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Speciation of heavy metals in non-volatile solids of sewage sludge

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ABSTRACT

The aim of this study was to investigate if the combustion of sewage sludge at 600°C (removal of organic matter) can influence the formation of immobile chemical forms of heavy metals (Zn, Cu, Ni, Pb, Cd, and Cr) in ash. Dried sewage sludge samples were collected at two different mechanical–biological wastewater treatment plants. For sewage sludge and residue on ignition (ash) heavy metal speciation analysis according to BCR procedure was conducted. It was demonstrated that metals found in sludge are mainly bound to organic/sulfide fraction. Zinc was present in significant amounts in hydrated iron and manganese oxide fractions, nickel and cadmium in exchangeable-carbonate fraction, and lead in residue fraction. In the ash obtained after calcination at the temperature of 600°C, mainly metal enrichment of nearly insoluble compound fraction (residual fraction) occurred. The content of lead in this fraction was 93–96%. The residual fraction is considered to be chemically stable and biologically inactive. For other metals: zinc, copper, nickel, cadmium, and chromium, their content in the residual fraction was 48–62; 50–68; 69–92; 44–48; and 91–97%, respectively. Metal accumulation in this non-mobile fraction is advantageous with respect to soil–water environment protection.

Keywords: Heavy metals; Fractionation; Sewage sludge; Ash

1. Introduction

Mobility of heavy metals depends on their distinctive chemical forms in sewage sludge. Identification of these forms as well as their quantification is crucial in order to evaluate a potential threat to the particular ecosystem that is posed by heavy metals accumulated in sludge. If research applies to available forms, excluding the determination of metal distribution in other fractions, it can be limited to one-step extraction with the use of solution that simulates natural conditions in which metals pass from sludge into liquid. If the aim of the research is the exact determination of forms in which heavy metals occur in sludge, then a speciation analysis is applied with the use of sequential extraction. In this case, solutions of reagents with increasing leaching force are used [1–3].

Transfer of heavy metals from sewage sludge into food chain takes place through plants which are cultivated in soils fertilized with this sludge. Therefore, it is really important to perform heavy metal speciation

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analysis in sewage sludge in the case of its agricultural application. In spite of the fact that some of the heavy metals in trace amounts (microelements) are essential for plant and animal metabolism they can became toxic and pose threat to plants, animals, and humans when their concentrations are above certain acceptable level [4–6].

Apart from agricultural applications, sewage sludge is composted along with other organic waste, it is used for degraded soil reclamation, biological consolidation of landfill surface, it undergoes thermal transformations, or it is stored. Thermal modification processes of sludge are drying and pyrolysis, whereas neutralization processes are combustion, co-combustion, gasification, and vitrification. Incineration is an important method because it can reduce the volume and the mass of the waste by 90 and 70%, respectively [7,8]. Fly ash formed during sludge combustion processes contains in its composition, among others, several volatile metals such as mercury, cadmium, and lead, which are subject to evaporation, and which are emitted with combustion gasses, whereas elements more resistant to temperature remain in slag and bottom ash. Volatility of a particular element depends on the form in which it occurs, its sludge properties, and conditions of combustion process [9–11]. Metals evaporate at temperatures near the boiling point of the element or compound, which suggests that high incineration temperatures will increase the emission of heavy metals [8].

Combustion of sewage sludge causes an increase in heavy metal concentration in the formed products; however, it can also contribute to chemical transitions into less mobile forms (metals bound to insoluble compound fraction). The aim of this research was to demonstrate whether sewage sludge combustion at the temperature of 600˚C (removal of organic matter) contributes to the formation of non-mobile forms of heavy metals in the final bottom ash. Results were supplemented by mineralogical examination of sewage sludge and ash.

2. Materials and methods

2.1. Materials

As an experimental material dried sewage sludge sampled from two municipal waste water treatment plants in Częstochowa and Myszków (Poland) was used. Wastewater treatment in the plant located in Myszków (M), with the capacity of 12,000 m^3/d, is being conducted by the means of activated sludge method with the use of nitrification and denitrification processes. Sewage sludge from settling tanks is dewatered with the use of mechanical press and afterwards it is dried in solar dryer.

Wastewater treatment in the plant located in Częstochowa (C), with the capacity of 46,000 m^3/d, is being conducted by the means of activated sludge with nitrification, denitrification, and biological and chemical dephosphatation. Sludge stabilization in this plant is performed by the means of mesophilic methane digestion process. Stabilized sludge is mechanically dewatered with tape presses, and afterwards it is dried at a temperature of 260˚C in column dryers.

For the research ash was also used, which was obtained after calcinations of dried sewage sludge in muffle furnace for 1 h at a temperature of 600˚C.

2.2. Analysis procedure

Properties of total solids and volatile solids (gravimetric method) were determined for the sludge (M and C) samples.

In order to determine the quantity of the forms in which heavy metals occurred in sludge and in their residues after ignition (ash), sequential extraction according to BCR procedure was conducted [12,13]. Three different samples of the same sludge and ash were prepared for the analyses.

Preparation of required reagents was performed according to the guidelines described in the research [14]. In the first stage, in order to extract exchangeable metals and metals bound to carbonates (F1) 0.11 M CH_3COOH was used; in the second stage, (reducible fraction—F2) 0.5 M $NH_2OH{\cdot}HCl$ was used. In the following stage, in order to extract metals bound to organic matter and sulfides (oxidizable fraction—F3), 8.8 M H_2O_2 and 1 M CH_3COONH_4 were used; in the final stage, (residual fraction—F4) HNO_3 (65%) and HCl (37%) were used, as shown in Table 1.

In order to determine the overall content of heavy metals, 0.5 ± 0.001 g of dry sludge and ash were placed into 15 mL glass test tubes. Next, 2 mL of HNO_3 (65%) and 6 mL of HCl (37%) (aqua regia) were added [15]. The material underwent mineralization at 120˚C for two hours.

The concentration of heavy metals (Zn, Cu, Ni, Pb, Cd, and Cr) in the extracts was determined by the means of atomic absorption spectrometry method with four repetitions (using a spectrometer novAA 400, Analytic Jena, Germany).

The overall concentration of metals (total) determined after mineralization with aqua regia was compared with the sum of the metal concentrations in the extracted fractions (F1 + F2 + F3 + F4). Recovery in

Table 1
Operating conditions required in the BCR sequential extraction method

Fraction	Extraction procedure per 1 g of dry matter material	Forms of metals
F1	40 mL 0.11 M CH_3COOH, temp. 22°C, shaking for 16 h	Exchangeable and bounded with carbonates
F2	40 mL 0.5 M $NH_2OH{\cdot}HCl$ (pH 2), temp. 22°C, shaking for 16 h	Bounded with Fe and Mn oxides
F3	10 mL 8.8 M H_2O_2 (pH 2–3), temp. 22°C, 1 h, 10 mL 8.8 M H_2O_2, temp. 85°C, 2 h 50 mL 1 M CH_3COONH_4 (pH 2 with HNO_3), temp. 22°C, shaking for 16 h	Bounded with organic matter, sulfides
F4	2 mL 65% HNO_3 + 6 mL 37% HCl, temp. 120°C, 2 h	Non-silicate minerals

the sequential extraction procedure was calculated as follows:

$$\text{Recovery }(\%) = \frac{F1 + F2 + F3 + F4}{\text{Total}} \times 100 \quad (1)$$

In order to identify crystal phases in the analyzed material, X-ray powder diffraction method was applied with the use of D8 ADVANCE BRUKER X-ray diffractometer with Cu Kα radiation. The accelerating voltage was kept at 40 kV and the current at 30 mA. Scans were made from 2 to 60° (2-Theta) with a step of 0.02° in 3 sec step time.

3. Results and discussion

The amount of sludges M and C contained in the organic matter were 70 and 61%, respectively. The total concentration of zinc, copper, nickel, lead, cadmium, and chromium in sludge M amounted to 1,450; 65; 58; 46; 4.1; and 14.1 mg kg^{-1} of dry matter, respectively; in sludge C—2,980; 312; 121; 130; 7.7; and 431 mg kg^{-1} of dry matter.

Heavy metal concentration in particular fractions of sludge and ash (mg kg^{-1}) is presented in Tables 2 and 3, whereas the percentage content is shown in Figs. 1 and 2. The sum of zinc, copper, nickel, lead, and cadmium content in the four analyzed fractions was 92–109% of the total concentration in the sludge determined without fractionation, confirming the correctness of the used methodology and reliability of the obtained results [16–18].

Zinc in sludge M occurred in a hydrated iron and manganese oxide fraction in the amount of 628 mg kg^{-1}, while in an organic/sulfide fraction—559 mg kg^{-1}. This constituted, respectively, 46 and 41% of total zinc concentration in sludge. In the residue after ignition (ash M) zinc was bound with insoluble compound fraction—2,305 mg kg^{-1} (48%) and to oxidizable fraction —1,720 mg kg^{-1} (36%). In sludge C, this metal occurred in the organic/sulfide fraction in the amount of 1825 mg kg^{-1} (58%), and in the iron and manganese oxide fraction—927 mg kg^{-1} (29%). In ash C, it was bound with insoluble compound fraction—5,165 mg kg^{-1} (62%).

About 88% of total copper concentration in sludge M appeared in the organic/sulfide fraction (56 mg kg^{-1}), while in ash—in insoluble compound fraction—108 mg kg^{-1} (50%). A large amount of this metal in ash was bound also with sulfide fraction—87 mg kg^{-1} (40%). In sludge C, copper also occurred in the organic/sulfide fraction—257 mg kg^{-1} (90%), whereas in residue after ignition of sludge C—in the insoluble compound fraction—478 mg kg^{-1} (68%) and the oxidizable fraction —150 mg kg^{-1} (21%).

Nickel in sludge M was present in an exchangeable-carbonate fraction—21 mg kg^{-1} (38% of total amount), while in ash in an insoluble compound fraction—72 mg kg^{-1} (69%). A significant amount of this metal (35%) in sludge M was also obtained in an iron and manganese oxide fraction. In sludge C nickel occurred in the organic/sulfide fraction—60 mg kg^{-1} (46% of total amount) and in the exchangeable-carbonate fraction (28%). In ash C it was bound to insoluble compound fraction—322 mg kg^{-1} (92%).

Lead concentration in the organic/sulfide fraction of sludge M amounted to 31 mg kg^{-1} (72%), and in ash in the insoluble compound fraction—117 mg kg^{-1} (93%). Both in sludge C and in its residue after ignition (ash), lead occurred in the insoluble compound fraction, from 89 mg kg^{-1} in sludge, up to 298 mg kg^{-1} in residue after ignition, which constituted, respectively, 74 and 96% of the total amount.

Cadmium in sludge M was bound to organic/sulfide fraction and exchangeable-carbonate fraction, 1.9 mg kg^{-1} (50%) and 1.1 mg kg^{-1} (29%), respectively, while in sludge C it occurred mainly in the organic/sulfide fraction—6.2 mg kg^{-1} (74%). In ash M it was present in the insoluble compound fraction—5.4 mg kg^{-1} (48%); in remaining fractions: exchangeable-carbonate, iron and manganese oxide, and sulfide ones, respectively, 19, 16, and 18 %. In ash C cadmium was bound to insoluble compound fraction—8.7 mg

Table 2
Chemical fractionation of heavy metals in sewage sludge

Sewage sludge	Metal	Content in fractions (mg kg^{-1}) Exchangeable/carbonates	Fe and Mn oxides	Organic matter/sulfides	Residual	Sum	Reco-very (%)
M	Zn	147.0	628.0	559.0	41.0	1,375.0	95
	Cu	0.8 2	1.0	56.1	5.8	63.7	98
	Ni	20.5	19.1	11.0	3.5	54.1	93
	Pb	2.0	1.9	31.3	8.3	43.5	95
	Cd	1.1	0.5	1.9	0.3	3.8	93
	Cr	<0.1	0.3	9.4	3.3	13.0	108
C	Zn	243.0	927	1,825.0	169.0	3,164.0	106
	Cu	1.5	1.5	257.0	25.0	285.5	92
	Ni	36.4	18.0	59.7	15.4	129.5	107
	Pb	10.5	8.7	12.0	88.8	120.0	92
	Cd	0.2	1.0	6.2	1.0	8.4	109
	Cr	2.3	3.6	335.0	104.4	445.3	103

Table 3
Chemical fractionation of heavy metals in ash

Ash	Metal	Content in fractions (mg kg^{-1}) Exchangeable/carbonates	Fe and Mn oxides	Oxidizable	Residual	Sum	Reco-very (%)
M	Zn	388.0	383.0	1720.0	2,305.0	4,796.0	94
	Cu	15.0	5.8	86.5	107.7	215.0	95
	Ni	8.3	9.8	13.6	72.0	103.7	92
	Pb	3.0	0.5	5.9	117.4	126.8	92
	Cd	2.1	1.8	2.0	5.4	11.3	93
	Cr	<0.1	3.1	0.8	38.0	41.9	108
C	Zn	583.0	1,001.0	1,583.0	5,165.0	8,332.0	93
	Cu	23.5	50.3	150.4.0	478.0	702.2	96
	Ni	7.0	8.0	11.8	322.0	348.8	93
	Pb	7.6	2.8	3.7	298.0	312.1	107
	Cd	3.0	4.8	3.5	8.7	20.0	98
	Cr	15.3	7.7	13.1	1,057.0	1,093.1	92

kg^{-1} (44%), and to iron and manganese oxide fraction (24%).

In sludge, chromium dominated in the organic/sulfide fraction—9.4 mg kg^{-1} (72%) in sludge M, and 335 mg kg^{-1} (75%) in sludge C, while in ash—in insoluble compound fraction, respectively, 38 mg kg^{-1} (91%) and 1057 mg kg^{-1} (97%).

The speciation analysis of metals conducted in dried sludge taken from two wastewater treatment plants and in their residue after ignition at a temperature of 600˚C (ash) demonstrated that in ash most of the metals were bound to insoluble compound fraction, while in sludge—to organic/sulfide fraction. The dominant role of sewage sludge organic/sulfide fraction in binding zinc, copper, cadmium, and chromium was confirmed by Fuentes et al. [17], Alonso et al. [19], Stylianou et al. [20], Hanay et al. [21]. In the case of zinc, a large amount of this metal was found also in the iron and manganese oxide fraction, in the case of nickel and cadmium—in sludge exchangeable-carbonate fraction. Strong zinc affiliation by iron and manganese oxides in sewage sludge was pointed out by Walter et al. [16], Chen et al. [18], Jamali et al. [22], whereas high concentration of nickel in sludge exchangeable-carbonate fraction was stated by Hanay et al. [21], Jamali et al. [22], Lasheen and Ammar [23]. Organic matter combustion in sewage sludge contributed to the formation of non-mobile forms of heavy metals, especially with respect to chromium, nickel, lead, and copper. However, metals were still found in the mobile, exchangeable-carbonate, ash fraction. The following concentrations were detected: 7–8; 3–7; 2–8; 2; 15–19; and 1% of the total content of zinc, copper, nickel, cadmium, lead, and chromium, respectively. In

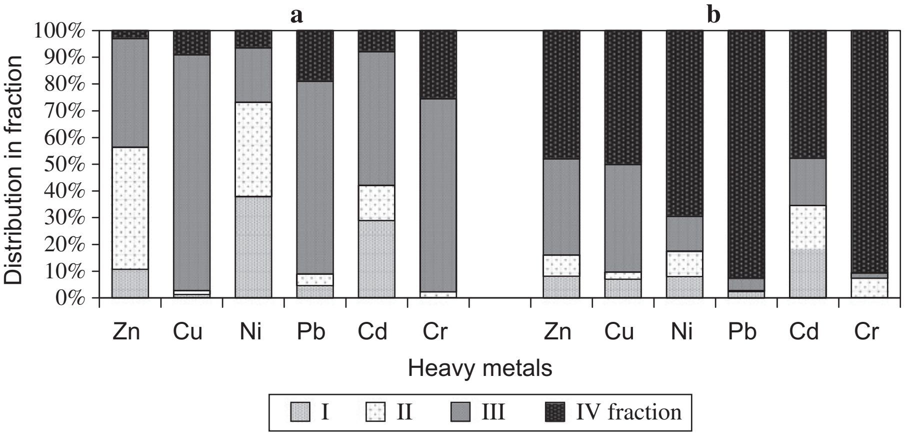

Fig. 1. Percentage distribution of heavy metals in fraction of sewage sludge M (a) and ash M (b); I—exchangeable/carbonates, II—Fe/Mn oxides, III—oxidizable, and IV—residual.

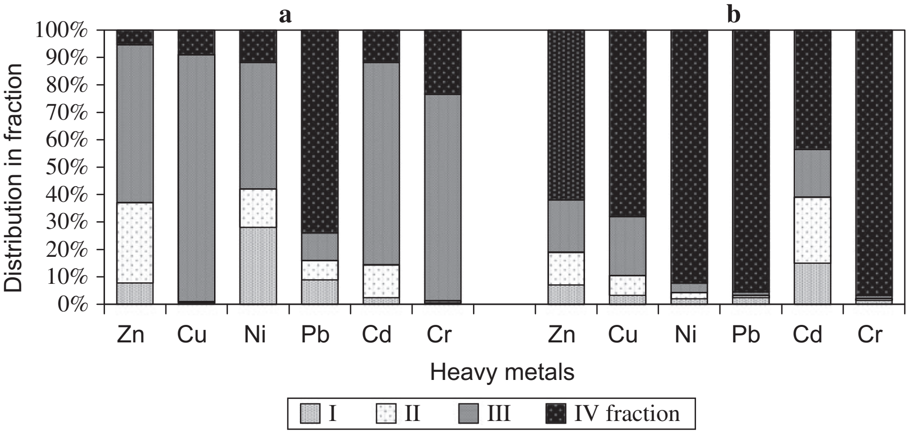

Fig. 2. Percentage distribution of heavy metals in fraction of sewage sludge C (a) and ash C (b); I—exchangeable/carbonates, II—Fe/Mn oxides, III—oxidizable, and IV—residual.

order to lower the concentration of metals in this fraction, the combustion of sewage sludge at higher temperatures can be performed as indicated by studies of Chen and Yan [8]. The highest concentration increase in this fraction in slag obtained at a temperature of 500˚C was observed for nickel and chromium, while also in slag obtained at a temperature of 900˚C for copper, cadmium, and zinc [8]. Residue fraction is considered to be chemically stabile and biologically inactive. It contains mostly metals incorporated in crystal lattice of primary and secondary minerals. Metals which are accumulated in this fraction of waste do not pose any threat to the water–soil environment.

X-ray diffraction measurements indicated that quartz (SiO_2) and hydroxywagnerite (Mg_2PO_4OH) were dominant crystal phases in sludge M. In ash M, the presence of quartz, illite ($KAl_2(Si_3AlO_{10})(OH)_2$), anhydrite ($CaSO_4$), dolomite ($CaMg(CO_3)_2$), giniite ferric ($Fe_5(PO_4)_4{\cdot}2H_2O$), and albite-calcian ordered ($(Na,Ca)Al(Si,Al)_3O_8$) was demonstrated.

Main crystal phases of sewage sludge C were: quartz (SiO_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), hematite—Fe_2O_3, and albite-calcian ordered ($(Na,Ca)(Si,Al)_4O_8$). However, identification was impeded due to a high amount of amorphous matter, which resulted in very high background. In ash C phases previously present in sludge C were concentrated (carbonates did not decompose at this temperature). Quartz was fully stable. Additionally concentration of illite ($(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$) occurred, and anhydrite ($CaSO_4$) typical for ash did as well. It was stated that a talc-like mineral was present, which was identified as willemseite ($(Ni,Mg)_3Si_4O_{10}(OH)_2$). The presence of quartz, calcite, phosphorus pentoxide (P_2O_5), hematite, and anhydrite in the product obtained during sludge sintering at the temperature of 800˚C was confirmed by Wang et al. [24].

4. Conclusions

Heavy metal speciation analysis performed for dewatered and dried sludge sampled in a wastewater treatment plant and for its residue on ignition (ash) showed that in sludge most metals were present in the organic/sulfide fraction, while in ash—in the insoluble compound (residue) fraction. The highest concentration in this fraction was observed for lead, chromium, and nickel. The residual fraction is considered to be chemically stable and biologically inactive.

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