Risk Analysis of Heavy Metal Accumulation from Sewage Sludge of Selected Wastewater Treatment Plants in Poland

Robert Kowalik *, Jolanta Latosińska * and Jarosław Gawdzik

Faculty of Environmental, Geomatic and Energy Engineering, Kielce University of Technology, 25-314 Kielce, Poland; ggawdzik@tu.kielce.pl
* Correspondence: rkowalik@tu.kielce.pl (R.K.); jlatosin@tu.kielce.pl (J.L.)

Abstract: Sewage sludge (SS) from wastewater treatment plants (WWTPs) has important soil-forming and fertilizing properties. However, it may not always be used for this purpose. One of the main reasons why SS cannot be used for natural purposes is its heavy metal (HM) content. SS from the wastewater treatment plant in Poland was subjected to an analysis of the potential anthropogenic hazard of HMs, especially in terms of their mobility and accumulation in soil. Calculations were made for the concentrations of HMs in SS from the analyzed wastewater treatment plants and in arable soil from measurement points in places of its potential use. The geoaccumulation index (GAI), potential environmental risk index (PERI), risk assessment code (RAC) and environmental risk determinant (ERD) were calculated. Then the values of the indicators were compared with the mobility of HMs, which was the highest risk of soil contamination. It was shown that a high level of potential risk and geoaccumulation indicators did not necessarily disqualify the use of SS, provided that HMs were in immovable fractions.

Keywords: heavy metals; sewage sludge; mobility; geoaccumulation index; potential ecological risk index; environmental risk determinant

1. Introduction

Sewage sludge is a by-product of municipal wastewater treatment processes. In Poland, as in other countries, an increase in the amount of sewage sludge generated has been observed [1–3]. The sewage sludge created can be utilized in many ways. Agricultural utilization of sewage sludge is particularly beneficial as it has high soil-forming and fertilizing properties [4]. The choice of sewage sludge management method is dictated especially by the quantity and the properties of the sewage sludge [5–7]. Moreover, it is subject to legal regulations, inter alia: The Act on Waste [8], the Regulation of the Minister of the Environment on municipal sewage sludge [9], the Regulation of the Minister of Economy on the criteria and procedures for allowing waste to be deposited at a given type of landfill [10]. Sewage sludge showing high fertilizer values may be used in agriculture as an organic fertilizer, provided that the content of micro-pollutants does not cause negative effects in the soil environment [11,12]. The limits of heavy metals in terms of the use of sewage sludge in Poland and worldwide are presented in [9,13–16].

In case of improper sludge management, environmental contamination and groundwater pollution may occur. Accumulation of heavy metals in the soil is particularly dangerous because it significantly affects the circulation of elements in the natural environment [17]. The natural source of heavy metals for humans and animals is consumed plants; therefore, heavy metals pose a significant threat to the quality of agricultural crops. Additionally, leaching pollutants with heavy metals from soils can significantly worsen the condition of the aquatic environment [18]. Plants that are the main recipients of mineral nutrients from soil and water, including heavy metals, are at the same time, the main source of them in the food of humans and animals. Even a minimal concentration of heavy metals in the body causes metabolic disorders, decreased efficiency of the organism and weakened...
immunological and enzymatic processes, which consequently lead to many diseases, and in some cases, may become the cause of death [19].

Mineral, organic and sorbed metals are not immediately absorbed by plants, but they can be slow to release metals into solution [20]. Essential elements such as Cu, Cr, Fe, Co, Mn, Mo, Ni, Se and Zn are needed by organisms in trace amounts and become toxic at higher levels. Non-essential elements including As, Sb, Cd, Pb, Hg, Sn and Ag are toxic and are not needed by organisms [21]. Most industrial effluents and wastes contain heavy metals in sufficient quantities to cause toxicity to crop plants [22]. The bioavailability of Cu, Co and Zn is moderate, while Ni, Cr and Mn show low bioavailability, indicating that these elements may pose a limited threat to crop quality. Cadmium is the main controlling contaminant, posing a moderate potential ecological risk [23].

Continued progress in wastewater treatment, by reducing the amount of pollutants released into the receiving water body and thereby improving water quality, will transfer more potentially harmful compounds to sewage sludge, making it unsafe for agricultural use [24].

Sewage sludge can also be used to remediate disturbed soil areas. Due to increased environmental awareness and stricter environmental regulations, measures have been taken worldwide for the reclamation of degraded soils. Among the methods adopted are isolation and encapsulation, mechanical separation, pyrometallurgical separation, biochemical processes, phytoremediation, soil flushing, soil washing, electrokinetics and vitrification [25,26]. The main disadvantage of most of these remediation methods is that they lack the soil fertility restoration aspects that sewage sludge application can provide.

Another beneficial way of utilizing sewage sludge is to valorize it into useful materials such as activated carbon or biochar for the remediation of pollutants. Sludge when pyrolyzed produces a carbonaceous residue called biochar [27]. The biochar, owing to its aromatic nature, high surface area, cation exchange capacity (CEC), micropore volume and the presence of multi-functional polar groups serves as a good sorbent for pollutant adsorption as well as carbon dioxide sequestration [27,28]. One of the most common methods used to remove heavy metals from water is chemical precipitation using hydroxides or sulfides. Chemical precipitation is a method of removing heavy metals from water in which the contaminants (in dissolved or suspended form) are separated from the solution as a precipitate, which can then be separated from the liquid portion [29]. The precipitate arises by the formation of a complex between the precipitating agent and the heavy metal ions, which reduces the bioavailability of the metals [30]. Chemical precipitation is an efficient and widely used process in industry. It is characterized by simplicity and is inexpensive to operate. It can be used to remove pollutants from municipal and industrial wastewater. Calcium carbonate, calcium hydroxide (slaked lime), calcium oxide (quicklime), sodium carbonate (soda ash), sodium hydroxide and ammonium hydroxide can be used to precipitate heavy metals from solution [31].

Metal sulfide precipitation is also an effective method for removing heavy metal ions. One of the main advantages of using sulfides is the lower solubility of metal compounds compared to hydroxide precipitates [24,32,33]. Alternative methods for the precipitation of heavy metals from aqueous solutions include precipitation using chelating ligands [34]. Matlock et al. in their study determined the efficiency of using three widely used commercial reagents for heavy metal binding: sodium potassium thiocarbonate (STC), 2,4,6-trimercaptotriazine, nonahydrate trisodium salt (TMT) and sodium dimethylthiocarbamate (SDTC) [34]. In order to develop more efficient, cheaper and stable compounds for heavy metal precipitation, a number of new ligands have been synthesized for irreversible heavy metal binding. One such ligand is 2,6-pyridinediamidoethanethiol (PyDET) [34]. Studies on the use of this compound to remove heavy metals from solution show that it effectively binds metals so that the final concentration is much lower than required. The precipitated product is insoluble in organic solvents and stable over a wide pH range of 0 to 14. Using PyDET, the mercury concentration decreased from 50 to 0.09 mg·L\(^{-1}\) and the lead concentration decreased from 50 to 0.05 mg·L\(^{-1}\) [35].
The aim of this study was to analyze sewage sludge from five wastewater treatment plants (WWTPs) located in Poland in terms of the heavy metal content and mobility and a risk analysis of their accumulation in the environment. The obtained results were used to calculate the geoaccumulation index (GAI), potential environmental risk index (PERI), risk assessment code (RAC) and environmental risk determinant (ERD). Then all the indicators were compared with the regulation of the use of sewage sludge in Poland and Europe.

2. Materials and Methods

2.1. Characteristics of Wastewater Treatment Plants and Sites of Agricultural Use of Sewage Sludge

Samples of sewage sludge were collected from five different WWTPs located in Poland (Figure 1). The characteristics of the WWTPs are presented in Table 1. All WWTPs were of the mechanical-biological type. The WWTPs varied in terms of the number of residents they serve, ranging from small WWTPs (1400 for WWTP3) to large WWTPs (172,569 for WWTP1). The measurement sites prepared by the Monitoring of Orne Soil Chemistry in Poland [36], located in close proximity to the places of sewage sludge formation, were used as the comparison sites of the heavy metal contents in the soil (Figure 1). The characteristics of sites of potential agricultural utilization of sewage sludge are presented in Tables 1 and 2. The pH of the soils ranged from 4.6 to 6.2. The humus content ranged from 0.95 to 2.13, while the C/N ratio oscillated between 5.5 and 9.0. The heavy metal content of the soils was low, as shown in Table 2.

### Table 1. Characteristics of wastewater treatment plants (WWTPs) and potential sites of agricultural use of sewage sludge [37,38].

| Wastewater Treatment Plant | WWTP1 | WWTP2 | WWTP3 | WWTP4 | WWTP5 |
|---------------------------|-------|-------|-------|-------|-------|
| Location of WWTP          | Siktówka-Nowiny | Cedzyna | Pacanów | Sandomierz | Jędrzejów |
| Type of WWTP              | Mech.-biol. | Mech.-biol. | Mech.-biol. | Mech.-biol. | Mech.-biol. PUB |
| Equivalent Number of Residents | 172,569 | 9466 | 1400 | 29,550 | 48,272 |
| SS treatment              | Fermentation | Oxygen stab. | Oxygen stab. | Oxygen stab. | Liming |
| Agricultural Use of Sewage Sludge | P1 | P2 | P3 | P4 | P5 |
| Location of potential use of SS: | Wola Kopcowa | Rzędów | Winiarki | Dyminy | Olszówka Nowa |
| -district                 | kielecki | buski | sandomierski | kielecki | jedrzejowski |
| -commune                  | Masłów | Tuczępy | Dwikozy | Morawica | Wodzisław |
| Distance of the WWTP from the point use of SS (km) | 21.5 | 9.1 | 21.3 | 12.0 | 24.2 |
| Soil type                 | leached brown soils | deer soils | brown soils appropriate | deer soils | deer soils |
| Bonitation class          | IVa medium quality arable land | IIb average good arable land | IIb average good arable land | IIb average good arable land | IIb average good arable land |
| Complex                   | 5 (rye good) | 4 (rye very good) | 3 (wheat defective) | 4 (rye very good wheat-rye) | 4 (rye very good) |
| Soil species              | light clay sand | light clay sand | clay dust | clay dust | sandy clay dusty |

Mech.-biol.—mechanical-biological; Oxygen stab.—Oxygen stabilization; EvU-Pearl®—carrier material is a high-performance filling material for wastewater treatment; PUB—biological treatment plant with increased removal of nitrogen (N) and phosphorus (P) compounds.
Figure 1. Location of wastewater treatment plants (own research) and potential sites of agricultural use of sewage sludge.

Table 2. Characteristics of analyzed sites of potential sewage sludge utilization [38–40].

| Parameter                  | Sites of Sewage Sludge Agricultural Use | IDL * |
|----------------------------|----------------------------------------|-------|
|                            | P1          | P2          | P3          | P4          | P5          |       |
| pH (H₂O)                   | 4.5         | 5.2         | 6.3         | 5.9         | 6.2         | 0.01  |
| Humus, %                   | 1.08        | 0.95        | 1.55        | 2.13        | 1.38        | 0.1   |
| Organic carbon, %          | 0.63        | 0.55        | 0.90        | 1.24        | 0.80        | 0.05  |
| Total nitrogen, %          | 0.08        | 0.10        | 0.10        | 0.15        | 0.10        | 0.01  |
| C/N ratio                  | 7.9         | 5.5         | 9.0         | 8.2         | 8.0         | 0.004 |
| Cu, mg kg⁻¹                | 3.2         | 5.3         | 8.5         | 4.6         | 6.2         | 0.003 |
| Cr, mg kg⁻¹                | 4.5         | 3.8         | 14.3        | 7.4         | 9.5         | 0.003 |
| Cd, mg kg⁻¹                | 0.12        | 0.11        | 0.12        | 0.37        | 0.31        | 0.005 |
| Ni, mg kg⁻¹                | 2.6         | 3.0         | 13.7        | 4.6         | 8.0         | 0.008 |
| Pb, mg kg⁻¹                | 12.1        | 10.3        | 9.5         | 22.4        | 15.0        | 0.006 |
| Zn, mg kg⁻¹                | 20.4        | 18.0        | 29.6        | 39.6        | 38.2        | 0.005 |

IDL * Instrumental detection limit.

2.1.1. Determination of pH

For pH testing, 10 g of air-dried sample was placed in a 100 mL breaker. We added exactly 40 mL of distilled water, mixed and set aside for 30 min. The pH electrodes were then introduced into the partially settled suspension and the results were taken.

2.1.2. Sewage Sludge Analysis

The dry matter and organic matter contents were analyzed according to the guidelines given in PN-EN 12880:2004 and PN-EN 12879:2004. The pH and redox potential (Eh) of the sewage sludge were measured using a multifunctional meter CPR-411 (Elmetron, Zabrze, Poland). The total concentrations and chemical forms of the selected heavy metals (Pb, Cd, Cr, Cu, Ni and Zn) were determined in the sludge samples collected fresh from the treatment plant after centrifugation processes.

2.2. Mobility of Heavy Metals of Sewage Sludge

Heavy metals can belong to four different mobility fractions, depending on their migratory capacity [41]. These are, respectively, the FI—carbonate-bound fraction, FII—amorphous iron and manganese oxides-bound fraction, FIII—organic and sulfide matter-bound fraction and FIV—silicate-bound metal density fraction. Sewage sludge samples collected from all the WWTPs before the hygienization process were used for the mobility
studies carried out according to the Community Bureau of Reference (BCR) sequential extraction method [42]. The BCR sequencing extraction methodologies are shown in Table 3.

Table 3. Method of metal speciation heavy metals in sewage sludge [43,44].

| Fraction | Form of Metal                  | Parameters of Fractionation                              | Time of Extraction, h |
|----------|--------------------------------|----------------------------------------------------------|-----------------------|
| FI       | Carbonate bound                | 0.11 M CH₃COOH, pH = 7.0, T = 20 °C                       | 16                    |
| FII      | Fe/Mn oxides bound             | 0.1 M NH₂OH·HCl pH = 2.0                                 | 16                    |
| FIII     | Organic                        | 30% H₂O₂ + 8.8 M H₂O₂ pH = 2.0, T = 85 °C                | 16                    |
| FIV      | Residual                       | 10 M HNO₃ + 10 M HCl, T = 100 °C                         | 3                     |

The content of heavy metals in the extracts was determined on an ICP-OES Perkin Elmer Optima 8000 optical emission spectrometer with an inductively coupled plasma (PerkinElmer, Waltham, MA, USA). Each process of determination was repeated four times for each sample, statistical analysis was carried out and Grubbs tests were performed to eliminate coarse errors based on the repeatability of the test.

2.3. Risk Indicators for Accumulation of Heavy Metals

2.3.1. Geoaccumulation Index of Heavy Metal in Soil (GAI)

In order to assess the degree of accumulation of heavy metals of anthropogenic origin in the soil, the GAI was used, which is described in the following equation [45,46]:

\[
GAI = \log_{2} \frac{C_n}{B_n} \cdot \frac{1}{1,5}
\]  

(1)

where:

- \(C_n\) — content of a given element from the group of heavy metals contained in sewage sludge, mg·kg⁻¹ d.m.;
- \(B_n\) — content of a given element from the group of heavy metals present in the soil, mg·kg⁻¹ d.m.

Table 4 presents the classification of the heavy metals according to the geoaccumulation index and the risk assessment code.

Table 4. Classification of the geoaccumulation index (GAI) and the risk assessment code (RAC) [46–49].

| Level of Risk | GAI     | Level of Risk | RAC       |
|---------------|---------|---------------|-----------|
| <0            | No pollution | <1            | No risk   |
| 0–1           | No pollution to moderate pollution | 1–10         | Low risk  |
| 1–2           | Moderate pollution | 11–30        | Medium risk|
| 2–3           | Moderate pollution to high pollution | 31–50      | High risk |
| 3–4           | High pollution    | >50           | Very high risk |

2.3.2. Risk Assessment Code (RAC)

The risk assessment code (RAC) was also used to assess the environmental risks posed by heavy metals. The RAC was used to assess soil contamination by heavy metals from sewage sludge and sewage sludge ashes [50,51]. The RAC takes into account the percentage of heavy metals present in the mobile fraction \(F_1\). The risk level can be classified into five categories as shown in Table 4. It is determined by the following formula [50]:

\[
RAC = \frac{F_1}{HM} \cdot 100\%
\]  

(2)
where: 
$F_1$—acid heavy metal concentration soluble/free fraction, mg·kg$^{-1}$; $HM$—total heavy metal concentration, mg·kg$^{-1}$.

2.3.3. Potential Environmental Risk Index (PERI)

The potential environmental risk index (PERI) is a measure of the environmental risk of soil with heavy metals and is described in the following formulas [45,47]:

$$C'_f = \frac{C'_D}{C'_R}$$

(3)

where: $C'_f$—pollution factor; $C'_D$—concentration of the $i$-th element from the group of heavy metals present in the sewage sludge, mg·kg$^{-1}$ d.m.; $C'_R$—concentration of the $i$-th element from the group of heavy metals in the soil, mg·kg$^{-1}$.

$$E'_i = T'_i \cdot C'_f$$

(4)

where: $E'_i$—indicator of the potential ecological risk of the $i$-th element from the group of heavy metals; $T'_i$—toxicity factor of the $i$-th element from the group of heavy metals.

Heavy metals differ in their degrees of toxicity, which takes into account the toxicity factor ($T'_i$): lead—5, cadmium—30, chromium—2, copper—5, nickel—5, zinc—1 [46].

The sum of the indicators of the potential ecological risk of heavy metals from sewage sludge in the ground is defined by the equation [22]:

$$\text{PERI} = \sum_{i=1}^{n} E'_i$$

(5)

Table 5 presents the classification of the heavy metals according to the potential environmental risk index.

| PERI Indicator Classification | PERI | Potential Environmental Risk |
|------------------------------|------|-----------------------------|
| $E'_i$                       |      |                             |
| <40                          | <150 | Low                         |
| 40–80                        | 150–300 | Medium                     |
| 80–320                       | 300–600 | High                       |
| >320                         | >600 | Very high                   |

2.3.4. Environmental Risk Determinant (ERD)

Considering the mobility of heavy metals, it can be noted that only fraction IV does not migrate to the soil—water environment under any conditions. The mobile fractions (F1,FII) are considered to be the most mobile, while FIII can be mobile under certain conditions, i.e., when the organic matter in the soil is fully processed by microorganisms and when an ozone storm occurs. Metals bound to iron and manganese oxides are released into the environment much more slowly. Under certain conditions of pH and oxidation-reduction potential, metals bound to FII can exhibit significant bioavailability [52]. An environmental risk assessment was performed based on the first three fractions, taking into account the level of individual predisposition of each fraction to release heavy metals into the soil environment. The ERD determines the elemental content of the heavy metal group according to its content in the four fractions. Each fraction is assigned an appropriate weight depending on a scale of 0–1. The authors proposed the use of the ERD index because none of the indicators of the mobility issue take into account the weight of each
fraction [45]. As the FI, FII and FIII fractions are mobile, but the FI fraction is much more mobile than FII and FIII, which takes into account the formula for the ERD index, the adopted weight ranges were proposed based on a scale analysis of the other indicators. Its determinant is described by the formula [53]:

$$ERD = Fp_1 + Fp_2 + Fp_3$$  (6)

where: $Fp_1 = F_1$; $F_1$—metal content in fraction FI on a scale of 0–1; $Fp_2 = F_2^2$; $F_2$—metal content in fraction FII on a scale of 0–1; $Fp_3 = F_3^3$; $F_3$—metal content in fraction FIII on a scale of 0–1.

The classification of the ERD resulted in the following: $0 < ERD \leq 0.35$—low risk; $0.35 < ERD \leq 0.6$—medium risk; $0.6 < ERD \leq 0.8$—high risk; $0.8 < ERD$—very high risk.

3. Results and Discussion

Table 6 shows the results of the speciation analysis of heavy metals in sewage sludge. Analyzing the level of heavy metal geoaccumulation in soil, it can be concluded that the dominant heavy metals causing high contamination are cadmium and zinc (Figure 2), while statistically the lowest risk of accumulation in soil is posed by nickel. However, in most cases, the results are not satisfactory and high risk of heavy metal geoaccumulation prevails, despite the fact that sewage sludge from wastewater treatment plants meets the requirements of permissible content of heavy metals for agricultural purposes according to the Regulation of the Minister of Environment of 6 February 2015 [9] and EU Directive 86/278/EEC [13]. The highest content of heavy metals was observed in the most stable fraction FI, and the conditionally-mobile fraction FIII. The metal content in the mobile fractions was negligible, with the exception of sediments from WWTP4. According to the literature data, the concentrations of particular heavy metals in sewage sludge can be ordered as follows: Zn > Cu > Cr > Ni > Pb > Cd [54]. The study showed that the trend of metal concentrations was as follows: Zn > Cr > Cu > Pb > Ni > Cd for WWTP1, Zn > Pb > Cr > Ni > Cu > Cd for WWTP2, Zn > Cu > Ni > Cr > Pb > Cd for WWTP3, Zn > Pb > Cu > Cr > Ni > Cd for WWTP4 and Zn > Cu > Pb > Cr > Ni > Cd for WWTP5. As can be seen, the results varied slightly between each other as well as compared to literature data. However, in each case, Zn showed the highest concentrations, while Cd showed the lowest.

Table 6. Chemical speciation of heavy metal * in sewage sludge, mg kg$^{-1}$ [31].

| Fraction | Cu  | Cr  | Cd  | Ni  | Pb  | Zn  |
|----------|-----|-----|-----|-----|-----|-----|
| **Sewage sludge—S1** |     |     |     |     |     |     |
| Fraction I | 0.8 ± 0.1 | 5.3 ± 0.6 | 0.3 ± 0.1 | 1.3 ± 0.2 | 3.5 ± 0.1 | 144.1 ± 15.9 |
| Fraction II | 0.0 ± 0.1 | 2.8 ± 0.4 | 0.5 ± 0.1 | 0.0 ± 0.1 | 4.0 ± 0.4 | 98.3 ± 10.3 |
| Fraction III | 60.9 ± 1.5 | 93.8 ± 1.7 | 2.5 ± 0.1 | 1.3 ± 0.3 | 3.4 ± 0.2 | 832.6 ± 24.6 |
| Fraction IV | 21.7 ± 0.6 | 136.5 ± 9.5 | 2.3 ± 0.2 | 49.2 ± 5.1 | 56.8 ± 3.7 | 240.5 ± 24.4 |
| ΣFI . . . IV | 83.5 ± 1.6 | 238.5 ± 9.7 | 5.6 ± 0.3 | 51.8 ± 5.1 | 67.7 ± 3.7 | 1315.0 ± 39.5 |
| **Sewage sludge—S2** |     |     |     |     |     |     |
| Fraction I | 0.2 ± 0.1 | 7.7 ± 0.3 | 1.2 ± 0.1 | 1.9 ± 0.1 | 7.0 ± 0.7 | 244.0 ± 0.8 |
| Fraction II | 0.2 ± 0.1 | 4.2 ± 0.2 | 1.5 ± 0.2 | 3.0 ± 0.3 | 11.0 ± 0.9 | 335.2 ± 0.9 |
| Fraction III | 10.4 ± 0.4 | 20.0 ± 0.9 | 3.9 ± 0.2 | 8.0 ± 0.6 | 16.0 ± 0.9 | 169.0 ± 0.8 |
| Fraction IV | 5.9 ± 0.3 | 54.0 ± 3.3 | 5.0 ± 0.4 | 9.0 ± 0.5 | 335.1 ± 9.9 | 726.1 ± 7.9 |
| ΣFI . . . IV | 16.7 ± 0.5 | 85.9 ± 3.4 | 11.6 ± 0.5 | 21.9 ± 0.8 | 369.1 ± 10.0 | 1474 ± 8.0 |
Table 6. Cont.

| Fraction | Cu   | Cr   | Cd   | Ni   | Pb   | Zn   |
|----------|------|------|------|------|------|------|
|          | (mg/kg s.m.) |   |   |   |   |   |
| Sewage sludge—S3 |   |   |   |   |   |   |
| Fraction I | 1.5 ± 0.1 | 0.0 ± 0.1 | 0.0 ± 0.1 | 2.6 ± 0.1 | 3.7 ± 0.4 | 328.9 ± 0.9 |
| Fraction II | 25.6 ± 0.2 | 24.1 ± 0.3 | 4.2 ± 0.1 | 19.6 ± 0.3 | 14.0 ± 2 | 743.2 ± 2.3 |
| Fraction III | 551.4 ± 0.9 | 45.1 ± 0.4 | 5.1 ± 0.1 | 57.0 ± 0.6 | 6.0 ± 0.7 | 152.3 ± 0.9 |
| Fraction IV | 4.7 ± 0.1 | 4.7 ± 0.1 | 0.8 ± 0.1 | 4.3 ± 0.2 | 26.7 ± 3 | 3.1 ± 0.1 |
| ΣFI...IV | 583.3 ± 0.9 | 74.0 ± 0.5 | 10.1 ± 0.2 | 83.5 ± 0.7 | 50.3 ± 3.7 | 1228 ± 2.6 |

| Sewage sludge—S4 |   |   |   |   |   |   |
| Fraction I | 47.8 ± 0.5 | 9.7 ± 0.3 | 4.6 ± 0.5 | 16.1 ± 0.3 | 103.4 ± 8.0 | 699.0 ± 7.0 |
| Fraction II | 86.9 ± 0.8 | 54.3 ± 0.9 | 2.5 ± 0.2 | 22.4 ± 0.5 | 177.3 ± 8.5 | 280.0 ± 3.0 |
| Fraction III | 83.3 ± 0.8 | 38.5 ± 0.7 | 1.3 ± 0.1 | 11.1 ± 0.3 | 73.1 ± 0.7 | 91.0 ± 0.8 |
| Fraction IV | 6.2 ± 0.1 | 23.7 ± 0.5 | 1.5 ± 0.1 | 9.8 ± 0.2 | 45.5 ± 0.4 | 31.0 ± 0.4 |
| ΣFI...IV | 224.3 ± 1.2 | 126.2 ± 1.3 | 9.9 ± 0.6 | 59.3 ± 0.7 | 399.4 ± 11.7 | 1101 ± 7.7 |

| Sewage sludge—S5 |   |   |   |   |   |   |
| Fraction I | 16.3 ± 0.2 | 1.4 ± 0.2 | 1.1 ± 0.2 | 1.9 ± 0.3 | 5.0 ± 0.4 | 4.0 ± 0.3 |
| Fraction II | 1.4 ± 0.2 | 0.2 ± 0.1 | 1.0 ± 0.1 | 1.3 ± 0.2 | 3.6 ± 0.5 | 3.9 ± 0.3 |
| Fraction III | 15.1 ± 0.3 | 0.1 ± 0.1 | 0.1 ± 0.1 | 1.8 ± 0.3 | 0.4 ± 0.2 | 20.5 ± 1.7 |
| Fraction IV | 73.5 ± 0.7 | 82.8 ± 0.9 | 3.5 ± 0.3 | 4.8 ± 0.3 | 90.5 ± 9.2 | 1208 ± 13 |
| ΣFI...IV | 106.4 ± 0.8 | 84.6 ± 0.9 | 5.8 ± 0.4 | 9.7 ± 0.6 | 99.4 ± 9.2 | 1237 ± 13.1 |

*Heavy metal content with standard deviation calculated for 4 samples using Grubbs’ statistical tests.

Figure 2. The geoaccumulation index (GAI) of HMs in SS.

The GAI index compares the content of metals in sludge to their content in soil. The value of this indicator is strongly dependent on the quality and condition of the soil, at the site of potential use. Figure 2 shows the GAI values for all analyzed samples.

In most cases, the level of RAC does not indicate a high environmental risk. This is due to the low content of heavy metals in the most mobile fraction (F1). The highest percentage share was recorded for zinc in sewage sludge from WWT4, measuring as much as 63.49% (Figure 3). The concepts of expressing mobility through the sum of fractions F1 and F2, as suggested by many authors [50,55], seem to be only partially correct. It should be noted that the F3 fraction also has potential mobility that will be higher than zero in an
oxidizing environment. Likewise, it is incorrect to consider only the F1 fraction as mobile. A better solution to this problem seems to be to define the opposite concept, which can be understood as the stability of heavy metals in sewage sludge. This indicator would be closely related to the residual F4 fraction.

Analyzing the results of the potential ecological hazard index, it can be concluded that the main element from the group of heavy metals causing very high PERI index value is cadmium (Figure 4), while other metals mostly show a low level of potential ecological hazard.

By analyzing the results of the ERD index, it can be concluded that most of the metals show a low level of risk (Figure 5). Only zinc for WWTPs 3 and 4 showed a high level of risk of environmental contamination. The RAC index indicated similar results; however, according to the RAC, the sludge taken from WWTP3 was significantly less toxic to the environment than the sludge from WWTP4. Yet, according to ERD, they are at an equally high level of toxicity to the ground environment. This difference is due to the fact that the RAC index does not take into account the second and third mobility fractions to any extent.
Figure 5. The environmental risk determinant (ERD) indicator of HMs in SS.

For the results of heavy metal toxicity according to the four analyzed indicators, non-compliance tables were created for each wastewater treatment plant. The tables include those heavy metals that did not meet the criterion qualifying them as not affecting the environment and causing pollution. This is shown in Table 7. As can be seen, the GAI and PERI indices turned out to be the strictest, resulting from the fact that these two indices took into consideration the heavy metal content in soils of potential use and did not take into account the mobility of heavy metals. The least critical was the RAC index, taking into account only the content of metals in fraction I, the most mobile fraction. The ERD index, taking into account the metal content in fractions FI, FII and FIII, showed additionally toxicity of copper and zinc for WWTP3 in comparison with the RAC index, which considered them nontoxic.

Table 7. Schedule of failure to meet heavy metal toxicity criterion from analyzed sites for four pollutant indicators.

| WWTP      | GAI          | RAC | PERI          | ERD |
|-----------|--------------|-----|---------------|-----|
| WWTP1     | Ni, Zn, Cu, Cr, Cd | —   | Cu, Cd       | —   |
| WWTP2     | Zn, Cr, Cd, Pb  | —   | Cd, Pb       | —   |
| WWTP3     | Ni, Zn, Cu, Cr, Cd | —   | Ni, Cu, Cd   | Zn, Cu |
| WWTP4     | Zn, Cu, Cd, Pb  | Cd, Zn | Cu, Cd, Pb  | Zn, Cd |
| WWTP5     | Zn, Cu, Cd    | —   | Cu, Cd       | —   |

4. Conclusions

The tested sewage sludge meets the applicable limits for heavy metal content, which is one of the basic criteria determining the possibility of using it for natural or agricultural purposes. However, the analysis of potential ecological risk showed that despite the acceptable concentrations of heavy metals in the sewage sludge, its use for natural purposes poses a rather high ecological risk.

The trend of toxicity for GAI and PERI indices is preserved, but the results are not equal. Comparing the given indices, the GAI was found to be more critical. Zinc and cadmium appeared to be the heavy metals with the highest potential for contamination. The PERI index also showed high ecological risk for the analyzed sewage sludge, which was due to very high ecological contamination risk values for cadmium, while the other heavy metals showed low risk levels.

A speciation analysis of the sewage sludge was also performed, which showed the percentage of heavy metals in four fractions. Heavy metals in the most mobile fractions
(F1 + F2) tended to migrate deep into the soil, causing soil contamination. The RAC index analyzing the percentage of the most mobile fraction F1 to the sum of all fractions showed that in most cases the contribution of heavy metals predominated in the non-mobile fractions. Only Zn and Cd for WWTP4 showed high levels of toxicity. According to the RAC index, the sludge from WWTP1 was completely nontoxic. The ERD, considering all mobile fractions by weight, showed high values for zinc and copper from WWTP3, and zinc and cadmium from WWTP4. The WWTP1, when compared with the RAC index, showed moderate toxicity levels for zinc and copper. Comparing RAC and ERD, it is very important to consider heavy metals from fractions II and III when analyzing the risk of environmental contamination.

**Author Contributions:** Conceptualization, J.L. and J.G.; methodology, J.G. and R.K.; formal analysis, J.L., J.G. and R.K.; investigation, J.G. and R.K.; writing—original draft preparation, J.L., R.K. and J.G; writing—review and editing, J.L., J.G., and R.K; visualization, J.L. and R.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** The APC were funded by The Programme of the Polish Ministry of Science and Higher Education—the Regional Initiative of Excellence, financed by the Polish Ministry of Science and Higher Education, on the basis of contract no. 025/RID/2018/19 of 28 December 2018, with the amount of funding: 12 million PLN.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The datasets supporting the results of this article are included within the article and its additional files.

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

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