The Ecological Risk Assessment and the Chemical Speciation of Heavy Metals in Ash after the Incineration of Municipal Sewage Sludge

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Received: 29 June 2020; Accepted: 9 August 2020; Published: 12 August 2020

Abstract: Popular incineration of sewage sludge results in the increase in heavy metals content in ash. The knowledge of the total content of heavy metals in sewage sludge 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 do not require the ecological risk assessment of the environmental burden with heavy metals for the choice of the method of the utilization of sewage sludge ash. The paper presents the research results on the mobility of heavy metals in sewage sludge ash after its incineration. The geo-accumulation index ($I_{GAI}$), the potential ecological risk index (PERI) and the risk assessment code (RAC) were used for the evaluation of the potential soil contamination with heavy metals. The authors also suggested a new formula, which took into consideration more factors influencing the risk of the contamination of a water-soil environment with heavy metals—the water and soil environment risk index (WSERI). The calculated indices for sewage sludge ash indicate the risk of soil contamination with heavy metals.

Keywords: heavy metals; speciation; sewage sludge ash; risk assessment

1. Introduction

One of the applied methods of municipal sewage sludge neutralization is a thermal treatment. The thermal treatment can be realized with the use of pyrolysis, gasification or incineration [1–5]. One of the popular solutions is the incineration and co-incineration that can be performed in a fluidized-bed furnace [6], a grate furnace [7,8] or a rotary kiln [9,10]. The incineration of sewage sludge, apart from the obvious advantages such as, among others, the application regardless of the sanitary characteristics of sludge and the possibility to recover phosphorous [11–13], causes an increase in the concentration of heavy metals in ash [14].

Apart from the initial concentration in sludge and the temperature of the incineration, the concentration of heavy metals in ash after the incineration of sewage is influenced by the volatility of heavy metals. The most volatile metals are mercury, cadmium and lead. Zinc is considered volatile, and copper a slightly volatile metal. Chrome and nickel are, however, considered non-volatile metals [15]. Approximately 78–98% of cadmium, chrome, copper, nickel, lead and zinc present in sewage sludge remain in ash. Furthermore, 98% of mercury is removed together with the fumes [16].

Sewage sludge ash can be utilized as a component of a raw material set for the production of building materials [17–19], soil stabilization [20] and for agricultural land [21]. However, the presence of sewage sludge ash in the environment is a potential source of contamination with heavy metals [22].
Potentially high concentrations of heavy metals in sewage sludge ash are the criterion determining the methods of its neutralization. However, the mobility and bioavailability of heavy metals in the environment depend not only on the total concentration but also on their form of occurrence. The most mobile are metals bound with carbonates (fraction FI). Metals bound to iron and manganese oxides are released more slowly into the environment (fraction FII). The temporarily immobile metals are the ones that form permanent bonds with the organic matter or occur in the form of sulphides (fraction FIII). Metals bound with aluminosilicates are considered immobile (fraction FIV) [23,24].

Heavy metals present in the environment, apart from the negative influence on all elements of the food chain, have a negative impact on the biological properties of soil and lead to the contamination of ground waters. The excess of the admissible limit of heavy metals causes a decrease in the soil fertility, changes its acidification and is the inhibitor of the enzyme activity of soil [25].

The prevailing norms do not require the ecological risk assessment of the environmental burden with heavy metals for the choice of the method of the utilization of sewage sludge ash. The ecological risk assessment of heavy metals in the environment is performed with two kinds of indicators: total content indices and speciation indices [26]. The most common are the ones from the first group, i.e., the geo-accumulation index (IGAI) and the potential ecological risk index (PERI) as well as from the second group, i.e., the risk assessment code (RAC) [25–27]. The usage of the IGAI and the PERI indices does not give a full picture of the risk because it does not take into consideration the form of the occurrence of heavy metals. However, taking into account only the mobile fraction of heavy metals (FI) for the determination of the RAC is also not a comprehensive description of the risk of the contamination of the water-soil environment. The answer to the lack of suitable tools for 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 ash, particularly in terms of their accumulation in the water-soil environment. The measures of assessment of the potential contamination of soil with heavy metals are the IGAI, the PERI, the RAC and the WSERI.

2. Materials and Methods

2.1. Materials

In this research, ash was taken from six installations of municipal sewage sludge incineration located in Poland (Table 1). Four installations are located in the northern part of Poland, one in the centre of the country and one in the South. The installations differ within the nominal capacity and the technology of sewage sludge incineration. Grate furnaces are used in the installations of lower capacity, whereas fluidized-bed furnaces are the domain of the installations of the highest capacities.

| Sample | Combustion Technology | Nominal Capacity of the Installation of Sewage Sludge Incineration, Mg d.m./Year |
|--------|------------------------|--------------------------------------------------------------------------------|
| S1     | grate furnaces         | 1500                                                                            |
| S2     | grate furnaces         | 3200                                                                            |
| S3     | grate furnaces         | 6000                                                                            |
| S4     | fluidized beds         | 7800                                                                            |
| S5     | fluidized beds         | 21,000                                                                          |
| S6     | fluidized beds         | 23,000                                                                          |

The phase composition of sewage sludge ash was determined with the Debye-Scherrer-Hull X-ray powder diffraction. An empyrean diffractometer was used for this purpose (PANalytical, Almeo, Niederlande). The test was conducted in the range of angles 5–60° 2θ with the use of a Cu lamp. The interpretation of the test results was performed in the HighScore Plus programme (PANalytical, Almeo, The Netherlands). The quality analysis was conducted on the basis of the database ICDD.
The data from the Crystallography Open Database (COD) was used for the quantity analysis, which was performed with the Rietveld method on the basis of the quality analysis.

2.2. Methods

The determination of the chemical form of the tested substance present in the environment, resulting from 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 a matrix in which it occurs [7,24]. In order to define the amount of forms of heavy metals occurring in sewage sludge ash, the sequential extraction was performed according to the European Community Bureau Reference (BCR) [7,28]. The content of heavy metals in extracts was determined on the ICP-OES Perkin Elmer Optima 8000 optical emission spectrometer with the inductively coupled plasma (Waltham, MA, USA). Every process of determination was repeated three times.

2.3. Contamination Assessment Methodology

2.3.1. Geo-Accumulation Index

The levels of contamination with heavy metals in sewage sludge ash can be characterised by the geo-accumulation index $I_{GAI}$ [29]. Originally, the $I_{GAI}$ was used for the ecological risk assessment of bottom sediments [30]. It is also used for the assessment of the contamination of soil and sewage sludge [31]. The $I_{GAI}$ is based on the individual levels of the accumulation of metals, however, without taking the toxicity into account [29]. The modified geo-accumulation index $I_{GAI}$ was used in this paper [32]:

$$I_{GAI} = \log_2 \frac{C_n}{1.5B_n}$$  \hspace{1cm} (1)

where:

$C_n$ is the measured individual concentration of a heavy metal in sewage sludge ash, $B_n$ is the geochemical background value of each heavy metal $n$ [33]. The constant value 1.5 is introduced for better analysis of the natural variability of the content of the chosen substance in the environment.

The $I_{GAI}$ values are divided into the following categories: uncontaminated ($I_{GAI} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{GAI} \leq 1$), moderately to heavily contaminated ($1 < I_{GAI} \leq 2$), moderately to heavily contaminated ($2 < I_{GAI} \leq 3$), heavily contaminated ($3 < I_{GAI} \leq 4$), heavily to extremely contaminated ($4 < I_{GAI} \leq 5$) and extremely contaminated ($5 < I_{GAI}$) [30]. Background values of heavy metals are presented in Table 2.

Table 2. Bn and $T_i^*$ of heavy metals from sewage sludge ash.

| $B_n$*, mg kg$^{-1}$ | Cu | Cr | Cd | Ni | Pb | Zn |
|----------------------|-----|----|----|----|----|----|
| $B_{S1}$             | 14.0| 0.12| 21.0| 17.8| 11.5| 37.3|
| $B_{S2}$             | 5.29| 3.61| 0.15| 1.97| 13.3| 14.4|
| $B_{S3}$             | 5.71| 13.1| 0.09| 7.30| 10.5| 27.4|
| $B_{S4}$             | 6.10| 7.37| 0.09| 6.06| 8.58| 26.9|
| $B_{S5}$             | 17.3| 20.1| 0.97| 15.1| 45.9| 158 |
| $B_{S6}$             | 3.21| 4.54| 0.12| 2.62| 12.6| 20.4|
| $T_i^*$              | 5   | 2  | 30 | 5  | 5  | 1  |

Note: * $B_n = C_i$-values determined on the basis of the report on the realization of the III stage of the procurement [33]. Measurement points were located adequately to the analysed wastewater treatment plants. ** $T_i$ on the basis of [34].
2.3.2. Potential Ecological Risk Index

The PERI suggested by Håkanson [34] is based on the toxicity, the sensitivity and the concentration of heavy metals. The PERI is characterized by a wide range of applications in different fields of study, such as environmental chemistry, ecology and toxicology. It can be used for the comprehensive environmental risk assessment caused by heavy metals. The PERI was used for the evaluation of the ecological risk of sewage sludge ash [29], and of the fly ash after the incineration of solid municipal wastes [35]. The PERI value was calculated with the following formulas [30,36,37]:

\[
C^i_f = \frac{C^i_D}{C^i_R}
\]

(2)

\[
E^i_i = T^i_i \times C^i_f
\]

(3)

\[
PERI = \sum_{i=1}^{n} E^i_i = \sum_{i=1}^{n} T^i_i \times C^i_f
\]

(4)

where:
- \(C^i_f\) is the contamination factor;
- \(C^i_D\) is the concentration of each heavy metal in sewage sludge ash;
- \(C^i_R\) is the background value of individual heavy metals and defined as \(B_n\);
- \(E^i_i\) is the potential ecological risk index of an individual heavy metal;
- \(T^i_i\) is the given heavy metal toxic response factor [34].

The \(T^i_i\) values are presented in Table 2. The PERI is the sum of potential ecological risks of each heavy metal.

For a single heavy metal element, \(E^i_i\) was used as follows: low potential ecological risk (\(E^i_i < 40\)), moderate potential ecological risk (\(40 \leq E^i_i < 80\)), considerable potential ecological risk (\(80 \leq E^i_i < 160\)), high potential ecological risk (\(160 \leq E^i_i < 320\)), and very high ecological risk at hand (\(320 \leq E^i_i\)).

The following ranges of values of the PERI were used: \(<150—low risk (LR)\); \(150 < PERI < 300—moderate risk (MR)\); \(300 < PERI < 600—considerable risk (CR)\); \(PERI > 600—very high risk (VHR)\) [25,26,29].

2.3.3. Risk Assessment Code (RAC)

The RAC was used for the evaluation of the contamination with heavy metals of soil [38] and of sewage sludge ash [29]. The RAC takes into account the percentage of heavy metals present in the form of exchangeable and carbonate fractions (F1). Heavy metals in 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), and very high risk—very dangerous to the environment (VHR > 50) [39,40].

The RAC was calculated as follows:

\[
RAC = \frac{HM}{F1} \times 100
\]

(5)

where:
- F1—the concentration of a heavy metal in acid-soluble/exchangeable fraction; fraction F1 (mg kg\(^{-1}\)),
- HM—the total concentration of a heavy metal (mg kg\(^{-1}\)).

2.3.4. 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 of heavy metals present in the assessed matrix. The lack the concentration of heavy metals present in the second fraction (reducible) and the third one (oxidizable), and the characteristics of the water-soil environment do not constitute a thorough description of the
ecological hazard. Taking into account the mobility of heavy metals and the metal toxic response factor ($T_i$) the author proposes the Water-Soil Environment Risk Index (WSERI) described with the formula:

$$\sum_{i=1}^{n} WSERI_i = \log_{10} \left[ T_i \times \left( \frac{F_1 + F_2}{C_{iw}} + \frac{F_3}{C_{si}} \right) \right]$$

(6)

where:

- $F_1$—the concentration of $i$-th metal in acid-soluble/exchangeable fraction; fraction $F_1$, mg·kg$^{-1}$;
- $F_2$—the concentration of $i$-th heavy metal bound with amorphous iron and manganese oxides; fraction $F_2$—reducible, mg·kg$^{-1}$; $F_3$—the concentration of the metal-organic and sulphide fractions of $i$-th metal; fraction $F_3$—oxidizable, mg·kg$^{-1}$; $C_{iw}$—the concentration of $i$-th heavy metal in the groundwater, mg·kg$^{-1}$; $C_{si}$—the concentration of $i$-th heavy metal in soil, mg·kg$^{-1}$.

The concentrations of heavy metals in 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;
- $WSERI > 19.9$—very high risk 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 (Table 3) [41,42]. The determination of such restrictive ranges of the $WSERI$ values was caused by the increase in concentrations of heavy metals from anthropogenic sources on agricultural terrains in Europe [43,44].

**Table 3.** Admissible concentrations of heavy metals in water intended for consumption [41].

|     | Cu  | Cr  | Cd  | Ni  | Pb  | Zn  |
|-----|-----|-----|-----|-----|-----|-----|
| Water intended for consumption | 2.00 | 0.05 | 0.003 | 0.02 | 0.05 | - * |

* not a defined limit

The method of the determination of the total content of heavy metals is not introduced. The usage of the total content of the heavy metal for the determination of the PERI, the GAI for the comparison with the RAC and the $WSERI$ calculated on the basis of the sum of fractions $F_1 + F_2 + F_3 + F_4$ are affected by an error. The values of the total content of the metal and the sum of the metal fractions are not 100% identical, which is proved by papers [45,46]. The differences between these values reach 30–50% [26,47]. Such differences are influenced by the precision of both methods, i.e., the BCR, the total content of heavy metals and the homogeneity of the tested matrix [24,48].

3. Results and Discussion

The characteristics of sewage sludge ash was presented in Table 4 and Figure 1. Regardless of the method of the incineration of sewage sludge, the dominant components of ashes are quartz, whitlockite, anhydrite and stanfieldite. A high content of silicon is the consequence of street cleaning, the erosion of pipelines, the drainage of rainwater rich in sand and the usage of aluminium sulfate for the removal of phosphorous from the treated sewage [48]. The obtained results of the characteristics of ashes are convergent with the research results presented in [11,13]. The pH value and the loss on ignition of the tested sewage sludge ash are consistent with the research results presented by Donatello et al. [22].

In S1 sewage sludge ash, heavy metals, except for copper, cadmium, nickel and zinc, occur in fraction IV—i.e., the immobile fraction (Table 5). In the mobile fraction FI, the greatest content was found for zinc, copper and nickel (Figure 2).

The analysis of the results of the BCR extraction of S3 sewage sludge ash leads to the conclusion that heavy metals occur mainly in fraction IV, i.e., are bound with aluminosilicates. In fraction FI, the greatest content was found for cadmium, which constitutes 83.2% of the total content of this chemical element in S3 ash.
Table 4. The characteristics and the phase composition of sewage sludge ash.

| Sample | S1       | S2       | S3       | S4       | S5       | S6       |
|--------|----------|----------|----------|----------|----------|----------|
| pH     | 8.90 ± 0.3 | 7.60 ± 0.1 | 7.30 ± 0.03 | 12.7 ± 0.05 | 10.6 ± 0.7 | 8.40 ± 0.3 |
| Loss on ignition, % w. | 2.56 ± 0.01 | 5.80 ± 0.3 | 3.28 ± 0.23 | 4.91 ± 0.25 | 0.85 ± 0.06 | 1.07 ± 0.03 |
| Phase composition of sewage sludge ash |          |          |          |          |          |          |
| Quartz, SiO$_2$, % w. | 27.7 | 19.8 | 14.8 | 10.7 | 17.2 | 38.5 |
| Whitlockite, Ca$_9$Mg$_5$(PO$_4$)$_6$(HPO$_4$)$_2$, % w. | 38.3 | 60.4 | 36.7 | 19.3 | 54.0 | 28.5 |
| Feldspar, % w. | 28.1 | 0.60 | 18.8 | 0.80 | 12.5 | 15.4 |
| Anhydrite, CaSO$_4$, % w. | - | - | - | 49.6 | 7.00 | 6.50 |
| Hematite, Fe$_2$O$_3$, % w. | 2.20 | - | - | - | 9.20 | 11.1 |
| Stanfieldite, Ca$_4$Mg$_5$(PO$_4$)$_6$, % w. | - | 19.2 | 29.7 | - | - | - |
| Calcite, CaCO$_3$, % w. | 1.60 | - | - | 10.7 | - | - |
| Tridymite, SiO$_2$, % w. | 2.20 | - | - | - | 2.80 | - |
| Apatite, % w. | - | - | - | 3.90 | - | - |
| Calcium–iron oxide, Ca$_2$Fe$_7$O$_{11}$, % w. | - | - | - | - | - | - |
| Phosphorous sulphate, P$_4$S$_3$, % w. | - | - | - | - | - | - |

Figure 1. Diffractograms of sewage sludge ash. Quartz—Q; Tridymite—T; Whitlockite—W; Stanfieldite—S; Hematite—H; Calcite—C; Anhydrite—A; Feldspar—F; Apatite—a; Calcium–iron oxide (Ca$_2$Fe$_7$O$_{11}$)—O; Phosphorous sulphate (P$_4$S$_3$)—P.

Table 5. Chemical speciation of heavy metals ** in sewage sludge ashes from grate furnaces, mg·kg$^{-1}$.

| Fraction * | Cu     | Cr     | Cd     | Ni     | Pb     | Zn     |
|------------|--------|--------|--------|--------|--------|--------|
| Sewage sludge ash—S1 |        |        |        |        |        |        |
| I          | 3.60 ± 2.96 | 0.01 ± 0.02 | 0.05 ± 0.07 | 1.85 ± 1.49 | 0.19 ± 0.17 | 60.1 ± 50.7 |
| II         | 3.10 ± 1.00 | 0.05 ± 0.09 | 0.01 ± 0.01 | 1.53 ± 1.76 | 0.21 ± 0.18 | 28.8 ± 3.28 |
| III        | 165 ± 152  | 1.14 ± 0.08 | 0.08 ± 0.14 | 4.95 ± 0.40 | 4.64 ± 0.03 | 282 ± 208 |
| IV         | 231 ± 175  | 37.7 ± 28.8 | 0.00 ± 0.00 | 12.5 ± 7.52 | 11.5 ± 1.99 | 317 ± 81.2 |
| Sum        | 403      | 38.9   | 0.14   | 20.9   | 16.5   | 688    |
| Sewage sludge ash—S2 |        |        |        |        |        |        |
| I          | 5.63 ± 2.50 | 0.12 ± 0.15 | 5.61 ± 6.48 | 2.96 ± 1.10 | 0.62 ± 0.40 | 121 ± 56.1 |
| II         | 4.61 ± 3.23 | 0.09 ± 0.16 | 0.26 ± 0.06 | 2.03 ± 1.16 | 0.63 ± 0.07 | 59.4 ± 7.76 |
| III        | 70.7 ± 10.9 | 1.13 ± 0.52 | 0.08 ± 0.15 | 8.25 ± 2.55 | 2.23 ± 0.73 | 162 ± 87.2 |
| IV         | 762 ± 200  | 67.9 ± 36.5 | 0.00 ± 0.00 | 29.0 ± 13.5 | 24.6 ± 6.81 | 682 ± 236 |
| Sum        | 843      | 69.3   | 5.95   | 42.3   | 28.1   | 1024   |
| Sewage sludge ash—S3 |        |        |        |        |        |        |
| I          | 23.0 ± 5.02 | 2.25 ± 3.90 | 0.68 ± 0.45 | 2.41 ± 0.72 | 0.64 ± 0.29 | 43.7 ± 9.75 |
| II         | 31.4 ± 44.2 | 0.39 ± 0.35 | 0.01 ± 0.02 | 1.48 ± 0.96 | 0.38 ± 0.32 | 45.2 ± 58.4 |
| III        | 135 ± 42.2  | 1.12 ± 0.31 | 0.12 ± 0.22 | 5.91 ± 0.54 | 4.21 ± 3.65 | 45.9 ± 10.2 |
| IV         | 413 ± 186  | 36.0 ± 2.73 | 0.00 ± 0.00 | 22.4 ± 3.99 | 9.07 ± 15.7 | 576 ± 85.4 |
| Sum        | 602      | 39.7   | 0.82   | 32.2   | 14.3   | 710    |

Note: * Fraction: I—exchangeable/carbonates, II—reducible, III—oxidizable, IV—residual; ** ± standard deviations.
Figure 2. Percentage distribution of heavy metals in fractions of sewage sludge ashes from grate furnaces.

In S4 sewage sludge ash in fraction FI, the greatest value was found for zinc. The contribution of fraction FI in the total content of zinc did not exceed 0.28% (Figure 3).

Figure 3. Percentage distribution of heavy metals in fractions of sewage sludge ashes from fluidized beds.

Similarly as for S4 sewage sludge ash, in S5 sewage sludge ash in fraction FI, the greatest value was found for zinc. The difference, however, is that the content of zinc in S5 sewage sludge ash was more than 42 times higher than in S4. In S5 sewage sludge ash, the contribution of fraction FI in the total content of zinc did not exceed 4.79% (Figure 3).

Similarly to the other tested ashes, heavy metals in S6 sewage sludge ash are mainly bound with aluminosilicates and occur in organic and sulphide bonds, i.e., the immobile fractions (FIII and FIV).

In all the tested ashes, the highest concentrations were for copper and zinc (Tables 5 and 6). The same tendency was shown in the test results of the mobility of heavy metals from sewage sludge ash conducted by Dąbrowska [23].

Regardless of the type of the installation of sewage sludge incineration, the lowest contributions in ash were for cadmium (Tables 5 and 6). Cadmium was the chemical element dominating by percentage in the FI mobile fraction (Figures 2 and 3). The presented results, similarly to the results of the previous tests [7], proved that the method of the incineration of sewage sludge did not influence the mobility of heavy metals from ash.
Table 6. Chemical speciation of heavy metals ** in sewage sludge ashes from fluidized beds, mg kg⁻¹.

| Fraction * | Cu   | Cr   | Cd   | Ni   | Pb   | Zn   |
|------------|------|------|------|------|------|------|
| Sewage sludge ash—S4 |      |      |      |      |      |      |
| I          | 0.05 ± 0.09 | 0.23 ± 0.13 | 0.73 ± 0.76 | 0.00 ± 0.00 | 0.32 ± 0.30 | 2.47 ± 2.69 |
| II         | 42.0 ± 5.04 | 0.00 ± 0.00 | 0.10 ± 0.18 | 1.35 ± 1.39 | 0.14 ± 0.13 | 54.2 ± 43.1 |
| III        | 154 ± 20.7  | 2.91 ± 1.23 | 0.28 ± 0.25 | 2.47 ± 0.33 | 5.61 ± 5.48 | 135 ± 18.7  |
| IV         | 233 ± 87.6  | 68.1 ± 3.95 | 0.00 ± 0.00 | 57.3 ± 11.7 | 16.4 ± 1.26 | 683 ± 49.4  |
| Sum        | 430       | 71.2  | 1.11 | 61.1 | 22.0 | 875 |

| Sewage sludge ash—S5 |      |      |      |      |      |      |
| I          | 27.9 ± 1.02 | 0.25 ± 0.04 | 0.76 ± 0.37 | 1.46 ± 0.05 | 0.49 ± 0.06 | 104.8 ± 5.84 |
| II         | 11.1 ± 0.46 | 0.23 ± 0.34 | 0.03 ± 0.06 | 1.44 ± 0.16 | 0.47 ± 0.08 | 55.5 ± 3.52 |
| III        | 84.0 ± 2.32 | 0.93 ± 0.17 | 0.26 ± 0.05 | 8.34 ± 0.40 | 4.58 ± 0.51 | 282 ± 21.7  |
| IV         | 710 ± 192   | 759 ± 200 | 0.00 ± 0.00 | 66.7 ± 15.0 | 60.1 ± 12.7 | 1745 ± 287  |
| Sum        | 833       | 761  | 1.06 | 78.0 | 65.6 | 2188 |

| Sewage sludge ash—S6 |      |      |      |      |      |      |
| I          | 12.0 ± 0.84 | 0.48 ± 0.83 | 0.88 ± 0.48 | 2.26 ± 1.61 | 0.12 ± 0.11 | 133 ± 57.7 |
| II         | 24.8 ± 4.00 | 0.42 ± 0.72 | 0.64 ± 1.10 | 2.35 ± 2.63 | 0.32 ± 0.29 | 134 ± 182 |
| III        | 72.1 ± 59.6 | 4.42 ± 7.10 | 0.99 ± 1.07 | 3.08 ± 0.33 | 10.9 ± 6.25 | 163 ± 56.8 |
| IV         | 256 ± 39.6  | 195 ± 25.1 | 0.00 ± 0.00 | 54.4 ± 9.70 | 87.1 ± 31.6 | 1560 ± 253 |
| Sum        | 364       | 200  | 2.51 | 62.1 | 98.5 | 1989 |

Note: * Fraction: I—exchangeable/carbonates, II—reducible, III—oxidizable, IV—residual; ** ± standard deviations.

Figure 4 presents the results of calculations of the geo-accumulation index of heavy metals in sewage sludge ashes. The I_GAI value of cadmium below zero for S2 ash indicates a favourable lack of the risk of contamination of the environment with the chemical element. The lowest I_GAI values for all sewage sludge ashes were of lead. The I_GAI values of lead, not exceeding two, indicate a moderate risk of contamination of this element, which is harmful for humans and animals [49]. The I_GAI values demonstrate that S1–S5 ashes constitute the highest risk of contamination of the environment with copper. Copper as a microelement is a necessary component of many enzymes and proteins. However, in the case of high concentrations, it is toxic, for example for plants sensitive to the presence of copper, its excess can cause the reduction of crops [49]. The I_GAI of zinc for S1–S6 ashes indicates a significantly higher risk of contamination than of nickel. The I_GAI of chrome varies from moderate risk (S3) to extremely high risk (S2). The order of the I_GAI values of heavy metals is not identical for all tested sewage sludge ashes. There is a tendency, for ashes obtained from the installations with the fluidized bed, that the lowest values of I_GAI are of lead and cadmium. However, the I_GAI values of other heavy metals do not have an identical order (Figure 4).
In comparison to the $I_{GAI}$ values presented in [50], the $I_{GAI}$ values indicate higher levels of risk. The reason of such a difference was the fact that Zhihua et al. [50] conducted the research on the sewage sludge ash with 10% and 30% additions of wood sawdust.

The results of the ecological risk assessment for heavy metals in sewage sludge ash are presented in Table 7. S2 ash is characterised by the highest values of $E_i$ for Cu and Cd, which indicate a very high potential risk of contamination of the environment. The lowest $E_i$ for Cu and Cd was noted for S1 ash. The highest value of $E_i$ of the tested samples was for Cd in S2 ash and equalled 1190. Simultaneously the lowest value of $E_i$ of the tested samples was for Cd in S1 ash. The dominant metals posing a potential ecological risk in the case of ashes from grate furnaces are Cu and Cd. In addition, for ashes from fluidized beds, the highest potential risk of contamination of the ecosystem is for Cu and Cd (Table 7).

Table 7. PERI of heavy metals in the sewage sludge ashes.

| Sample | Potential Ecological Risk Factor of Individual Heavy Metal $E_i$ | PERI |
|--------|---------------------------------------------------------------|------|
|        | Cu    | Cr    | Cd    | Ni    | Pb    | Zn    |      |
| S1     | 144   | 649   | 0.20  | 5.86  | 7.17  | 18.5  | 824  |
| S2     | 797   | 38.4  | 1190  | 107   | 10.6  | 71.1  | 2215 |
| S3     | 527   | 6.08  | 273   | 22.1  | 6.83  | 25.9  | 861  |
| S4     | 353   | 19.3  | 369   | 50.4  | 12.8  | 32.6  | 838  |
| S5     | 241   | 75.9  | 32.8  | 25.9  | 7.14  | 13.9  | 397  |
| S6     | 568   | 88.2  | 626   | 118   | 39.1  | 97.5  | 1538 |

The PERI was calculated in order to assess the total potential ecological risk caused by heavy metals from ash after the incineration of sludge. The PERIs of heavy metals in all sewage sludge ash were above 390, suggesting a very high potential ecological risk (Table 7).

Similarly to the publication [50], the potential ecological risk factor of an individual heavy metal had the highest risk of the emission to the environment for copper and cadmium.

The obtained values of the PERI are higher than the values presented in the paper [50] 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 [50].

Environmental risk assessment results in accordance with the RAC are shown in Figure 5. Taking into consideration the mobile fraction (FI) of heavy metals in the risk analysis proved that the majority of tested sewage sludge ashes constituted a low risk of contamination of the environment with copper, chrome, nickel, lead and zinc. Simultaneously, the RAC values indicate that all the tested ashes constituted a high or very high risk of contamination with cadmium (Figure 5). In addition, the ashes tested by Zhihua et al. [50] were characterized by a low risk of contamination with zinc, copper and cadmium.

Figure 5. Risk assessment code of sewage sludge ashes.
For all the tested matrices, the highest values of the individual water and soil environment risk index were for cadmium, and the lowest for copper and chrome (Figure 6).

![Figure 6](image-url). Individual water and soil environment risk indices for sewage sludge ashes with heavy metals.

All the tested sewage sludge ashes are characterized by the high WSERI, which indicates a high risk of the accumulation of heavy metals in the water-soil environment (Figure 7). The highest WSERI value for ashes obtained from the incineration of sewage sludge in the grate furnace (S1) does not constitute an argument against this technology because the lowest value of the WSERI for ash from the installation using the fluidized bed furnace is only 16% lower and also belongs to the range indicating the high risk of accumulation of heavy metals (Figure 7).

![Figure 7](image-url). Water and soil environment risk indices for sewage sludge ashes with heavy metals.

Further research on the risk assessment of the contamination of the environment with heavy metals from sewage sludge ash will concentrate on the optimization of the choice of the index. The value of the optimal index will be an unequivocal criterion allowing or prohibiting the introduction of the ash into the natural environment.

4. Conclusions

The conducted research allows for drawing the following conclusions:

The method of the incineration of sewage sludge did not influence the tested properties of ash. For the tested matrices, the high contribution of zinc in fraction FI did not cause high values of the potential ecological risk index for zinc. It was mainly the consequence of the relatively low coefficient of the toxicity of this chemical element.

The results of the comparison of the risk assessment of environmental contamination with the use of the PERI, the I\textsubscript{GAJ} and the RAC demonstrated that there were a few differences between the approaches in the classification.
The ecological risk assessment on the basis of the I_{GAI} and individual heavy metals (E_i) indicates that the highest hazard for the water and soil environment is copper. However, on the basis of the RAC values, the most hazardous metal is cadmium.

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 ash into the environment without the prior processing poses a high risk. The use of the WSERI in comparison to the popular indices such as the PERI, the I_{GAI} and the RAC covers a broader range of parameters, i.e., heavy metals in all mobile fractions (FI and FII) and the temporarily immobile fraction (FIII). The WSERI can be used in the situations when the potential risk of the accumulation of metals is unclear, for instance when the values of the above mentioned indices are different.

Author Contributions: J.L.: conceptualization, methodology, software, formal analysis, investigation, developing potential risk of the accumulation of metals is unclear, for instance when the values of the above mentioned indices are different.

Funding: This research and the APC were funded by the Polish Ministry of Science and Higher Education, The Programme of the Polish Ministry of Science and Higher Education—the Regional Initiative of Excellence on the basis of the contract no 029/RID/2018/19 of 28 December 2018; the amount of funding: 12 million PLN.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Hassen, B.; Trabelsi, A.; Zayoud, R.; Zaafouri, K. Sewage Sludge as Source of Energy: Experimental and Numerical Investigations of Thermochemical Conversion of Sewage Sludge via Pyrolysis. In Recent Advances in Environmental Science from the Euro-Mediterranean and Surrounding Regions; Kallel, A., Ksibi, M., Ben Dhia, H., Khellifi, N., Eds.; EMCEI 2017, Advances in Science, Technology & Innovation (IEREK Interdisciplinary Series for Sustainable Development); Springer: Cham, Switzerland, 2018.
2. Zhai, Y.; Peng, W.; Zeng, G.; Fu, Z.; Lan, Y.; Chen, H.; Fan, X. Pyrolysis characteristics and kinetics of sewage sludge for different sizes and heating rates. J. Therm. Anal. Calorim. 2012, 107, 1015–1022. [CrossRef]
3. Staf, M.; Buryan, P. Slow pyrolysis of pre-dried sewage sludge. Chem. Pap. 2016, 11, 1479–1492. [CrossRef]
4. Niu, S.; Chen, M.; Li, Y.; Lu, T. Combustion characteristics of municipal sewage sludge with different initial moisture contents. J. Therm. Anal. Calorim. 2017, 129, 1189–1199. [CrossRef]
5. Jin, Y.; Li, Y.; Liu, F. Combustion effects and emission characteristics of SO₂, CO, NO x and heavy metals during co-combustion of coal and dewatered sludge. Front. Environ. Sci. Eng. 2016, 1, 201–210. [CrossRef]
6. Hartman, M.; Pohořelý, M.; Trnka, O. Behaviour of inorganic constituents of municipal sewage sludge during fluidized-bed combustion. Chem. Pap. 2007, 61, 181–185. [CrossRef]
7. Latosinska, J.; Gawdzik, J. The impact of combustion technology of sewage sludge ash on mobility of heavy metals in sewage sludge ash. Ecol. Chem. Eng. S. 2014, 3, 465–475.
8. Lin, H.; Ma, X. Simulation of co-incineration of sewage sludge with municipal solid waste in a grate furnace incinerator. Waste Manag. 2012, 3, 561–567. [CrossRef]
9. Nadal, M.; Schuhmacher, M.; Domingo, J.L. Cost-benefit analysis of using sewage sludge as alternative fuel in a cement plant: A case study. Environ. Sci. Pollut. R 2009, 3, 322–328. [CrossRef]
10. Freda, C.; Cornacchia, G.; Romanelli, A.; Valerio, V.; Grieço, M. Sewage sludge gasification in a bench scale rotary kiln. Fuel 2018, 212, 88–94. [CrossRef]
11. Römer, W.; Steingrobe, B. Fertilizer Effect of Phosphorus Recycling Products. Sustainability 2018, 10, 1166.
12. Donatello, S.; Tong, D.; Cheeseman, C.R. Production of technical grade phosphoric acid from incinerator sewage sludge ash (ISSA). Waste Manag. 2010, 30, 1634–1642. [CrossRef] [PubMed]
13. Herzl, H.; Krüger, O.; Hermann, L.; Adam, C. Sewage sludge ash—a promising secondary phosphorus source for fertilizer production. Sci. Total Environ. 2016, 542, 1136–1143. [CrossRef] [PubMed]
14. Latosinska, J. The influence of temperature and time of sewage sludge incineration on the mobility of heavy metals. Environ. Prot. Eng. 2017, 4, 105–122. [CrossRef]
15. Vogel, C.; Adam, C. Heavy metal removal from sewage sludge ash by thermochemical treatment with gaseous hydrochloric acid. Environ. Sci. Technol. 2011, 45, 7445–7450. [CrossRef] [PubMed]
16. Werther, J.; Ogada, T. Sewage sludge combustion. Prog. Energy Combust. 1999, 25, 55–116. [CrossRef]
17. Vouk, D.; Nakic, D.; Stirmer, N. Influence of combustion temperature on the performance of sewage sludge as a supplementary cementitious material. *J. Mater. Cycles Waste* 2018, 3, 1458–1467. [CrossRef]
18. Lin, D.F.; Luo, H.L.; Cheng, J.F.; Zhuang, M.Z. Strengthening tiles manufactured with sewage sludge ash replacement by adding micro carbon powder. *Mater. Struct.* 2016, 9, 3559–3567. [CrossRef]
19. Yadav, S.; Agnihotri, S.; Gupta, S.; Tripathi, R.K. Incorporation of STP Sludge and Fly ash in Brick Manufacturing: An attempt to save the Environment. *Int. J. Adv. Res. Technol.* 2014, 3, 138–144. [CrossRef]
20. Al-Sharif, M.M.; Attom, M.F. A geoenvironmental application of burned wastewater sludge ash in soil stabilization. *Environ. Earth Sci.* 2014, 3, 2453–2463. [CrossRef]
21. Wierzbowska, J.; Sienkiewicz, S.; Sternik, P.; Busse, M.K. Using ash from incineration of municipal sewage sludge to fertilize Virginia fanpetals. *Ecol. Chem. Eng. A* 2015, 22, 497–507.
22. Donatello, S.; Tyrer, M.; Cheeseman, C.R. EU landfill waste acceptance criteria and EU Hazardous Waste Directive compliance testing of incinerated sewage sludge ash. *Waste Manag.* 2010, 30, 63–71. [CrossRef]
23. Dąbrowska, L. Speciation of heavy metals in non-volatile solids of sewage sludge. *Desal. Water Treat.* 2014, 52, 3761–3766. [CrossRef]
24. Gawdzik, J. Mobility of heavy metals in sewage sludge. In *Monograph*; Kielce University of Technology: Kielce, Poland, 2013.
25. Weissmannová, H.D.; Pavlovský, J. Indices of soil contamination by heavy metals—Methodology for calculation of pollution assessment (minireview). *Environ. Monit. Assess.* 2017, 189, 1–25.
26. Tytla, M. Assessment of heavy metal pollution and potential ecological risk in sewage sludge from municipal wastewater treatment plant located in the most industrialized region in Poland—Case study. *J. Environ. Res. Public Health* 2019, 16, 2430. [CrossRef] [PubMed]
27. Dąbrowska, L. Fractions of heavy metals in residue after incineration of sewage sludge. *Environ. Prot. Eng.* 2013, 39, 105–113. [CrossRef]
28. Ming, C.; Xiao-Ming, L.; Qi, Y.; Guang-Ming, Z.; Ying, Z.; De-Xiang, L.; Jing-Jin, L.; Jing-Mei, H.; Liang, G. Total concentrations and speciation of heavy metals in municipal sludge from Changsha, Zhuzhou and Xiangtan in middle-south region of China. *J. Hazard. Mater.* 2008, 160, 324–329.
29. Xiao, Z.; Yuan, X.; Leng, L.; Jiang, L.; Chen, X.; Zhibin, W.; Xin, P.; Jiachao, Z.; Zeng, G. Risk assessment of heavy metals from combustion of pelletized municipal sewage sludge. *Environ. Sci. Pollut. Res.* 2016, 23, 3934–3942. [CrossRef]
30. Müller, G. Index of geo-accumulation in sediments of the Rhine River. *Geol. J.* 1969, 3, 108–118.
31. Huang, H.; Yuan, X.; Zeng, G. Quantitative evaluation of heavy metals’ pollution hazards in liquefaced residues of sewage sludge. *Bioresour. Technol.* 2011, 102, 10346–10351. [CrossRef]
32. Loska, K.; Wiechula, D.; Korus, I. Metal contamination of farming soils affected by industry. *Environ. Int.* 2004, 30, 159–165. [CrossRef]
33. Monitoring of Agricultural Soil Chemistry in Poland in the Years of 2015–2017; Institute of Soil Science and Plant Cultivation, State Research Institute in Pulawy: Pulawy, Poland, 2017.
34. Håkanson, L. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res.* 1980, 14, 975–1001. [CrossRef]
35. Zhikun, Z.; Aimin, L.; Xuexue, W.; Lei, Z. Stabilization/solidification of municipal solid waste incineration fly ash via co-sintering with waste-derived vitrified amorphous slag. *Waste Manag.* 2016, 56, 238–245.
36. He, J.; Zhang, H.; Zhang, H.; Guo, X.; Song, M.; Zhang, J.; Li, X. Ecological risk and economic loss estimation of heavy metals pollution in the Beijiang River. *Ecol. Chem. Eng. Sci.* 2014, 21, 189–199. [CrossRef]
37. Maanan, M.; Saddik, M.; Maanan, M.; Claibi, M.; Assobhei, O.; Zourarah, B. Environmental and ecological risk assessment of heavy metals in sediments of Nador lagoon, Morocco. *Ecol. Indic.* 2015, 48, 616–626. [CrossRef]
38. Cheng, S.W.; Liu, G.J.; Zhou, C.C.; Sun, R.Y. Chemical speciation and risk assessment of cadmium in soils around a typical coal mining area of China. *Ecotox. Environ. Safe* 2018, 160, 67–74. [CrossRef] [PubMed]
39. Singh, J.; Lee, B. Reduction of environmental availability and ecological risk of heavy metals in automobile shredder residues. *Ecol. Eng.* 2015, 81, 76–81. [CrossRef]
40. Zhang, J.; Tian, Y.; Zhang, J.; Li, N.; Kong, L.; Yu, M. Distribution and risk assessment of heavy metals in sewage sludge after ozonation. *Environ. Sci. Pollut. Res.* 2017, 24, 5118–5125. [CrossRef]
41. The Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption. *J. Laws* 2017, 3, 2294.
42. The Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. OJ L 1998, 330, 32–54.
43. Panagos, P.; Van Liedekerke, M.; Yigini, Y.; Montanarella, L. Contaminated sites in Europe: Review of the current situation based on data collected through a European network. J. Environ. Public Health 2013, 2013, 158764. [CrossRef]
44. Panagos, P.; Ballabio, C.; Lugato, E.; Jones, A.; Borrelli, P.; Scarpa, S.; Orgiazzi, A.; Montanarella, L. Potential Sources of Anthropogenic Copper Inputs to European Agricultural Soils. Sustainability 2018, 10, 2380. [CrossRef]
45. Wang, L.; Skjevrak, G.; Hustad, J.E.; Grenli, M.G. Sintering characteristics of sewage sludge ashes at elevated temperatures. Fuel Process Technol. 2012, 96, 88–97. [CrossRef]
46. Xiao, Z.; Yuan, X.; Li, H.; Jiang, L.; Leng, L.; Chen, X.; Zeng, G.; Li, F.; Cao, L. Chemical speciation, mobility and phyto-accessibility of heavy metals in fly ash and slag from combustion of pelletized municipal sewage sludge. Sci. Total Environ. 2015, 536, 774–783. [CrossRef] [PubMed]
47. Fuentes, A.; Lloréns, M.; Sáez, J.; Aguilar, M.L.; Ortuño, J.F.; Meseguer, V.F. Comparative study of six different sludges by sequential speciation of heavy metal. Bioresour. Technol. 2008, 99, 517–525. [CrossRef] [PubMed]
48. Yuan, X.; Huang, H.; Zeng, G.; Li, H.; Wang, J.; Zhou, C.; Zhu, H.; Pei, X.; Liu, Z.; Liu, Z. Total concentration and chemical speciation of heavy metals in liquefaction residues of sewage sludge. Bioresour. Technol. 2011, 102, 4104–4110. [CrossRef]
49. Wilk, M.; Gworek, B. Heavy metals in sewage sludge. Environ. Prot. Nat. Res. 2009, 39, 40–59.
50. Zhihua, X.; Xihgzhong, Y.; Leng, L.; Longbo, J.; Xiaohong, C.; Wu, Z.; Xin, P.; Zhang, J.; Guangming, Z. Risk assessment of heavy metals from combustion of pelletized municipal sewage sludge. Environ. Sci. Pollut. Res. 2017, 23, 3934–3942.

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