum hydroxide precipitates and an increase of the mobile species of K. Despite the varying percentage of sum extractions in the analyzed samples, the highest percentage of Na and K was extracted in the exchangeable fraction, which was between 1.2 and 2.2 times higher than that in the water-soluble fraction.

High sum BCR extraction close to 100% was obtained for Ca. Its distribution shows mainly the presence of easily mobile species in the exchangeable fraction, which represent more than 50% of the total extracted Ca independent of the sample pH. The total extracted percentage of Mg is lower and ranges from 60% to 89%. In all the samples, Mg is also predominantly associated with the exchangeable phase. Main binding in the exchangeable fraction of Na, K, Ca and Mg was also found in [23]. High mobility and sum extraction close to 100% were observed for Mn. In the acidic Sewage sludge 1 it is predominately associated with the exchangeable fraction (57%), in ERM-CC144 it is evenly distributed in the exchangeable and oxide fractions (45%, resp. 47%), in CRM 029 the percentage of Mn in the oxide fraction dominates over the exchangeable (31% *vs*. 63%), which is even more pronounced in Sewage sludge 2 (25%-68%). The fractionation of P also shows a strong dependence on sample pH and the differences in sum extraction are consistent with the water solubility data. The highest degree of sum extraction (average 50%) was observed in the acidic Sewage sludge 1 and CRM 029. In both samples, P was relatively evenly distributed in the three fractions. In ERM-CC144, the sum extraction was below 30%, predominantly in the form of organic complexes. A very low degree of mobility (total 1.4%) was found in the alkaline Sewage sludge 2, due to the formation of insoluble compounds which reduce its availability. The sum extraction of Fe was in the range from 23% to 38%, the main part of it being in the oxide fraction, which also corresponds to the low water solubility. The total extracted fraction of B varied between 31% and 86%, and decreased with increasing the sample pH from 4.86 to 6.6. The fractionation also depends on the sample matrix. In the acidic Sewage sludge 1, it is fairly even distributed in the three fractions, while in ERM-CC144 and CRM 029 binding to the exchangeable fraction predominates. The data in Fig. 2 show that the total solubility of Zn amounts to 100% in all the samples. It is mainly bound in exchangeable and oxide fractions in Sewage sludge 1 and ERM-CC144 and in the oxide fraction in CRM 029 and Sewage sludge 2. The data show that main binding to the organic fraction in all the samples was found only for Mo, Cu and Cr. The total extracted percentages varied from 13% to 99% for Mo, from 27% to 96% for Cr, and above 98% for Cu. The percentage of the elements in the organic fraction does not depend on the organic carbon concentration in the sewage samples. The fractionation of Cu and Cr confirmed literature data on the high tendency of these elements to form organic complexes [14, 22], which suggests their low mobility and bioavailability.

High degree of sum extraction from 73% to 100% was also obtained for Cd with more than 60% of it was bound in the oxide fraction in all samples. For the remaining PTEs, the sum extraction and the fractionation depended on both the sample matrix and the element itself. The sum BCR extraction of Ni in the acidic sludge SS1 was 87%, evenly distributed in the oxide and organic fractions, and least in the exchangeable fraction. The sum extraction tended to 100% in the alkaline SS2, but it was mostly bound in the oxide fraction and had a lower and approximately equal tendency to bind to the other two fractions.

In ERM-CC144 the sum extraction was 38%, half of which in the organic fraction, followed by oxide and exchangeable fractions, while in CRM 029 the sum extraction of 61% was mainly due to the formation of oxide and exchangeable species. Very low sum extraction, below 4%, was found for Pb, except for the acidic Sewage sludge 1, in which the total extracted percentage was 19.7%. The extracted part of Pb was mainly bound in the form of oxides and organic complexes, similar to the data obtained in [14, 28, 33, 34]. The present results indicate low mobility of Pb in sewage sludge due to its binding in immobilized forms in sewage sludge samples. Hg was below the limit of detection in SS1 and SS2. In ERM-CC144 and CRM 029 the total extraction was below 1%, and 6.2%, resp., mainly in the form of organic complexes. Due to the low total extraction percentages, and the predominant binding of Pb and Hg in the oxide and organic fractions, they also do not pose an environmental pollution risk. The data for As show sum extraction below 50% in the acidic SS1 and alkaline SS 2, and an increase to 100% in ERM-CC144. Regardless of the varying sum extraction, a major binding in the oxide fraction was established for these samples. Different fractionation was observed in CRM 029. The total mobility reached 77%, 30% of which were in the exchangeable, 28% in the organic and 19% in the oxide fraction. A fractionation study for Cd, Cr, Cu, Ni, Pb, Zn and Hg in ERM-CC144 was conducted in [15] as well. The obtained concentrations in the individual fractions differ from the present data for some elements, the most significant differences being for Cd in Fraction 1, Ni in Fraction 2 and Fraction 3, Pb in Fraction 2 and Fraction 3 and Hg in Fraction 1. However, in both studies an identical distribution of the elements in the studied fractions is obtained.

CONCLUSIONS

The main aim of this study was to conduct a fractionation study of essential and potentially toxic elements in domestic (SS1, ERM CC-144 and CRM 029) and industrial (SS2) sewage sludge. The total concentrations of the studied elements showed statistically significant differences between the samples. The results from the sequential extraction showed that the most mobile metals are Na, K, Ca and Mg, being concentrated in the exchangeable fraction. Mn, Fe and B are mainly accumulated in the easily assimilable fractions (exchangeable and reducible) which indicates their high bioavailability. Low mobility is expected for Mo with dominant binding to the organic phase and for P, concentrated in the organic phase or distributed among the three phases. Metals contained in the sludge can be rereleased, when added to soil, depending on the soil pH, soluble metals, acid rain, dissolved oxygen content, decomposition of organic substances with the participation of microorganisms, redox potential, etc. [34]. The storage of sludge under different atmospheric conditions, may cause release of metals from the sludge.

The concentrations of the PTEs in Bulgarian sewage sludge samples are far below the permitted levels. The data show water leachability below 12%. The BCR fractionation indicates low tendency to form exchangeable species for Cu, Pb, Cr and Hg. Although Ni, Zn, Cd and As show high affinity to the oxide fraction, significant percentages are extracted as exchangeable species. Because the exchangeable, followed by the reducible fraction are highly mobile, the data indicate a potential risk of soil and plant pollution with Ni, Zn, Cd and As.

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