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Risk assessment of soil contamination with heavy metals from sewage sludge and ash after its incineration

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ABSTRACT

The knowledge of the total content of heavy metals in sewage sludge and ash does not demonstrate a potential hazard. The toxicity of heavy metals in great measure depends on the form of their occurrence. The prevailing norms defining the maximal content of heavy metals in municipal sewage sludge used for environmental purposes apply to the total content of lead, cadmium, mercury, nickel, zinc, copper, and chrome. The possibility of using the soil for agricultural purposes also depends on the total concentration of the above-mentioned metals. The paper presents the research results on the mobility of heavy metals in sewage sludge and ash. The geo-accumulation index, the potential ecological risk index, and the risk assessment code were used for the evaluation of the potential soil contamination with heavy metals. A new formula was suggested for the risk assessment of the accumulation of heavy metals in soil (the water and soil environment risk index (WSERI). The WSERI covers a wider range of parameters in comparison to the formulas applied so far. The calculated indexes for sewage sludge and ash indicate the risk of soil contamination with heavy metals. The increase of the concentration of heavy metals in ash after the incineration of sewage sludge was noted with the simultaneous increase of the contribution of the immobile fraction in ash. It was found legitimate to use the methods taking into consideration the form of heavy metals for the risk assessment of the environmental influence of the anthropogenic substances.

Keywords: Sewage sludge; Ash; Heavy metals; Contamination risk

1. Introduction

Heavy metals, considered permanent contaminants, are removed from wastewater during its treatment and concentrate in sewage sludge, which requires final utilization. Sewage sludge containing the organic matter at the level of 30% d.m. can be used for the improvement of the physical–chemical properties of soil [1]. However, high levels of concentrations of heavy metals in sewage sludge prevent its agricultural usage [2]. The criteria determining the agricultural usage of municipal sewage sludge are defined by the directive EEC/1986 [3]. The directive [3] describes the limit values of the content of heavy metals in sewage sludge, the admissible metal loads in soil, and the admissible doses of heavy metals. High contribution of the organic matter in sewage sludge constitutes the basis for the ban on its deposition on landfills without a suitable treatment [4].

One of the applied methods of the utilization of municipal sewage sludge is thermal treatment. The thermal treatment can be realized with the use of pyrolysis, gasification, or incineration [5–9]. One of the popular solutions is the incineration and the co-incineration that can be performed in a fluidized-bed furnace [10], a grate furnace [11,12], or a rotary kiln [13,14]. The incineration of sewage sludge,

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apart from the obvious advantages such as, among others, the application regardless of the sanitary characteristics of sludge and the possibility to recover phosphorous [15–17], causes the increase of the concentration of heavy metals in ash [18].

It has been reported that sewage sludge ash has been used as a raw material for the production of construction materials [19,20], soil stabilization [21], and for agriculture [22]. The presence of sewage sludge ash in the natural environment constitutes a potential source of contamination with heavy metals [23]. The concentration of heavy metals in ash after the incineration of sewage sludge depends, apart from the initial concentration in sludge and the temperature of the incineration, on the volatility of metals. The most volatile metals are mercury, cadmium, and lead. Zinc is considered volatile, and copper a little volatile metal. Whereas, chrome and nickel are considered non-volatile metals [24]. Approximately 78%–98% of cadmium, chrome, copper, nickel, lead, and zinc present in sewage sludge remain in ash. Ninety-eight percent of mercury is removed together with the fumes [25]. Potentially high concentrations of heavy metals in sewage sludge ash are one of the criteria determining the methods of utilization.

The mobility and bioavailability of heavy metals in the environment depend not only on the total concentration but also on the form of their occurrence [26,27]. The most mobile metals are considered the ones bound to carbonates (*F*1). Metals bound to iron and manganese oxides are released more slowly into the environment (*F*2). The temporarily immobile metals are the ones that form permanent bonds with the organic matter or occur in the form of sulfides (*F*3). The immobile metals are the ones bound with aluminosilicates (*F*4) [28,29]. The determination of the chemical form of the tested substance occurring in the environment, originating from the natural and anthropogenic sources, is performed on the basis of speciation. The chemical speciation differentiates the reactivity of the chemical compound and the durability of the matrix in which it occurs [28].

According to the prevailing norms, the risk assessment of the ecological influence of heavy metals on the environment is not a factor determining the environmental usage of sewage sludge and sewage sludge ash. The potential ecological risk index (PERI), the geo-accumulation index (GAI), and the risk assessment code (RAC) are most commonly used for the ecological risk assessment of heavy metals in the environment [30,32]. The usage of the GAI and the PERI does not present a full picture of the risk because it does not take into consideration the forms of the occurrence of heavy metals. Whereas, taking into account only the mobile fraction (FI) of heavy metals for the determination of the RAC is not also a comprehensive description of the risk of the contamination of the water-soil environment. The remedy for the lack of suitable methods of the risk assessment is the suggested water and soil environment risk index (WSERI).

The aim of the paper is the potential risk assessment of the anthropogenic influence of heavy metals from sewage sludge and from ash after the incineration of municipal sewage sludge, particularly in terms of their accumulation in soil. The measures of assessment of the potential contamination of soil with heavy metals are the PERI, the GAI, the RAC, and the WSERI.

2. Materials and methods

2.1. Materials

Sewage sludge (SS1, SS2) and sewage sludge ash (SSA1, SSA2) were taken from two wastewater treatment plants of different sludge incineration technologies.

The first wastewater treatment plant is located in Olsztyn (SS1, SSA1). Its capacity equals 350,000 PE. The maximum capacity of sewage incineration equals 15 mg d^{-1}. The installation of sewage sludge incineration consists of a belt drier and a combustion chamber equipped with a grate.

The second wastewater treatment plant receives wastewater from the sewer system in Kielce – the capital of this region, Sitkówka–Nowiny municipalities and part of the Masłów municipality (SS2, SSA2). The nominal flow capacity of this sewage treatment plant equals 270,000 PE. The maximum amount of incinerated sludge equals 88.8 mg d^{-1}. This thermal utilization of sewage sludge is performed in a fluidized bed.

2.2. Methods

The chemical composition of the studied sewage sludge and sewage sludge ash was defined with the use of the X-ray fluorescence spectroscopy method.

In order to define the amount of forms of heavy metals occurring in sewage sludge and ash after the incineration of sewage sludge, the sequential extraction was conducted according to the BCR procedure [18]. The content of heavy metals in extracts was determined on the Inductively coupled plasma optical emission spectrometry (ICP-OES) Perkin Elmer Elmer Optima 8000, (Waltham, MA, USA) optical emission spectrometer with the inductively coupled plasma.

2.3. Potential ecological risk index

The PERI is based on the toxicity and the concentrations of heavy metals. It is used for the comprehensive ecological risk assessment caused by heavy metals [31]. It is used for the ecological risk assessment of coastal waters and sediments [30], municipal sewage sludge, sewage sludge ash, sewage sludge slag [30], and volatile ash from the incineration of solid municipal wastes [32]. The PERI was calculated with the use of the following formulas [31,33]:

$$C_f^i = \frac{C_D^i}{C_R^i} \tag{1}$$

$$E_r^i = T_r^i \times C_f^i \tag{2}$$

$$\text{PERI} = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_f^i \tag{3}$$

where C_f^i is the contamination factor, C_D^i is the concentration of each heavy metal in a sample of sewage sludge or sewage sludge ash, C_R^i is the background value of individual heavy metals, E_r^i is the PERI of an individual heavy metal, T_i is the toxicity response coefficient of heavy metals, which

reflects the toxicity level of heavy metals and the sensitivity of organisms to the pollution (Table 1) [30].

The PERI is the sum of potential ecological risks of each heavy metal.

For a single heavy metal element, E_r^i was advised by Maanan et al. [34] as follows:

- low potential ecological risk (LPER); $E_r^i < 40$,
- moderate potential ecological risk (MPER); $40 \le E_r^i < 80$,
- considerable potential ecological risk (CPER); $0 \le E_r^i < 160$,
- high potential ecological risk (HPER); $160 \le E_r^i < 320$,
- very high ecological risk (VHPER); $320 \le E_r^i$.

According to Fu et al. [35], the following ranges of values of the PERI were accepted: <150 – low risk (LR); 150 < PERI < 300 – moderate risk (MR), 300 < PERI < 600 – considerable risk (CR), PERI > 600 – very high risk (VHR).

2.4. Geo-accumulation index

Originally, the GAI was used for the ecological risk assessment of bottom sediments [37]. It is also used for the assessment of the contamination of soil and sewage sludge [38]. The GAI is based on the individual levels of the accumulation of metals, however without taking the toxicity into account [39]. The GAI was used in this paper [39]:

$$\mathrm{GAI} = \log_2 \frac{C_i}{1.5C_R^i} \tag{4}$$

where C_i is the content of an individual heavy metal in sewage sludge or sewage sludge ash, C_R^i is the geochemical background value of each i heavy metal. The constant value 1.5 is introduced for a better analysis of the natural variability of the content of the chosen substance in the environment.

The GAI values are divided into the following categories: uncontaminated (GAI ≤ 0), uncontaminated to moderately contaminated (0 < GAI ≤ 1), moderately contaminated (1 < GAI ≤ 2), moderately to heavily contaminated (2 < GAI ≤ 3), heavily contaminated (3 < GAI ≤ 4), heavily to extremely contaminated (4 < GAI ≤ 5), and extremely contaminated (5 < GAI) [37].

2.5. Risk assessment code

The RAC was also used for the environmental risk assessment caused by heavy metals. The RAC was used for the assessment of the contamination of soil with heavy metals from sewage sludge [40] and sewage sludge ash [31]. The RAC takes into account the percentage of heavy metals present in the exchangeable and carbonate fractions ($F1$). Heavy metals in sewage sludge or sewage sludge ash can be categorized by the RAC as no risk – safe to the environment (NR < 1), low risk – relatively safe to the environment (1 < LR < 10), medium risk – relatively dangerous to the environment (11 < MR < 30), high risk – dangerous to the environment (31 < HR < 50), VHR – very dangerous to the environment (VHR > 50) [40,41]. The RAC was calculated as follows:

$$\mathrm{RAC} = \frac{F1}{\mathrm{HM}} \times 100 \tag{5}$$

Table 1
C_r^{i*} and T_r^i of heavy metals

	$C^i_{R\,(SS1,\,SSA1)}$, mg kg^{-1}	$C^i_{R\,(SS2,\,SSA2)}$, mg kg^{-1}	T_r^{i**}
Cu	13.96	3.21	5
Cr	0.12	4.54	2
Cd	21.02	0.12	30
Ni	17.81	2.62	5
Pb	11.53	12.60	5
Zn	37.28	20.40	1

*C_r^i-values determined on the basis of the report on the realisation of the III stage of the procurement [36]. Measurement points were located adequately to the analyzed wastewater treatment plants.
**on the basis of [30].

where $F1$ is the concentration of a heavy metal in acid-soluble/exchangeable fraction, faction $F1$ (mg kg^{-1}), HM is the total concentration of an individual heavy metal (mg kg^{-1}).

2.6. Water and soil environment risk index

Some of the formulas used for the determination of the potential ecological risk take into consideration the exchangeable fraction $F1$ of heavy metals present in the assessed matrix. Whereas, they lack the concentration of heavy metals present in the second fraction (reducible) and the third one (oxidizable) as well as the characteristics of the water-soil environment. Taking into account the mobility of heavy metals and the metal toxic response factor (T_r^i), the author proposes the WSERI described with the formula (WSERI):

$$\sum_{i=1}^{n} \mathrm{WSERI}_i = \log_{10}\left\{T_r^i \times \left[\frac{F1_i + F2_i}{C_{\mathrm{wi}}} + \frac{F3_i}{C_{\mathrm{si}}}\right]\right\} \tag{6}$$

where $F1_i$ is the concentration of i-th metal in acid-soluble/exchangeable fraction; fraction $F1$, mg kg^{-1}; $F2_i$ is the concentration of i-th heavy metal bound with amorphous iron and manganese oxides; fraction $F2$ is reducible, mg kg^{-1}; $F3_i$ is the concentration of the metal-organic and sulfide fractions of i-th metal; fraction $F3$ is oxidizable, mg kg^{-1}; C_{wi} is the concentration of i-th heavy metal in the groundwater, mg kg^{-1}; C_{si} is the concentration of i-th heavy metal in soil, mg kg^{-1}.

The concentrations of heavy metals in sludge and sewage sludge ash can be categorized by the WSERI values as: WSERI < 5.3 – low risk of accumulation of heavy metals, 5.3 < WSERI < 10.6 – medium risk of accumulation of heavy metals, 10.6 < WSERI < 19.9 high risk of accumulation of heavy metals, WSERI > 19.9 VHR of accumulation of heavy metals. The categorization of the WSERI levels was determined on the basis of the norms concerning the quality of water intended for human consumption [42,43] and the admissible amounts of heavy metals in soil when municipal sewage sludge is used in agriculture and for the recovery of soils intended for agricultural purposes [3] (Table 2). The determination of such restrictive ranges of the WSERI values was caused by the increase of concentrations of heavy

metals from anthropogenic sources on agricultural terrains in Europe [44,45].

3. Results and discussion

The characteristics of sewage sludge and sewage sludge ash were presented in Table 3. The incineration of sewage sludge caused the increase of the contribution of silicon, aluminum, iron, calcium, and phosphorous oxides.

In SS1 sewage sludge, heavy metals, except for cadmium, nickel, and zinc, occur in fraction IV – that is, the immobile fraction (Table 4). In the mobile fraction FI, the greatest content was found for zinc 14.93 (mg kg^{-1}), nickel (4.47 mg kg^{-1}), and cadmium (0.47 mg kg^{-1}). In the extract of fraction FII, the greatest concentrations were discovered for zinc (33.14 mg kg^{-1}) and copper (1.16 mg kg^{-1}). The average percentage of the tested heavy metals in the separated fractions in SS1 sludge was presented in the following lines of decreasing values (Fig. 1):

- Cu: FIV (82.8%) > FIII (16.5%) > FII (0.36%) > FI (0.35%),
- Cr: FIV (92.0%) > FIII (7.0%) > FI (0.5%) > FII (0.48%),
- Cd: FII (42.6%) > FIV (36.1%) > FIII (14.7%) > FI (6.6%),
- Ni: FIV (50.3%) > FIII (28.5%) > FI (15.8%) > FII (5.4%),
- Pb: FIV (98.4%) > FIII (0.9%) > FII (0.6%) > FI (0.2%),
- Zn: FIII (65.0%) > FIV (23.1%) > FII (8.2%) > FI (3.7%).

The tests on SS2 sludge proved that heavy metals occur, except for cadmium, mainly in immobile bonds. In the mobile fraction FI, the greatest value was found for zinc (6.85 mg kg^{-1}). However, this value constitutes only 2.0% of the total content of zinc in SS2 sludge. Cadmium was present mainly in fraction III. The average percentage of the tested heavy metals in the separated fraction in SS2 sludge was presented in the following lines of decreasing values (Fig. 1):

- Cu: FIV (95.3%) > FIII (3.1%) > FI (1.0%) > FII (0.6%),
- Cr: FIV (97.7%) > FIII (1.3%) > FI (0.7%) > FII (0.3%),
- Cd: FIII (39.7%) > FII (36.0%) > FI (24.3%) > FIV (0.0%),
- Ni: FIV (73.4%) > FIII (12.3%) > FI (10.1%) > FII (4.1%),
- Pb: FIV (99.2%) > FIII (0.5%) > FI (0.17%) > FII (0.15%),
- Zn: FIV (60.2%) > FIII (33.8%) > FII (4.0%) > FI (2.0%).

The analysis of the results of the European Community Bureau Reference extraction of SSA1 ash leads to the conclusion that heavy metals occur mainly in fraction IV,

Table 2
Admissible concentrations of heavy metals in water intended for consumption [42,43] and admissible amounts of heavy metals in soil when sewage sludge is used in agriculture [3]

	Water intended for consumption, mg dm^{-3}	Soil, mg kg^{-1} d.m.
Cu	2.0	25
Cr	0.05	50
Cd	0.005	1.0
Ni	0.02	20
Pb	0.01	40
Zn	–*	80

*Non-standard

Table 3
Characteristics of sewage sludge and sewage sludge ash

Component	SS1	SS2	SSA1	SSA2
pH	7.5	7.5	9.4	11.5
Humidity, %	15.8	72.6	4.3	0.2
Loss on ignition, %	71.51	69.98	8.46	1.95
SiO_2, %	8.15	8.81	25.77	35.72
Al_2O_3, %	2.99	2.11	9.54	6.70
Fe_2O_3, %	1.56	3.74	5.12	9.56
CaO, %	6.43	5.66	20.70	17.46
MgO, %	1.42	1.42	4.48	4.51
SO_3, %	0.04	0.01	0.30	1.21
K_2O, %	0.58	0.58	1.87	1.61
Na_2O, %	0.16	0.16	0.55	0.52
P_2O_5, %	6.75	7.06	21.58	19.0
TiO_2, %	0.24	0.32	0.77	1.00
Mn_2O_3, %	0.04	0.03	0.13	0.14
SrO, %	0.03	0.02	0.10	0.05
BaO, %	0.02	0.04	0.09	0.11
TOC, % m.	32.95	33.69	5.39	0.09
Density, g cm^{-3}	–	–	42.28	2.74
Phase composition	Quartz, dolomite, kaolinite, Feldspar, and amorphous phase	Quartz, calcite, dolomite, and amorphous phase	Quartz, feldspars	Quartz, hematite, orthoclase, and albite

that is, are bound with aluminosilicates. In fraction FI, the greatest content was found for zinc (120.7 mg kg^{-1}), which constitutes 11.8% of the total content of this chemical element in SSA1 ash. The average percentage of the tested heavy metals in the separated fraction in SSA1 ash was presented in the following lines of decreasing values (Fig. 2):

- Cu: FIV (90.4%) > FIII (8.4%) > FI (0.7%) > FII (0.5%),
- Cr: FIV (98.1%) > FIII (1.6%) > FI (0.2%) > FII (0.1%),
- Cd: FI (94.4%) > FII (4.4%) > FIII (1.3%) > FIV (0.0%),
- Ni: FIV (68.6%) > FIII (19.5%) > FI (7.0%) > FII (4.8%),
- Pb: FIV (87.6%) > FIII (7.9%) > FII (2.24%) > FI (2.21%),
- Zn: FIV (66.5%) > FIII (15.9%) > FI (11.8%) > FII (5.8%).

Similarly, as for SSA1 ash, in SSA2 ash in fraction FI the greatest value was found for zinc (120.7 mg kg^{-1}). The contribution of fraction FI in the total content of zinc did not exceed 10% (Fig. 2). The average percentage of the tested heavy metals in the separated fraction in SSA2 ash was presented in the following lines of decreasing values (Fig. 2):

- Cu: FIV (73.4%) > FIII (21.5%) > FI (3.0%) > FII (2.1%),
- Cr: FIV (97.5%) > FIII (2.0%) > FI (0.4%) > FII (0.1%),
- Cd: FIII (69.6%) > FI (16.6%) > FII (13.8%) > FIV (0.0%),
- Ni: FIV (63.4%) > FIII (21.8%) > FII (8.4%) > FI (6.5%),
- Pb: FIII (73.4%) > FIV (26.5%) > FII (0.036%) > FI (0.002%),
- Zn: FIV (45.7%) > FIII (34.7%) > FII (9.9%) > FI (9.7%).

The levels of heavy metals in SS1 and SS2 sewage sludge did not exceed the admissible limits valid in the EU for sludge designed for environmental usage (Table 3). The researched municipal sewage sludge can be used for agricultural purposes, on condition that other parameters are met in accordance with the prevailing norms.

The consequence of the application of sludge incineration is the increase in the concentration of heavy metals in ash (Table 4). The increase of the concentrations of heavy metals in ash was caused mainly by the decrease of the organic mass and depended on the volatility of heavy metals [18]. Simultaneously, the tendency of the increase in the contribution of fraction FIV is noticeable for ash.

SS1 and SS2 sludge can be used in agriculture and/or the process of land reclamation for other than agricultural purposes. The environmental or agricultural usage of SS1 and SS2 can be authorized for realization on condition that suitable terrains are available, that is, they meet the limits of concentrations of heavy metals. The prevailing norms do not assess the risk of contamination with heavy metals

Table 4
Chemical speciation of heavy metals in sewage sludge ash, mg kg^{-1} (means ± standards deviation, n = 3)

Fraction*	Cu	Cr	Cd	Ni	Pb	Zn
			Sewage sludge – SS1			
I	1.13 ± 0.08	0.34 ± 0.06	0.47 ± 0.03	4.47 ± 0.06	0.05 ± 0.16	14.93 ± 0.09
II	1.16 ± 0.06	0.33 ± 0.001	3.01 ± 0.07	1.52 ± 0.05	0.21 ± 0.11	33.14 ± 0.24
III	52.93 ± 0.24	4.85 ± 0.53	1.04 ± 0.02	8.07 ± 0.08	0.34 ± 0.17	262.54 ± 1.97
IV	265.08 ± 8.67	62.99 ± 0.06	2.55 ± 0.06	14.26 ± 0.21	36.78 ± 0.24	93.50 ± 2.22
Sum	320.30	68.50	7.06	28.34	37.39	404.11
			Sewage sludge – SS2			
I	2.20 ± 0.15	0.42 ± 0.06	0.33 ± 0.02	2.66 ± 0.03	0.22 ± 0.01	6.85 ± 0.12
II	1.42 ± 0.04	0.16 ± 0.04	0.49 ± 0.01	1.09 ± 0.03	0.20 ± 0.04	13.65 ± 0.05
III	6.84 ± 0.16	0.78 ± 0.06	0.54 ± 0.01	3.23 ± 0.05	0.59 ± 0.07	116.54 ± 0.82
IV	211.95 ± 1.23	60.64 ± 1.18	0.000 ± 0.00	19.29 ± 0.11	129.5 ± 0.93	207.64 ± 2.58
Sum	222.42	61.98	1.36	26.27	130.51	344.68
			Sewage sludge ash – SSA1			
I	5.63 ± 2.50	0.12 ± 0.15	5.61 ± 6.48	2.96 ± 1.10	0.62 ± 0.40	120.70 ± 56.09
II	4.61 ± 3.23	0.09 ± 0.16	0.26 ± 0.06	2.03 ± 1.16	0.63 ± 0.07	59.36 ± 7.76
III	70.72 ± 10.94	1.13 ± 0.52	0.08 ± 0.15	8.25 ± 2.55	2.23 ± 0.73	162.81 ± 87.20
IV	762.25 ± 200.76	67.92 ± 36.51	0.00 ± 0.00	29.01 ± 13.48	24.61 ± 6.81	681.88 ± 236.38
Sum	843.22	69.26	5.95	42.26	28.09	1024.75
			Sewage sludge ash – SSA2			
I	11.98 ± 0.2085	0.3316 ± 0.019	0.9002 ± 0.0036	2.9722 ± 0.0202	0.0094 ± 0.094	71.651 ± 1.0246
II	8.2368 ± 0.0799	0.082 ± 0.0788	0.7432 ± 0.0056	3.8101 ± 0.0419	0.1587 ± 0.1786	72.961 ± 0.3502
III	85.419 ± 1.2642	1.4879 ± 0.1278	3.7626 ± 0.0497	9.9175 ± 0.0238	310.89 ± 2.0208	256.21 ± 2.8183
IV	290.99 ± 6.4018	73.918 ± 5.2851	0.000 ± 0.0000	28.897 ± 0.052	112.47 ± 0.9672	336.85 ± 5.4907
Sum	396.6258	75.8195	5.40	45.5968	423.5281	737.672

*Fraction: I – exchangeable/carbonates, II – reducible, III – oxidizable, and IV – residual.

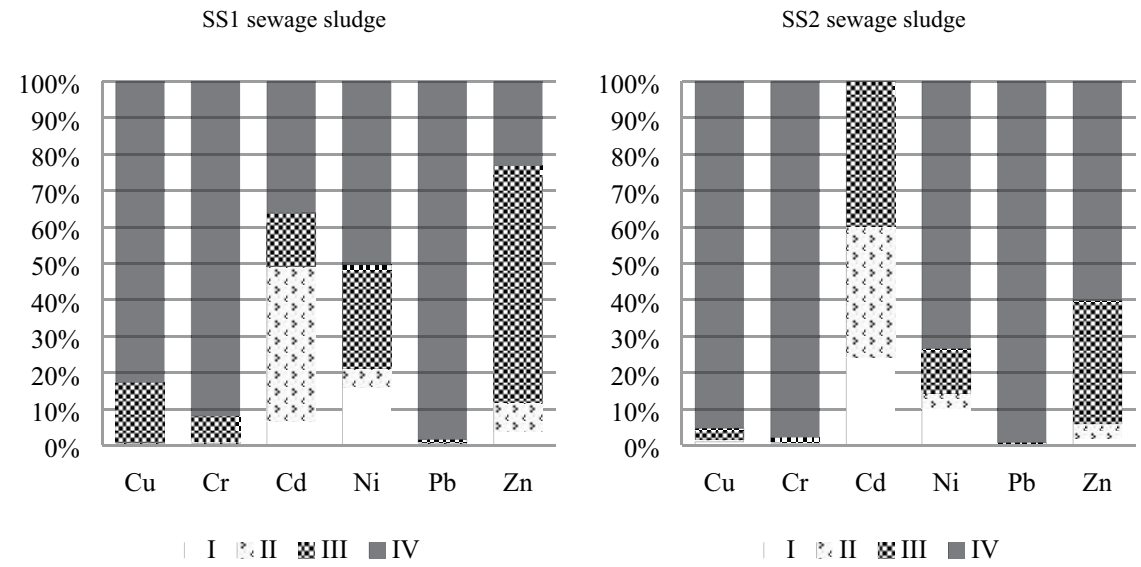

Fig. 1. Percentage distribution of heavy metals in fractions of SS1 sewage sludge and SS2 sewage sludge.

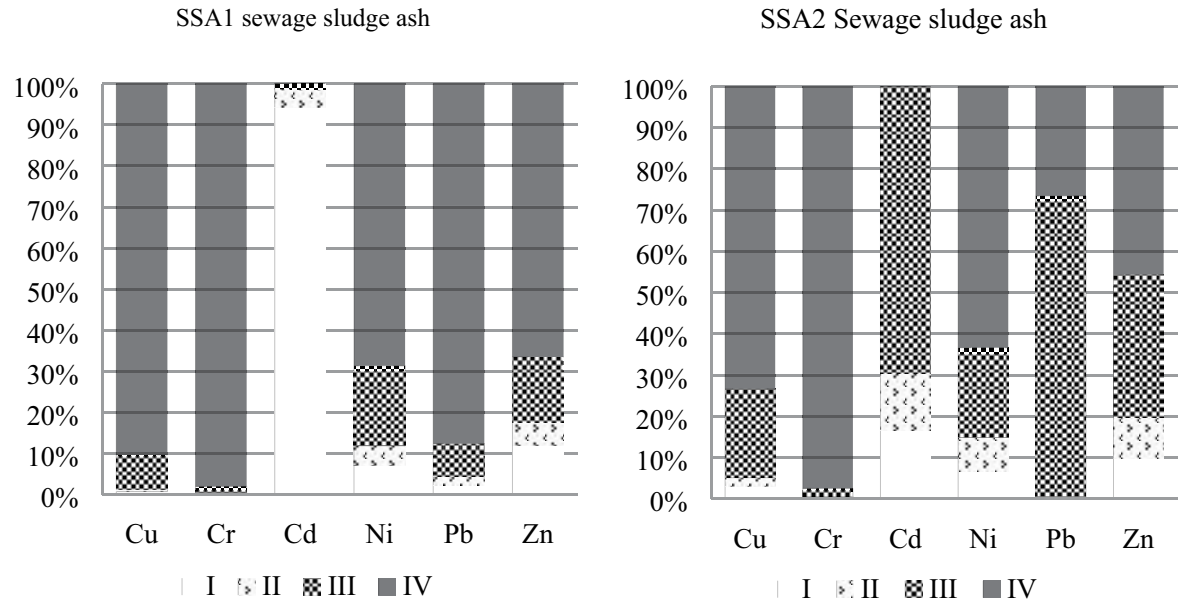

Fig. 2. Percentage distribution of heavy metals in fractions of SSA1 sewage sludge ash and SSA2 sewage sludge ash.

thoroughly because they do not cover the individual toxicity of heavy metals and their mobility.

The results of the ecological risk assessment for heavy metals in sewage sludge and sewage sludge ash are presented in Figs. 3 and 4. It is demonstrated that the potential ecological risk indexes of individual heavy metals (E_r^i) are ranked in the following order:

- SS1: Ni (LPER) < Cd (LPER) < Zn (LPER) < Pb (LPER) < Cu (CPER) < Cr (VHPER),
- SS2: Zn (LPER) < Cr (LPER) < Ni (MPER) < Pb (MPER) < Cd (VHPER) < Cu (VHPER),
- SSA1: Cd (LPER) < Ni (LPER) < Pb (LPER) < Zn (LPER) < Cu (HPER) < Cr (VHPER),
- SSA2: Cr (LPER) < Zn (LPER) < Ni (CPER) < Pb (HPER) < Cu (VHPER) < Cd (VHPER).

The E_r^i values for Ni, Cd, Zn, Pb, and Cu in SS1 sewage sludge were lower than in SS2 sewage sludge. The E_r^i values for Ni, Cd, Zn, and Pb in SS1 sewage sludge were at the level indicating low potential ecological risk. The E_r^i values for Cd and Cu in SS2 sewage sludge were 340 and 346.45, respectively, revealing very high potential risk. The E_r^i values for Ni, Zn, Cu, and Cr in SSA1 sewage sludge ash were higher than for SS1 sewage sludge.

The E_r^i value for Cr in SSA1 sewage sludge ash was above 320, suggesting VHR to the local ecosystem. The E_r^i values for Cu and Cd in SSA2 sewage sludge ash were 617.8

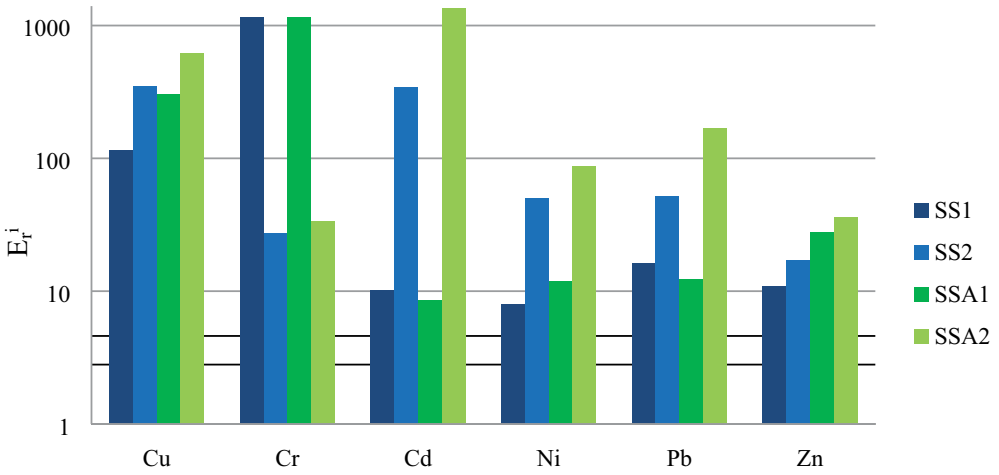

Fig. 3. Potential ecological risk index of individual heavy metals (E_r^i) in sewage sludge (SS1, SS2), and sewage sludge ash (SSA1, SSA2).

and 1,350, respectively, revealing very high potential ecological risk. The E_r^i values for all heavy metals in SSA2 sewage sludge ash were higher than the values for metals in SS2 sewage sludge. The dominant metal posing a potential ecological risk in the case of SS1 sewage sludge and SSA1 sewage sludge ash was chrome, and in the case of SS2 and SSA2 – cadmium and copper. For SS1 sludge and SSA1 ash, the highest values of E_r^i were for Cr, as they exceeded 1,140. For SS2 sludge the highest values of E_r^i were for Cd and Cu, 340, and 346.45, respectively. The highest value of E_r^i of the tested samples was for Cd in SSA2 ash and equaled 1,350.

The PERI was calculated in order to assess the total potential ecological risk caused by heavy metals from sewage sludge and ash after the incineration of sludge. The PERIs of heavy metals in sewage sludge and sewage sludge ash were above 600, suggesting a very high potential ecological risk (Fig. 4). Environmental risk caused by heavy metals would be posed if sewage sludge or sewage sludge ash were directly discharged into the environment without any treatment. Higher values of the PERI of tested ash than the values of the PERI of sewage sludge indicate that the incineration of sludge did not cause the decrease of the potential risk of the environmental contamination with heavy metals. Xiao et al. [31] proved that the incineration of sewage sludge reduces the potential risk of environmental contamination with heavy metals. However, it has to be highlighted that the authors [31] obtained the ash after the incineration of sewage sludge with 10% and 30% additives of wood sawdust.

The obtained values of the PERI are higher than the values presented in the paper [31], both for sewage sludge and for sewage sludge ash. It is caused by the significantly different contribution of heavy metals in the tested samples in comparison to the ones presented in the paper [31].

In SS1 sludge and SSA1 ash, the greatest contribution in the PERI was for chrome, 88%, and 76% respectively. Similarly, to the paper [31], in SS2 sludge the greatest contribution in the PERI was for copper (42%), and in SSA2 ash for cadmium (59%).

Fig. 5 presents the results of calculations of the GAI of heavy metals in sewage sludge and sewage sludge ash. The GAI values of sewage sludge and sludge ash were in the following increasing order:

- SS1: Cd < Ni < Pb < Zn < Cu < Cr,
- SS2: Ni < Pb < Cd < Cr < Zn < Cu,
- SSA1: Cd < Ni < Pb < Zn < Cu < Cr,
- SSA2: Cr < Ni < Zn < Cd < Pb < Cu.

For SS1, sludge and SSA1 ash the GAI values for cadmium were below zero, which suggests a favorable lack of contamination risk with this chemical element. The GAI for nickel of 0.09 for SS1 sludge indicates a moderate level of contamination. However, the GAI for chrome at the level above 8 suggests extreme contamination. For SS2 sludge, the level of contamination with nickel, lead, and cadmium is heavy, with chrome and zinc – within the heavy to extreme contamination range, with copper reaches the extreme contamination level.

The GAI values for all metals are higher for SSA1 and SSA2 ash than the values for SS1 and SS2 sludge with the exception of cadmium for SS1 sludge. It can be justified by the volatility of this chemical element. The order of the GAI values of the tested heavy metals for SS1 sludge and SSA1 ash was identical.

Environmental risk assessment results in accordance with the RAC are shown in Fig. 6. The RAC values of the tested samples have the following values in the increasing order:

- SS1: Pb < Cu < Cr < Zn < Cd < Ni,
- SS2: Pb < Cr < Cu < Zn < Ni < Cd,
- SSA1: Cr < Cu < Pb < Ni < Zn < Cd,
- SSA2: Pb < Cr < Cu < Ni < Zn < Cd.

The RAC values for sewage sludge and sewage sludge ash indicate the no risk of contamination of the ecosystem with heavy metals. For all the tested samples and all heavy metals, the RAC values are above the value of 1.0, which is the limit value for the no risk ranges. The incineration of sewage sludge was accompanied by the highest increase of the RAC values for Cd, Zn, Pb, and Cu. The increase of

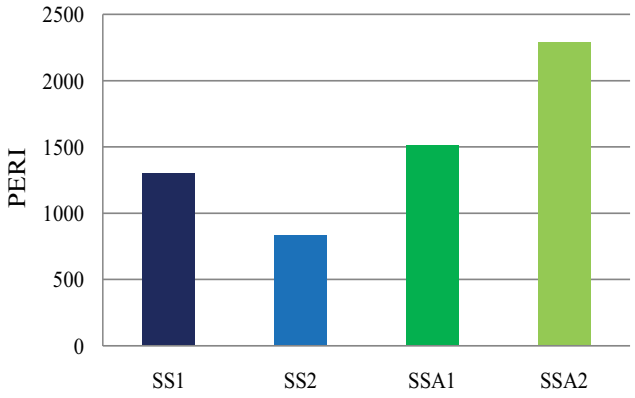

Fig. 4. Potential ecological risk index (PERI) of heavy metals in sewage sludge (SS1, SS2) and sewage sludge ash (SSA1, SSA2).

the concentration of these heavy metals was caused by their characteristics, that is, the lack of volatility.

For all the tested matrices, the highest value of the individual WSERI was for cadmium and the lowest for copper and chrome. For no heavy metal, the value of the individual WSERI was from the range of the zero potential contamination risk (Fig. 7). The calculated index of the water and soil environment risk had the following values (Fig. 7):

- SS1 sewage: 14.78,
- SS2 sewage: 13.09,
- SSA1 sewage sludge ash: 15.85,
- SSA2 sewage sludge ash: 15.28.

The obtained values of the WSERI proved that the incineration of sewage sludge causes the increase of the contamination risk of the water-soil environment with heavy metals. The highest percentage in the WSERI value was for cadmium, nickel, and lead. For all the tested sludge and ash the values of the WSERI indicate a high risk of accumulation of heavy metals in the environment.

4. Conclusions

The conducted research and calculations allow for drawing the following conclusions:

- In accordance with the obtained values of the PERI and the GAI, the incineration of sludge did not decrease the potential levels of contamination risk of the environment with heavy metals. Thus, the ash should undergo processing before the final usage or landfilling.
- The use of the RAC proved that taking into consideration the mobile fraction *F*1 is responsible for the decrease of the value of the parameter assessing the risk of the contamination with heavy metals. The use of the GAI did not prove the results obtained for the PERI and the RAC for all the tested samples because in the case of cadmium for the tested sewage sludge the negative values suggested the lack of contamination with this chemical element.
- For the tested matrices, the high contribution of zinc in fraction I did not cause high values of the PERI for zinc. It was mainly the consequence of the relatively low coefficient of the toxicity of this chemical element.
- The increase of the concentration of heavy metals in ash after the incineration of sewage sludge and the simultaneous increase of the contribution of the immobile fraction in ash prove the legitimacy of using the methods, which take into consideration the form of metals for the risk assessment of the environmental influence of the anthropogenic substances.
- The use of a new formula for the assessment of the accumulation risk of heavy metals proved that the introduction of the tested sewage sludge and ash into the environment without prior processing poses a high risk. The use of the WSERI in comparison to the popular indexes such as the PERI, the GAI, and the RAC covers a broader range of parameters, that is, heavy metals in all mobile fractions (FI and FII) and the temporarily immobile fraction (FIII). The WSERI can be used in situations when the potential risk of the accumulation of metals is unclear, for

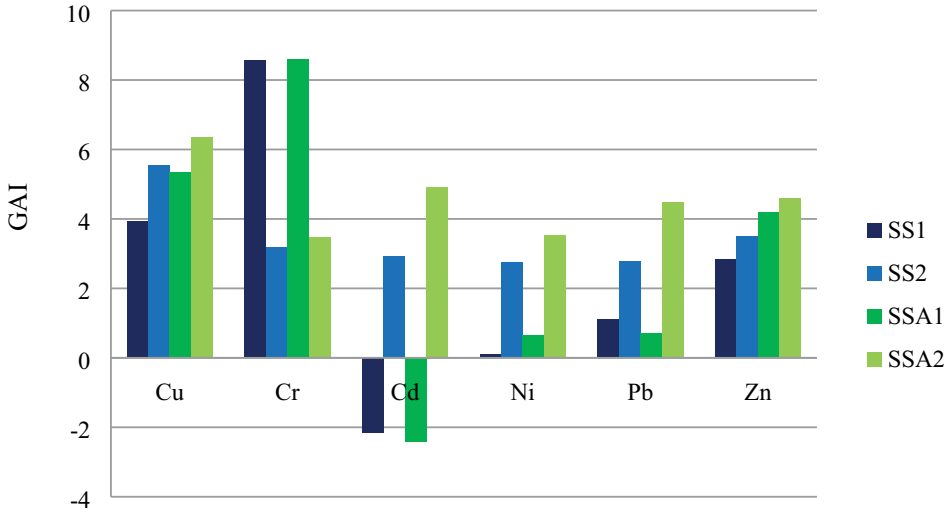

Fig. 5. Geo-accumulation index of heavy metals in sewage sludge (SS1, SS2) and sewage sludge ash (SSA1, SSA2).

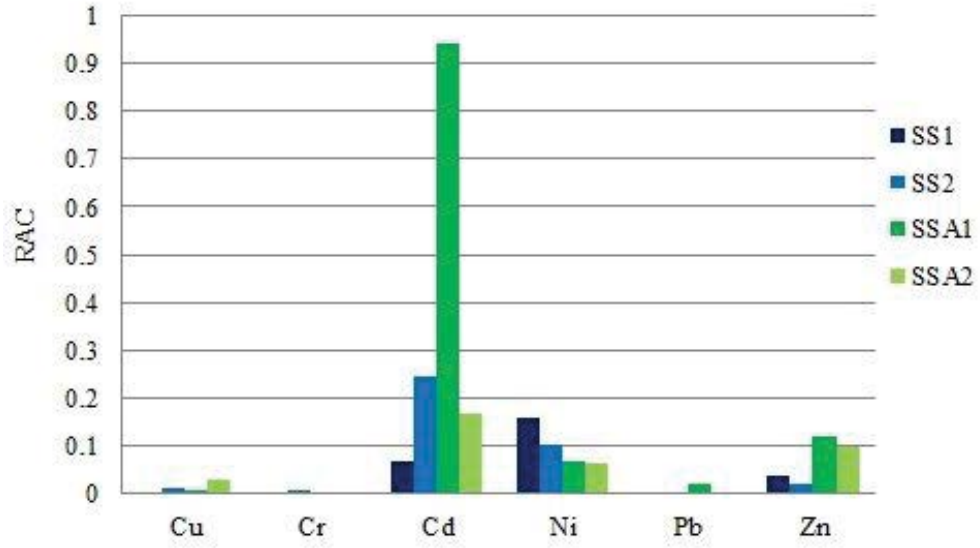

Fig. 6. Risk assessment code (RAC) of sewage sludge (SS1, SS2) and sewage sludge ash (SSA1, SSA2).

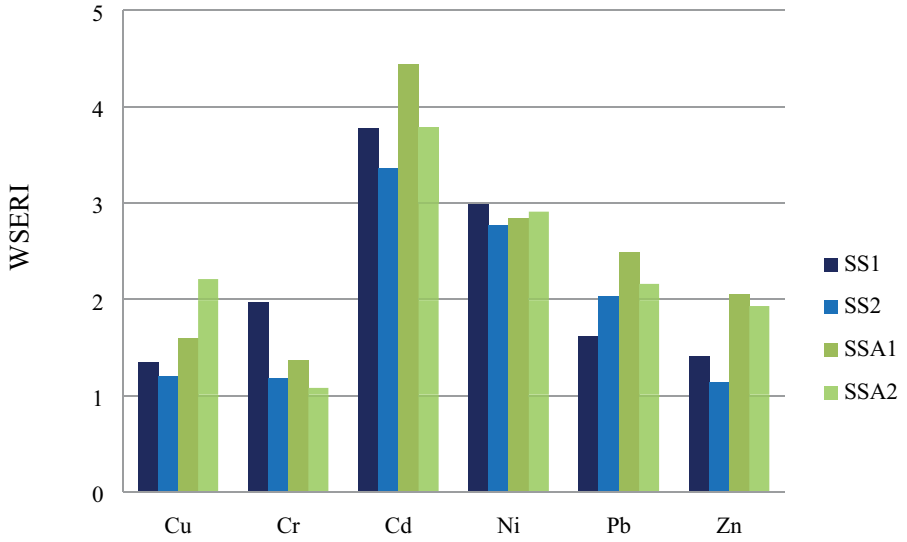

Fig. 7. Individual water and soil environment risk indexes for sewage sludge (SS1, SS2) and sewage sludge ash (SSA1, SSA2) with heavy metals.

instance when the values of the above-mentioned indexes are different.

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