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Heavy Metal Speciation in Sewage Sludge

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Abstract

Sewage sludge is a rich source of organic matter and nutrients, so there is a possibility of their broader agricultural utilization. However, agricultural utilization of this material is limited by excessive quantities of heavy metals.

In accordance with this, the current paper presents the results of investigations referring to the speciation of heavy metals in selected sewage sludge.

It was found that there were differences among metals in the preferential formation of bonds, but also such phenomena occurred in the individual sludge samples for the same element. This was mainly observed for cadmium and nickel.

Especially important are the amounts of metals associated with water soluble plus exchangeable fraction (1 mol-L^{-1} NH4NO3) as well as fraction of metals extracted by 1 mol-L^{-1} NH_4OAc (pH = 6.0), corresponding to weakly adsorbed and bound with carbonates and labile organic compounds. With reference to this, it was stated that the percentage share of such combinations decreased in the order: Cu < Cr < Zn < Cd < Ni, reaching values of 2.9, 7.2, 8.8, 19.5 and 21.6% respectively. It shows those copper forms the lowest number of fast released combinations, whereas Ni and Cd - the highest.

Keywords: heavy metals, speciation, sewage sludge, sequential extraction, bioavailability

Introduction

A lot of attention has been paid in professional literature to sewage sludge due to its increasing amounts every year and the simplicity of its use. As it is characterised by an abundance of organic matter and nutrients [7, 8, 16, 17], it is often used in agriculture. While applying sewage sludge, its advantageous effect on the physical and chemical soil properties is taken into account, including the increase in bioavailability of phosphorus, the increase in cation exchange capacity and supplying the soil with exchangeable ions of Ca^{2+} and Mg^{2+} [4].

However, the addition of sewage sludge to soil is strictly limited by the presence of toxic compounds in its chemical composition, including heavy metals. As the effects of the negative impact of these elements on the environment are commonly known and thoroughly described, sewage sludge undergoes a strict process of verification in terms of total heavy metal content. On the other hand, [9] total metal contents are not the best indicators of their bioavailability and do not determine the character of bonds in which they occur. Thus, it is possible to establish the degree of their solubility and mobility in the environment only by taking into account various physical and chemical forms created by these elements. In this way it is also possible to determine their availability for plants. The mobility of heavy metal combinations in sludge in terms of the rate of their release and potential negative effect on soil and plants is assessed using the sequential chemical extraction procedures. These methods facilitate the determination of the percentage of water-soluble, exchangeable and easily soluble forms in the total metal content in sludge. On the basis of such information, the amount of a given element is established as it may be either a potential source of the nutrient for plants, or a threat both for plants and the whole environment.

In order to realise the above-mentioned task in the

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Table 1. Chemical composition of used sewage sludge.

Specification	Number of sewage sludge							
	1	2	3	4	5	6	7	8
Dry matter [%]	42.6	16.2	31.2	33.5	18.2	27.6	45.1	53.7
Organic matter [%]	46.3	73.3	64.0	60.0	50.3	69.2	42.3	31.2
Organic carbon [%]	21.3	33.9	32.0	35.5	30.5	57.4	22.8	12.4
pH	7.5	7.5	5.9	7.0	6.6	6.6	6.1	7.8
Total content of heavy metals [$mg \cdot kg^{-1}$]								
Cu	180	800	970	128	372	511	143	196
Cd	4.8	7.5	29	5.2	6.3	4.9	5.7	5.2
Zn	1450	1937	3249	2625	1150	1900	2754	1077
Cr	50	595	666	83	496	440	153	263
Ni	34	225	235	44	66	100	92	100

case of sewage sludge from mechanical biological sewage treatment plants in the Wielkopolska region, the Zeien and Brummer method [18] was used in the paper, taking into account seven fractions describing the type of metal combinations in the sludge.

Materials and Methods

Sewage sludge used in the study came from eight mechanical biological sewage treatment plants located in the Wielkopolska province. Sludge samples were taken from each plant from heaps from various places in the pile, using an auger. The samples were generally not taken from the outer layer of the heat, as the material tended to be very dry in those places. After 6-10 individual samples were taken from one heat, they were all mixed together and one average sample was compiled for analysis.

The collected material was prepared by drying and ground to pass through a 0.5 mm stainless steel sieve. The sewage sludge were analysed for basic physico-chemical properties using standard procedures:

Dry matter - the samples were heated to 105°C overnight to dry.

pH - was measured with a glass electrode in 1 mol • L^{-1} KC1 (1:2.5 ratio).

Organic matter (OM) - weighed samples were ignited at 550°C for 8 h, weight loss representing the loss of organic material.

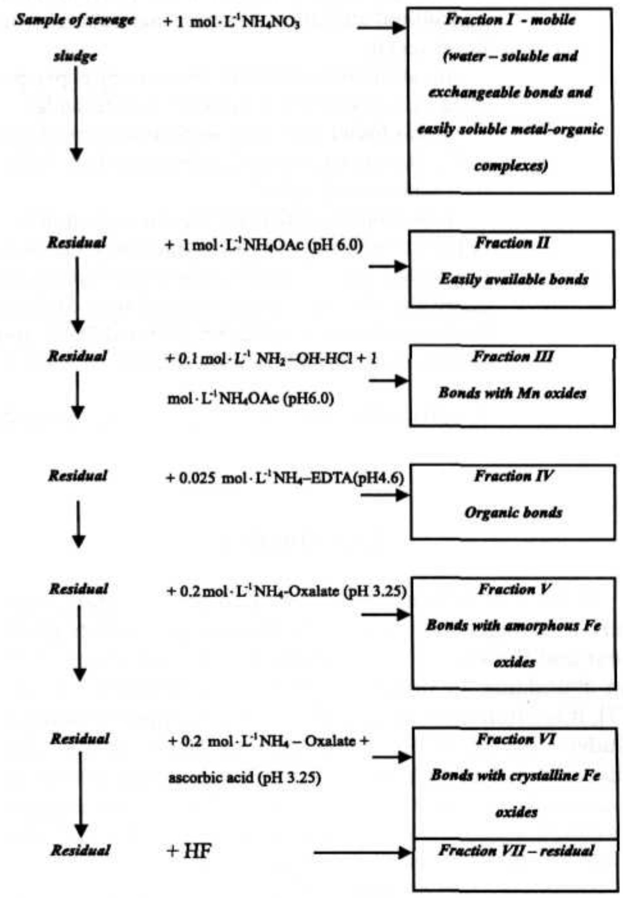
Organic carbon - by wet dichromate oxidation with sulphuric acid

Ca^{2+} - by flame atomic absorption following ashed at 450°C and then residual was dissolved in 3 mol • L^{-1} HC1.

Total heavy metal content of samples was determined following HF digestion. The mixture was evaporated to dryness and the residue taken up in 2 mol • L^{-1} HNO_3. All used in studies reagents were pure for analysis.

Total contents as well as amounts of heavy metals in sequential extractions were assessed by atomic absorption spectophotometry (Varian, SprectrAA - 250).

Sequential chemical extraction of heavy metals were undertaken using a sequential extraction procedure described by Zeien and Brummer [18] according to the following scheme:



The analyses of heavy metals were carried out in triplicate and all the reported results are their averages.

The obtained data were subjected to statistic analysis to evaluate the correlation coefficient (R) at two levels of significance ($p < 0.01$ and $p < 0.05$) and standard deviation (SD). Above analysis were made by using the program STATOBL.

Results

It results from the data in Table 1 that the investigated sewage sludge are characterised by varying chemical composition. From the point of view of their agricultural usage, the contents of dry matter, organic matter and organic carbon are essential. The quantities varied in a wide range of values, assuming in sludge no. 8 the lowest ones for organic matter and C org. at 31.2% and 12.4%, respectively, with the simultaneous highest dry matter content of 53.7%. In turn, the lowest amount of dry matter among the investigated sludge (16.5%) was accompanied by the highest MO content (73.3%), which were observed for sludge no. 2. The highest C org. content of 57.4% was found in sludge no. 6. In contrast to the above-mentioned properties, the reaction of the analysed sludge was similar in all samples, ranging from 5.9-7.8. Such pH values undoubtedly result from the presence of calcium, found in large quantities, i.e. between 0.7% (sludge no. 1) to 4.0% (sludge no. 6).

Among the numerous group of elements present in sewage sludge, heavy metals are undoubtedly the most crucial and at the same time the most controversial ones as those responsible for pollution. It primarily concerns cadmium, zinc, copper, chromium and nickel. Data presented in Table 1 indicate that total content of the above mentioned elements showed significant differences between the investigated sludge samples. It was most pronounced in sludge no. 3, which was characterised by high total contents of heavy metals, considerably exceeding Polish standards of admissible concentrations of elements in sludge (Polish statute book ,,Dziennik Ustaw" no. 72, dated August, 31st, 1999). However, in spite of the wide ranges of metals found in the samples (Table 1), their mean quantities from the eight plants met the above-mentioned standards (Fig. 1). The only exception was nickel, which slightly exceeded the admissible amount of 100 of sludge dry matter.

The conducted sequential analysis of metals revealed that in spite of the significant effect of the nature of this element on the rate and direction of the formation of chemical combinations, the similarly dominant quantities of Cu, Cd, Zn and Ni were also found in the organic combinations (fraction IV), as well as all the investigated elements in fraction VII (residual fraction) (Tab. 2).

It is worth noting that not only were there differences among metals in the preferential formation of combinations, but also such phenomena occurred in the individual sludge samples for the same element. It was mainly observed for cadmium and nickel. For the most active combinations described by fraction I, total cadmium contents ranged from 4.4% (sludge no. 7) to 20.2% (sludge no. 1); the figures for nickel were from 1.1% (sludge no. 7) to 25.1% (sludge no. 2) (Table 2). The percentage distribution in fractions II and III revealed that contrasts of this type in the rate of solubility are also found for zinc

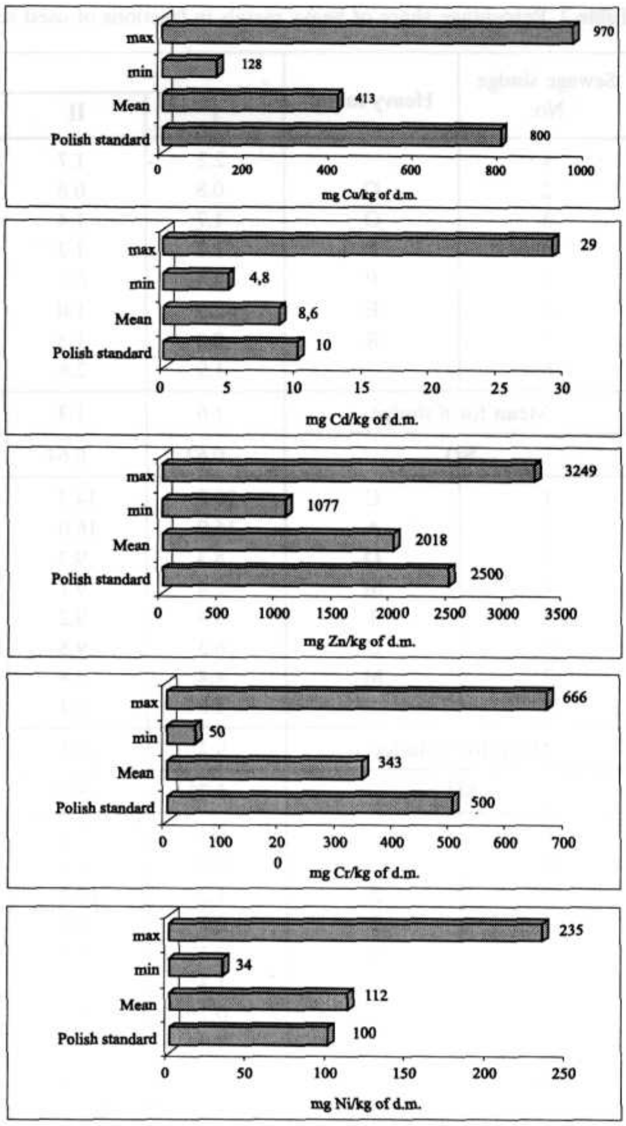


Fig. 1. Heavy metals content in sewage sludge in relation to Polish standards.

(from 2.2% in case of sludge no. 1 to 25.3% for sludge no. 8 in fraction II), as well as for chromium (from 0.4% in sludge no. 6 to 27.8% for sludge no. 4 in fraction III). Both form the ecological and agricultural points of view; it is essential to analyse the water-soluble and exchangeable combinations, as well as readily available metals, indicating the possibility of their fast transfer to the soil solution, and thus their high potential activity in the soil environment.

For this reason, the sequential distribution of the investigated elements was analysed, based on their percentage in fractions I and II. This results from the data presented in Table 2 that the percentage share of such bonds decreased in the order: Cu < Cr < Zn < Cd < Ni, reaching the values of 2.9, 7.2, 8.8, 19.5 and 21.6%, respectively. It shows those copper forms the lowest number of fast released bonds, whereas Ni and Cd - the highest. The above-mentioned dependencies are additionally con-

Table 2. Percentage share of heavy metals in fractions of used sewage sludge.

Sewage sludge No.	Heavy metal	Fractions of sewage sludge						
		I	II	III	IV	V	VI	VII
1	C	2.2	1.7	2.6	5.8	10.0	4.9	72.8
2	O	0.8	0.8	0.8	4.7	10.3	2.5	80.1
3	P	1.7	1.4	0.9	34.0	25.0	2.6	34.4
4	P	1.2	1.2	1.4	2.4	2.0	1.4	90.4
5	E	2.4	0.5	1.3	3.6	3.0	1.2	88.0
6	R	2.0	1.0	1.3	3.5	7.2	2.0	83.0
7		0.8	1.3	1.3	11.2	11.9	3.1	70.4
8		1.9	2.6	1.1	22.5	13.7	2.4	55.8
Mean for 8 sludge		1.6	1.3	1.3	11.0	10.4	2.5	71.9
SD		0.62	0.64	0.55	11.38	7.19	1.15	18.74
1	C	20.2	14.7	8.5	10.5	6.3	10.5	29.3
2	A	16.0	16.0	20.0	17.3	9.3	8.0	13.4
3	D	8.3	9.3	15.2	23.4	12.6	9.0	22.2
4	M	7.4	9.1	3.3	13.8	9.7	2.7	54.0
5	I	5.4	9.2	11.9	20.7	19.1	14.6	19.1
6	U	6.3	9.8	14.2	23.6	8.6	10.8	26.7
7	M	4.4	5.8	6.9	19.0	10.8	16.5	36.6
8		5.6	8.4	14.4	19.5	14.0	14.9	23.2
Mean for 8 sludge		9.2	10.3	11.8	18.5	11.3	10.9	28.0
SD		5.73	3.37	5.32	4.53	5.52	4.48	12.55
1		0.4	2.2	5.3	43.9	16.2	19.9	12.1
2		0.9	6.8	16.5	7.0	20.8	9.8	38.2
3	Z	1.2	13.3	13.8	46.2	14.3	4.4	6.8
4	I	0.2	1.0	1.2	7.9	12.1	12.4	65.2
5	N	2.3	3.3	4.3	12.1	9.6	24.1	44.3
6	C	1.3	5.2	12.2	43.4	9.6	11.7	16.6
7		0.7	5.6	9.6	14.5	8.9	7.8	52.9
8		1.0	25.3	9.9	35.0	5.4	3.4	20
Mean for 8 sludge		1.0	7.8	9.1	26.3	12.1	11.7	32.0
SD		0.64	7.99	5.17	17.42	4.85	7.19	21.18
1	C	6.2	11.9	9.1	3.8	13.7	10.1	45.2
2	H	3.0	3.2	0.7	5.9	27.6	26.9	32.7
3	R	3.7	1.5	0.7	3.1	48.5	25.8	16.7
4	O	6.0	12.7	27.8	7.5	13.1	14.5	18.4
5	M	0.1	0.1	1.6	2.6	28.8	2.9	63.9
6	I	0.5	0.6	0.4	3.1	41.2	38.1	16.1
7	U	1.4	5.9	4.6	6.9	8.2	13.4	59.6
8	M	0.5	1.1	3.2	8.4	26.0	20.8	40.0
Mean for 8 sludge		2.6	4.6	6.0	5.2	25.9	19.1	36.6
SD		2.46	5.08	9.27	2.28	14.05	11.12	18.98
1		8.5	12.6	8.2	21.8	10.6	14.7	23.6
2	N	25.1	12.4	6.3	20.6	12.6	6.0	17.0
3	I	7.6	7.8	5.4	22.2	25.1	10.9	21.0
4	C	4.6	11.2	14.9	9.6	11.7	10.2	37.8
5	K	6.0	12.2	9.8	14.7	18.2	9.4	29.7
6	E	17.2	22.6	7.8	22.7	10.2	4.4	15.1
7	L	1.1	3.1	3.4	4.4	4.1	6.9	77
8		4.0	16.0	10.6	21.8	14.7	5.9	27
Mean for 8 sludge		9.3	12.2	8.2	17.2	13.4	8.6	30.9
SD		7.96	5.68	3.54	6.93	6.20	3.38	19.94

firmed by the decreasing percentage share of the elements (from 71.9% of Cu to 28.0% Cd) in the combinations most firmly bound, described by fraction VII (Tab. 2).

In terms of the above assessment of the element solubilities, a relatively low percentage of zinc in the mobile fraction (I) and in the easily soluble fraction (II) is worth noting (Table 2), with the found high total contents of metals in the investigated sludge (Table 1).

The expected effect of the chemical properties of the sludge on the speciation of metals was not statistically confirmed in an unambiguous way. The influence of the sludge organic matter was observed only on cadmium in fraction II ($R = 0.716$ at $p < 0.05$). However, reaction - although with similar values observed in the investigated sludge samples - had a significant effect only in the case of copper in fraction II ($R = 0.725$ at $p < 0.05$) and III ($R = 0.808$ at $p < 0.05$), and nickel in fraction VI ($R = 0.868$ at $p < 0.01$). Thus, as the dependencies are so fractional, it is difficult to draw unambiguous conclusions or present any trends.

Discussion

Sewage sludge, being a product of the mechanical and biological treatment of sewage, are treated as wastes with fertilising properties, indicated by a considerable amount of organic substances and macroelements [13, 17].

The conducted analysis of the tested sewage sludge from mechanical biological sewage treatment plants confirmed their natural diversified chemical composition. It was connected with the type of sewage treatment plants and sewage quality, which were determined, among other things, by the degree of urbanisation and industrialisation of a given area. The latter factor was to a large extent responsible for the heavy metal contents, which often exceed the admissible concentrations, thus limiting the agricultural use of the sludge. The main hazard connected with the application of sludge stems from the unstable amounts of metals and the formation of combinations with various degrees of their release to the environment. Their type and character is established using the sequential extraction method. According to Hooda and Alloway [9], methods of Stover et al. and Tessier et al. are widely used in this respect. The Zeien and Brummer method [18] used in the author's study is comparable with the latter, and at the same time it facilitates a thorough analysis of speciation of heavy metals in sludge on the basis of seven obtained fractions.

The different profile of fractionation found in this paper resulted indirectly from the geochemical character of each element, and thus - its preferences to form more or less soluble combinations.

The speciation of copper obtained in the study in a conventional way confirmed results obtained by different authors [3, 12, 13, 14, 15], who showed the lowest mobility of that element. It is manifested by the firm binding with the mineral fraction of sludge, expressed in the adsorption on iron oxides and in the bonds of organic and residual fractions. High stability of the complexes with slightly soluble humic acids and other components of organic matter having high molecules [5] is definitely of significance in this context. The stability and resistance to dissolution of such copper combinations were confirmed indirectly by Rudd et al. [15], who showed a decreasing percentage share of copper in organic bonds with an increasing percentage of the less stable ones under the influence of high acidity (pH 0.5) of sewage sludge.

A similar type of speciation to that of copper was found for zinc, which was prevalent in forms difficult to activate. Data in literature [1, 3,12,15] first of all emphasise the occurrence of complexes with organic matter and significant amounts in the residual fraction. The applied method made it possible to determine that a relatively high percentage share of zinc was adsorbed on amorphous and crystalline iron oxides, i.e. in combinations of low solubility, the stability of which increases along with the increase in pH [2]. The obtained results confirmed the geochemical character of Zn, which in the soil environment is firmly bound, among others, by Fe oxides [11]. Irrespective of that, zinc is one of the more mobile elements in soil. It exhibited the same degree of mobility in sewage sludge [12]. However, the authors' own research does not confirm this. The phenomenon is even more significant as total Zn contents in sludge samples were high and as such did not affect increased solubility.

Slight quantities of mobile and readily soluble combination of Cu and Zn found during the tests, from the point of view of plant nutrition, must be considered as disadvantageous since both elements are microelements. In this case, high reaction should be maintained, as according to Brummer et al. [2] at the reaction above 6 and 7 the amount of soluble metal organic complexes increases at the expense of stable bounds with humic acids, the stability of which in the case of copper is high even at a pH of 3.0.

On the other hand, it is advantageous when cadmium and nickel, which are phytotoxic in the environment, are found in forms which are difficult and very difficult to activate. However, the presented results from the conducted investigations, as well as data in literature [3, 9, 12, 15] do not indicate such a character of speciation in cases of these elements. Both cadmium and nickel exhibited an almost identical distribution of fractions, at very similar percentages in individual fractions of sludge. This was especially visible in fraction I describing water-soluble and exchangeable combinations, as well as easily soluble metal organic complexes. The interpretation of the obtained results indicating high activity of Ni and Cd in sludge should be based on their typical reactions in the environment. First of all, mobility characteristic for both elements should be emphasised here [11], which - among other things - results from their preferential formation of soluble complexes with fulvic acids at neutral pH [2, 5]. Moreover, it should also be stressed that in spite of fast specific adsorption on Mn oxides, the stability of the process is low, as is indicated by the high pK values for both metals presented by Brummer et al. [2]. Thus, the assessment of the degree of bonds, in which Cd and Ni occur, should also include the total quantities of metals obtained for fractions from I to III, which will make it possible to estimate their bioavailable concentrations in sewage sludge in a reliable and objective way.

Chromium, similarly to the metals discussed above, enters into complexes with fulvic acids [6]. It may to some extent explain its comparatively high quantities in fractions I and II, indicating a potential set-off of the element to soil solution. As reported by Kabata - Pendias and Pendias [11], however, the mobility of chromium in the environment is limited by the dominating oxidation degree $^{3+}$, giving the formed compounds their low solubility, especially with iron oxides and hydroxides. It is confirmed by data from the authors' own studies, where the highest metal percentages were observed in fractions V and VII. Moreover, research done by Imai and Gloyna [10] indicate that, irrespective of the oxidation degree, the dominant part of Cr (80 - 90%) was bound firmly, difficult to dissolve in sludge.

Summing up it should be stated that in spite of the effect of organic matter on heavy metal speciation not being proven statistically, the effect was visible in the determination of the degree of solubility of combinations formed by them in sewage sludge. The major role is ascribed to the easily soluble metal organic complexes, which intensify the mobility of metals, leading to an increase in their concentration in soil solution. Moreover, this type of combination is more available for plants than inorganic precipitated forms or firmly bound with the mineral fraction of the sewage.

Research results presented here indicate that the hazard connected with heavy metals does not result from their total contents - even those exceeding admissible standards - which was rare in the analysed material, but rather from the quantitative distribution in the fractions easily transferred to the soil solution.

Conclusions

1. Investigated sewage sludge exhibited differed chemical composition, which was especially evident in the total amounts of heavy metals.
2. Among the analysed heavy metals, copper showed the least preference to form easily soluble bonds, where as cadmium and nickel showed the highest.
3. The undertaken speciation of heavy metals revealed differences between elements in the preferential formation of chemical combinations, which to a large extent was determined by their geochemical character.

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