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Research Article

FRACTIONATION OF HEAVY METALS (Pb, Cr AND Cd) IN MUNICIPAL SEWAGE SLUGES FROM PODLASIE PROVINCE

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ABSTRACT

In the samples of fresh dehydrated sewage sludges from municipal treatment plants in Grajewo, Bielsk Podlaski, Sokółka, Dąbrowa Białostocka, Knyszyn, Mońki, Augustów, Suwałki, Sejny and Suchowola the following determinations were made: pH, pseudo-total content of Pb, Cd and Cr, organic matter and dry mass. The contents of the above-mentioned elements in fractions were evaluated using modified BCR method (four fractions: 1-acid soluble and exchangeable, 2-reducible, 3-oxidizable, 4-residual). The lead content (mean values) in particular fractions can be arranged quantitatively in a sequence: F4 (51.4%) > F2 (30.3%) > F3 (19.2%) > F1 (7.2%), in the case of cadmium: F4 (49.0%) > F2 (23.6%) > F3 (18.9%) > F1 (15.5%) and in the case of chromium: F4 (65.0%) > F3 (30.6%) > F2 (6.8%) > F1 (3.1%). Cumulative content of lead in mobile fractions (F1+F2+F3) ranged from 20.7% to 89.9%; for cadmium from 32.9% to 76.9% and for chromium from 27.5 to 58.6% of pseudo-total content.

Keywords: lead, cadmium, chromium, metal fractions, sewage sludge

INTRODUCTION

The utilisation of sewage sludges is nowadays one of the most important problems in sewage management of cities in majority of European countries. The amount of the produced municipal sewage sludge is systematically increasing [Wilk, Gworek 2009]. Better utilisation of biogenic substances from sludges is planned, keeping all the regulations related to sanitary and chemical safety [Bień, Wystalska 2008].

The use of municipal sewage sludge in agriculture according to regulations is a current problem. The biggest threat is connected with heavy metals, which contained therein. Once introduced into natural environment, heavy metals remain therein as they are not biodegradable. These metals can be cumulated by plants and thus create potential negative effect on animals and human health.

Lead and cadmium belong to a group of toxic elements for plants [Łukowski, Wiater 2011]. Chromium was never recognised as an essential element for plant growth, but some of its stimulating effects were reported [Sanghamitra et al. 1998]. These metals accumulate mainly in kidneys, the adrenal gland, liver, lungs, hair and skin, and they may cause high blood pressure, cancerous changes, damage to kidneys, liver and brain. In some cases they may also lead to mental disorders and loss of brain function [Szyczewski et al. 2009].

The total content of heavy metals in sewage sludge does not provide information about their availability for plants and thus about the amount of element, which will be introduced into biological cycle. The percentage of metals in mobile, or potentially mobile form available for plants, can be estimated using sequential extraction [Shrivastava, Banerjee 2004; Szumska, Gworek 2009; Rao et al. 2008]. The most often sequential extraction procedures involve extraction of metals from the following fractions: exchangeable, bound with carbonates, bound with Fe/Mn oxides, bound with organic matter and residual (metals associated with crystal lattice of minerals).

Investigation of fractional composition of metals in municipal sewage sludges is important in particular when they will be applied into light and acidic soils with low content of potassium, phosphorus as well as magnesium, and such a soils occur mainly in Podlasie Provice. That is because the above-mentioned factors of soil quality can influence the movement of heavy metals [Wiater, Łukowski 2010].

EXPERIMENTAL PROCEDURES

The study was based on fresh dehydrated sewage sludges collected in the year 2010. They came from municipal treatment plants in Grajewo, Bielsk Podlaski, Sokółka, Dąbrowa Białostocka, Knyszyn, Mońki, Augustów, Suwałki, Sejny and Suchowola. The sludges were hygenized (mainly with burnt lime), except these from Sokółka, Augustów and Suchowola. The fractionation was made in average samples (three individual dried samples were mixed and homogenized). In collected samples the following determinations were made: pH potentiometrically, dry mass by drying at 105 ºC, organic matter by heating in oven at 600 ºC until a constant weight was achieved, pseudo-total content of Pb, Cr, Cd (after previous digestion in HNO_3 with 30% H_2O_2) by means of FAAS technique and content of studied metals in fractions by means of GFAAS technique using Varian AA-100 apparatus. The percentage of individual fractions in pseudo-total content of each element was calculated. Recovery was defined as a ratio of metal content in four fractions (F1, F2, F3 and F4) to the pseudo-total content.

Modified BCR method with a use of ultrasonic probe Sonics VCX 130 was used to evaluate fractional composition of Pb, Cd and Cr in sludge samples. Extraction included four stages:

1. Acid soluble and exchangeable fraction (F1) – 1 g of sludge in 100 cm^3 centrifuge tube with 40 cm^3 of 0.11 $mol·dm^{-3}$ acetic acid was sonicated for 7 minutes (power – 20W) at temperature 22±5 ºC. Then, the mixture was centrifuged for 20 minutes at 3000 g. The extract was separated for analysis. Residue with 20 cm^3 of deionized water was sonicated for 5 minutes (power – 20W) and centrifuged for 20 minutues at 3000 g. Water was discarded.
2. Reducible fraction, bound to Fe/Mn oxides (F2) – to the residue from the first step was added 40 cm^3 of 0.5 $mol·dm^{-3}$ hydroxylamine hydrochloride fresh solution, pH 1.5, and sonicated for 7 minutes (power – 20W) at temperature 22±5 ºC. Then, the mixture was centrifuged for 20 minutes at 3000 g. The extract was separated for analysis. The residue was rinsed with deionized water, alike in the first step.
3. Oxidizable fraction, bound to organic matter (F3) – to the residue from the second step was added 20 cm^3 of 30% hydrogen peroxide and sonicated for 2 minutes (power – 20W) at temperature 22±5 ºC. Then, the volume of H_2O_2 reduced to approx. 1 cm^3 using water bath. 50 cm^3 of 1 $mol·dm^{-3}$ ammonium acetate and sonicated for 6 min. (power – 20W) at temperature 22±5 ºC was added to the moist residue. Then, the mixture was centrifuged for 20 minutes at 3000g. The extract was separated for analysis. The residue was rinsed with deionized water, alike in the previous steps.
4. Residual fraction (F4) – the residue from the third step was extracted using concentrated HNO_3 with addition of 30% H_2O_2.

RESULTS AND DISCUSSION

The studied sludges were characterized by alkaline reaction (Table 1), what is beneficial to immobilization of metals. However, selected metals (Zn and Cu for example) tend to increase solubility also at alkaline reaction, what is connected with the ability to form anion complexes and bonds of metal ions with ammonium com-

Table 1. Physico-chemical characteristics of sewage sludges (mean ± SD, n=3)

Location	pH	DM	Organic matter
		%	
Dąbrowa Białostocka	9.43 ±0.01	17.9 ±0.23	29.8 ± 2.1
Grajewo	8.91 ±0.22	43.5 ±6.05	16.2 ± 3.6
Sokółka	8.20 ±0.08	15.4 ±5.03	62.5 ± 6.5
Bielsk Podlaski	8.14 ±0.06	17.1 ±1.65	62.8±13.4
Knyszyn	7.79 ±0.34	6.6 ± 0.76	41.6±18.6
Augustów	8.02 ±0.05	13.3 ±1.04	30.2 ± 7.9
Sejny	8.38 ±0.07	11.1 ±0.14	15.4 ± 4.0
Suwałki	9.03 ±0.19	20.6 ±0.92	36.5 ± 3.0
Mońki	9.42 ±0.05	13.1 ±0.63	29.8±13.7
Suchowola	7.78 ±0.16	10.6 ±1.07	73.9 ± 5.1

pounds or low molecule organic matter. The reaction is the main factor, which influences the solubility of metal compounds in environment [Wilk, Gworek 2009].

The content of dry mass ranged from 6.6 to 43.5%. The lime-treated sludges contained the highest amounts of dry matter, in general.

The sludges contained from 15.4 to 73.9% DM of organic matter. According to Mazur [Mazur 1995], the content of organic matter in sewage sludge rage from 17 to 87% (60% on average). It has the ability to form stabile complexes, which appreciably can decrease the mobility of metals. The biggest affinity to organic matter have elements such as Ni, Cu and Pb [Karczewska 2002].

The pseudo-total amounts of studied elements were below values intended for agricultural use of sludge (Table 2). As stated by Maćkowiak [2000], the average content of cadmium in municipal sludges is 3.3 mg·kg^{-1} DM. In 40% of studied sludges the Cd content was higher. The content of lead and chromium in all samples was lower, than the average (92 and 175 mg·kg^{-1} DM respectively) reported by above-mentioned author.

The content of metals in particular fractions, in general, was differentiated. It's related to varied sources and initial form of metals in sewage sludges, their pH, conductivity, content of organic matter and redox properties [Wilk, Gworek 2009].

Table 2. Pseudo-total content of Pb, Cr and Cd in sewage sludges (mean ± SD, n=3)

Location	Pb	Cr	Cd
	mg·kg^{-1} DM		
Dąbrowa Białostocka	29.80 ± 0.77	90.10 ± 2.44	3.85 ± 0.14
Grajewo	26.24 ± 1.54	45.11 ± 3.56	3.83 ± 0.25
Sokółka	23.80 ± 1.39	78.20 ± 1.22	2.38 ± 0.10
Bielsk Podlaski	21.80 ± 0.77	63.23 ± 3.14	2.49 ± 0.23
Knyszyn	23.58 ± 0.77	49.82 ± 0.82	2.74 ± 0.00
Augustów	28.25 ± 1.02	81.34 ± 8.80	2.74 ± 0.13
Sejny	27.80 ± 2.14	74.20 ± 3.82	3.02 ± 0.20
Suwałki	28.47 ± 1.93	109.69 ± 25.81	2.98 ± 0.20
Mońki	31.81 ± 1.02	80.47 ± 1.91	3.40 ± 0.13
Suchowola	29.85 ± 0.43	89.23 ± 1.94	3.34 ± 0.07

Lead

The highest amount of lead (51.4% on average) was bound to residual fraction and ranged from 26.1 to 82.6% (Table 3). According to Piotrowska and Dudka [1987] considerable differentiation of metal content in this fraction is dependent on source of sewage sludge. The results of other authors' studies confirm a high content of Pb in residual fraction [Wang et al. 2008; Fuentes et al. 2004; García-Delgado et al. 2007], which is unavailable for plants. The content of metals in this fraction is almost constant (changes can occur, to a small degree, only in extreme acid environment or due to the microorganisms' activity).

The results of the study have proved slight solubility and thus bioavailability of lead in sewage sludges, because only 7.2% of pseudo-total Pb content was noted in fraction F1. Metals bound to this fraction can be easily released after application of sludge into soil, due to the small bond strength [Wang et al. 2008, Kazi et al. 2005], during fractionation of sludges from the treatment plant located in Hyderabad city (Pakistan), with BCR method, have noted 4% of pseudo-total lead

Table 3. Content, percentage in fractions and recovery of Pb in the sewage sludges

Location	F1	F2	F3	F4	F1	F2	F3	F4	Recovery
	mg·kg^{-1} DM				%				
Dąbrowa Białostocka	2.80	12.00	6.50	10.29	9.4	40.3	21.8	34.5	106
Grajewo	2.35	12.51	1.50	11.10	8.9	47.7	5.7	42.3	105
Sokółka	2.80	5.60	2.00	18.92	11.8	23.5	8.4	79.5	123
Bielsk Podlaski	3.20	0.80	0.50	18.01	14.7	3.7	2.3	82.6	103
Knyszyn	2.40	6.80	12.00	4.27	10.2	28.8	50.9	18.1	108
Augustów	1.60	6.98	7.50	15.73	5.7	24.7	26.6	55.7	113
Sejny	0.80	7.60	8.00	12.10	2.9	27.3	28.8	43.5	103
Suwałki	0.40	7.20	4.50	18.19	1.4	25.3	15.8	63.9	106
Mońki	1.79	18.40	5.00	8.30	5.6	57.9	15.7	26.1	105
Suchowola	0.40	7.11	4.75	20.16	1.3	23.8	15.9	67.5	109
	Average								
	1.85	8.50	5.23	13.71	7.2	30.3	19.2	51.4	108

content in fraction mentioned before. Wang et al. [2008] obtained similar result, below 5% of Pb as compared to total content, in acid soluble and exchangeable fraction of sewage sludge from plant in Loujiang (China).

The average lead content in F2 fraction constituted 30.3% of pseudo-total content. This fraction is thermodynamically unstable. Anaerobic conditions and microorganisms' activity in sludges are leading to reduction and disintegration of Fe/Mn oxides, what can cause metal desorption [Jamali et al. 2007]. These factors may have influenced the content of Pb in above-mentioned fraction of sludge came from Bielsk Podlaski, which was very low. Fuentes at al. [2004] have stated in the reducible fraction of non-stabilized sewage sludge 20.7% of total lead.

The oxidizable fraction bound 19.2% of pseudo-total Pb content on average. According to Wang et al. [2006] this fraction dominate in sewage sludge, in the case of lead. Similar conclusions are presented by the earlier mentioned Kazi et al. [2005], who stated in fraction bound with organic matter 42% Pb, as compared to pseudo-total content.

The most of lead content (89.9% of pseudo-total content) in mobile pool (F1+F2+F3), i.e. available and potentially available for plants, was noted in the sludge from plant in Knyszyn. It was caused by low content of primary and secondary minerals, which comprise residual fraction. The same factor was responsible for the least cumulative Pb content (20.7%) in three fractions of sewage sludge from Bielsk Podlaski. Due to the high content of minerals mentioned before, fraction F4 gathered in this case 82.6% of pseudo-total Pb, that means the most among studied sludges.

Chromium

Residual fraction bound the highest amount of chromium (65% on average) and its content ranged from 37.1 to 87.5%, as compared to pseudo-total content (Table 4). Gawdzik and Gawdzik [2012] investigating fractional composition of heavy metals in sewage sludge came from treatment plant in Cedzyna have stated similar content (approx. 62%) of Cr in the discussed fraction using BCR method. Kazi et al. [2005], noted 41% of pseudo-total chromium in residual fraction. According to the authors, such a content indicates that this element occurs in a high degree as sulphides.

The lowest amount of the studied element (3.1% on average) was observed in fraction F1. The low content of chromium in exchangeable fraction (less than 5% of total content) have stated the above-mentioned Fuentes et al. [2004]. A similar result was obtained by Pérez-Cid et al. [1999] during the investigation of sewage sludge from a plant in Ourense (Spain) using Tessier method. The content of chromium in the exchangeable and bound with carbonates fractions (both fractions correspond to the first fraction of BCR method) was below determination limit.

Fraction bound to Fe/Mn oxides comprised 6.8% of psedo-total content on average. Similar chromium content (approx. 5 %) in this fraction was observed by Gawdzik and Gawdzik [2012]. Kabata-Pendias and Pendias [1999] report that

Table 4. Content, percentage in fractions and recovery of Cr in the sewage sludges

Location	F1	F2	F3	F4	F1	F2	F3	F4	Recovery
	mg·kg^{-1} DM				%				
Dąbrowa Białostocka	2.79	7.89	30.65	58.11	3.1	8.8	34.0	64.5	110
Grajewo	1.64	2.70	11.90	36.02	3.6	6.0	26.4	79.9	116
Sokółka	2.58	3.70	39.60	28.99	3.3	4.7	50.6	37.1	96
Bielsk Podlaski	3.61	5.86	17.43	31.09	5.7	9.3	27.6	49.2	92
Knyszyn	1.21	3.89	12.60	38.09	2.4	7.8	25.3	76.5	112
Augustów	1.36	5.65	23.99	65.10	1.7	6.9	29.5	80.0	118
Sejny	1.22	2.63	26.31	35.99	1.6	3.6	35.5	48.5	89
Suwałki	3.57	6.98	36.20	73.27	3.3	6.4	33.0	66.8	109
Mońki	3.06	5.31	21.85	48.18	3.8	6.6	27.1	59.9	97
Suchowola	2.01	7.50	15.00	78.10	2.3	8.4	16.8	87.5	115
	Average								
	2.31	5.21	23.55	49.29	3.1	6.8	30.6	65.0	105

low mobility of chromium is related to domination of Cr(III), which forms weak soluble compounds, especially with iron oxides and hydroxides.

Organic matter of sludge bound 30.6% of pseudo-total chromium content on average. Metals bound to this fraction can be released due to the minetalization in oxidizing conditions [Wilk, Gworek 2009]. It can be stated that chromium, like in the soil [Karathanasis, Pils 2005], is bonded the most strongly to fraction of organic matter, as compared to other heavy metals. This thesis is confirmed by investigations of Wang et al. [2008]. The authors noted in disccused fraction 59% of total chromium, what was the highest content among all the fractions.

Mobile pool of chromium was the largest (58.6 %) in sludge from plant in Sokółka. It was caused by high content of organic matter and simultaneously low content of primary and secondary minerals, what was confirmed by the amount of Cr (37.1%) in fraction F4 of this sludge, which was the lowest among all sewage sludges.

Cadmium

Similarly, like in the case of lead and chromium, the highest percentage of cadmium (49% on average) was observed in residual fraction and ranged from 26.6 to 72.7% of pseudo-total content (Table 5). Investigations of Wang et al. [2008] confirm, that discussed fraction binds the largest amounts of Cd (approx. 65%) in sewage sludge. Rosazlin et al. [2007], using modified Tessier method, also have stated in residual fraction came from treatment plant in Taman Sri Gombak (Malaysia) the largest amount of cadmium (34% of total content).

The exchangeable fraction gathered the least of Cd (15.5% on average) among all fractions. Metals in this fraction might be attached to negatively-charged exchange sites or through relatively weak adsorption.

It is anticipated that the content of element in this fraction is proportional to its total content [2007]. Changes in the ionic composition, influencing adsorption-desorption reactions, or lowering of pH could cause remobilisation of metals from this fraction [Filgueiras et al. 2002]. Wang et al. [2008] also observed in discussed fraction the least amount of Cd (below 5%).

Fraction F2 comprised 23.6% of pseudo-total content on average. It is a similar result to that obtained by Kazi et al. [2005] (22% of pseudo-total content) and higher as compared to that presented by Rosazlin et al. [2007] (according to these authors, approx. 15.0 % of total Cd in sludge was in fraction of Fe/Mn oxides). The oxides, especially Mn oxides, can bind cadmium strongly [Onyatta, Huang 2006]. Several times lower content of Cd in discussed fraction of sludge from Sokółka, as compared to the rest of sludges, could be caused by reducible conditions in studied sludge.

Fraction F3 gathered 18.9% of cadmium, as compared to pseudo-total content. Similar percentage of Cd in this fraction (21%) was noted by Wang et al. [2008]. Different result (approx. 10% of pseudo-total content) was presented by Rosazlin et al. [2007]. Metallic pollutants associated with oxidizable phases are assumed to remain in the soil for longer periods but may be mobilised by decomposition processes [Onyatta, Huang 2006]. According to Ridgway and Price [1987] organic fraction is very important

Table 5. Content, percentage in fractions and recovery of Cd in the sewage sludges

Location	F1	F2	F3	F4	F1	F2	F3	F4	Recovery
	mg·kg^{-1} DM				%				
Dąbrowa Białostocka	1.56	1.00	0.40	1.03	40.5	26.0	10.4	26.6	104
Grajewo	0.96	1.18	0.65	1.13	25.1	30.7	17.1	29.4	102
Sokółka	0.16	0.20	0.50	1.42	6.7	8.4	21.0	59.8	96
Bielsk Podlaski	0.04	0.47	0.45	1.65	1.6	18.9	18.1	66.0	105
Knyszyn	0.08	0.52	0.30	1.99	2.9	19.0	11.0	72.7	106
Augustów	0.44	0.80	0.40	1.35	16.1	29.2	14.6	49.2	109
Sejny	0.48	0.76	0.65	1.67	15.9	25.1	21.5	55.3	118
Suwałki	0.54	0.84	0.55	1.32	18.1	28.2	18.5	44.4	109
Mońki	0.56	1.07	0.90	1.44	16.5	31.4	26.4	42.2	116
Suchowola	0.40	0.64	1.00	1.48	12.0	19.2	30.0	44.3	105
	Average								
	0.52	0.75	0.58	1.45	15.5	23.6	18.9	49.0	107

and in sewage sludges can determine the distribution of metals.

The largest pool of mobile cadmium (76.9%) was found in sludge from treatment plant in Dąbrowa Białostocka. Similarly, like in the case of lead and chromium, it was caused by the low content of minerals which form the residual fraction. The content of Cd in fraction F4 comprised 26.6% of pseudo-total content and was lowest, as compared to the rest of sludges.

CONCLUSIONS

1. All sludges met the standards related to agricultural use, according to heavy metal content.
2. The lead content (mean values) in particular fractions can be arranged quantitatively in a sequence: F4 (51.4%) > F2 (30.3%) > F3 (19.2%) > F1 (7.2%), in the case of cadmium: F4 (49.0%) > F2 (23.6%) > F3 (18.9%) > F1 (15.5%) and in the case of chromium: F4 (65.0%) > F3 (30.6%) > F2 (6.8%) > F1 (3.1%).
3. Assuming the cumulative content of metal in mobile fractions (F1+F2+F3) as the solubility criterion, it can be stated that cadmium was most soluble and chromium – the least soluble.

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