water

MDPI

Article

The Assessment of Sewage Sludge Utilization in Closed-Loop Economy from an Environmental Perspective

Agata Janaszek [1], Alessandra Furtado da Silva [2], Nebojša Jurišević [3], Maria Kanuchova [4], Ľubica Kozáková [4] and Robert Kowalik [1,*]

[1] Faculty of Environmental Engineering, Geomatics and Renewable Energy Kielce, Kielce University of Technology, 25-314 Kielce, Poland; ajanaszek@tu.kielce.pl
[2] Department of Chemistry, Federal University of Technology-Paraná, Brazil (UTFPR), Avenida João Miguel Caram 3131, Jardim Morumbi, Londrina 86036-370, PR, Brazil; alessandrasilva@utfpr.edu.br
[3] Department for Energy and Process Engineering, Faculty of Engineering, University of Kragujevac, 34000 Kragujevac, Serbia; jurisevic@kg.ac.rs
[4] Faculty of Mining, Ecology, Process Control and Geotechnologies, Technical University of Kosice, Letna 9, 042 00 Kosice, Slovakia; maria.kanuchova@tuke.sk (M.K.); lubica.kozakova@tuke.sk (Ľ.K.)
* Correspondence: rkowalik@tu.kielce.pl

Abstract: Sewage sludge, a by-product of wastewater treatment, is garnering increasing attention in the pursuit of closed-loop economy practices due to its highly beneficial fertilizing properties. However, like any technique, using sewage sludge as fertilizer has potential and limitations. Heavy metals within sewage sludge are a primary limitation curtailing its application as a fertilizer. This study collected sewage sludge samples from four wastewater treatment plants and soil from potential application sites. The mobility of heavy metals was then examined using a sequential BCR analysis. Furthermore, a comprehensive environmental risk assessment associated with the agricultural use of sewage sludge was conducted, using various risk indicators such as I_{geo} and Nemerov, to compare the cumulative metal concentrations in the sewage sludge and soil. Additionally, risk assessment codes, ecological risk indices of metal mobility, and environmental risk indices were calculated, specifically focusing on the mobility of metals in the soil environment. This research demonstrates that sewage sludge failing to meet conventional criteria for agricultural use based on total metal content does not necessarily pose a high-risk application. Understanding the mobility forms of metals in sewage sludge is crucial, influencing the analysis of their potential utilization. Importantly, sewage sludge from wastewater treatment plants utilizing biological bed technology tends to exhibit a higher tendency of heavy metals to exist in mobile forms, migrating within the soil environment.

Keywords: heavy metals; sewage sludge; soil; pollution

check for updates

Citation: Janaszek, A.; Silva, A.F.d.; Jurišević, N.; Kanuchova, M.; Kozáková, Ľ.; Kowalik, R. The Assessment of Sewage Sludge Utilization in Closed-Loop Economy from an Environmental Perspective. *Water* **2024**, *16*, 383. https://doi.org/10.3390/w16030383

Academic Editor: John Zhou

Received: 26 December 2023
Revised: 20 January 2024
Accepted: 22 January 2024
Published: 24 January 2024

1. Introduction

Sewage sludge, a residual product of wastewater treatment procedures, has seen a significant increase in global production driven by growing population numbers and economic advancements. Managing this escalating volume of sewage sludge poses a challenge, particularly in urban settings where available space for its disposal is limited [1,2].

Renowned for its rich content of organic compounds and essential nutrients crucial for plant growth, sewage sludge is a potential resource for agricultural use, offering a natural solution to its management predicament [3,4]. However, the presence of pathogens, heavy metals, and other toxic substances in sewage sludge presents a risk to human health and the environment if not managed properly.

One of the critical elements of a closed-loop economy is the use of sludge in a closed resource cycle process. A closed-loop economy is based on the idea of minimizing waste by reusing resources in the production cycle. In this context, sludge, usually a waste, can be transformed into a valuable product.

Appropriate treatment and technologies can transform sludge into a sustainable and useful product, e.g., as a natural fertilizer, land reclamation material, or energy source. In this way, instead of treating sludge solely as an environmental problem, it becomes a valuable resource that can be reused in various sectors of the economy.

However, in order for sludge to be used in a closed-loop economy, it is necessary to maintain strict standards regarding its quality and safety. Appropriate treatment, chemical composition monitoring, and pollution control are key to ensuring that the transformed sludge becomes a safe and effective resource for the closed loop economy.

Recognizing the pressing need for sewage sludge management, the Municipal Sewage Sludge Management Strategy [5] emphasizes the encouragement of its natural utilization, bolstered by economic and environmental considerations [6,7]. Despite its potential benefits, this method also has its constraints and prerequisites. Adhering to the Ministry of the Environment Regulation of 6 February 2015 on municipal sewage sludge [8], it can only be applied to land if it meets specific requirements to ensure its safe use for human health, life, and environmental welfare.

The primary hindrance to the agricultural use of sewage sludge lies in its heavy metal content [9]. While average concentrations of trace elements offer some insight, they are insufficient for a comprehensive risk assessment concerning the natural use of sewage sludge. This inadequacy stems from the ability of heavy metals to migrate between soil layers, potentially infiltrating groundwater and surface water, posing contamination risks to plants, and potentially harming humans [10–12]. The mobility of heavy metals predominantly hinges on their chemical composition within the environment [13].

In Figure 1, we depict diverse strategies employed by several EU nations for managing sewage sludge. Concurrently, Table 1 delineates the prescribed thresholds governing the viability of utilizing sewage sludge for ecological purposes.

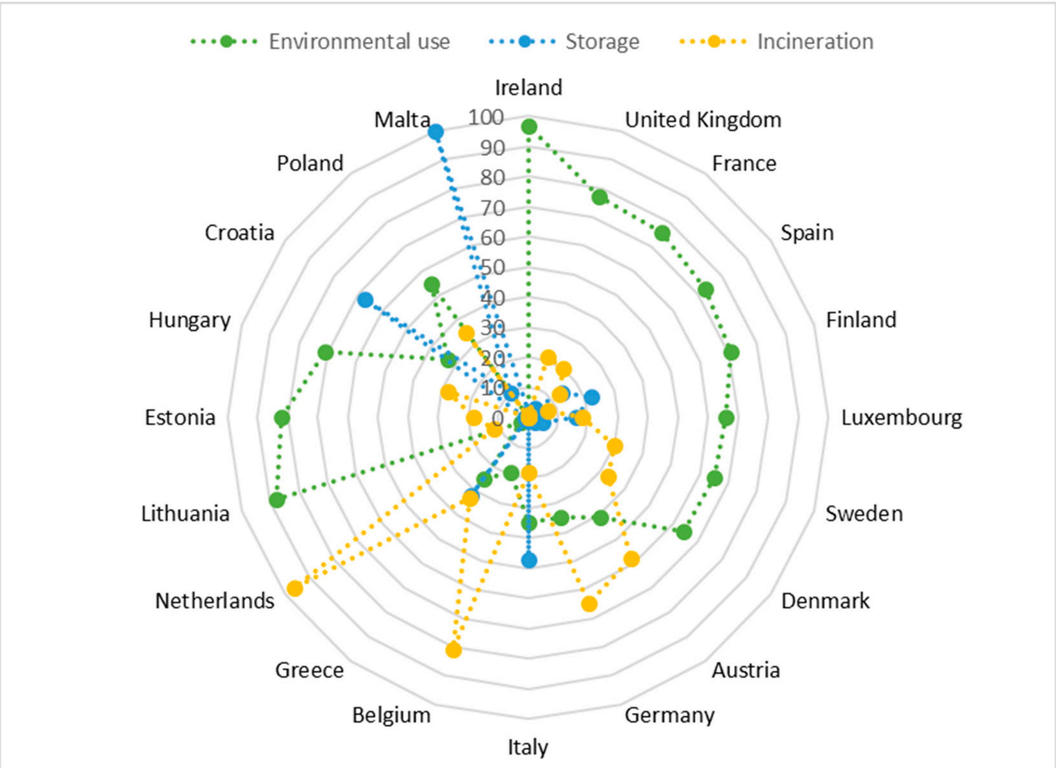

Figure 1. Percentage representation of sludge handling in EU countries as of 2020 [14].

Table 1. The allowable upper limits for heavy metal concentrations in sewage sludge intended for natural applications are indicated in milligrams per kilogram of dry matter (mg/kg d.m.).

Heavy Metal	The Permissible Levels of Heavy Metal Content in Sewage Sludge Intended for Natural Use								
	Poland [8]	EU [15]	Chinese [16]		United States [17]	South African [18]	Netherlands [19]	Ireland [20]	Malta [21]
			pH < 6.5	pH > 6.5					
Cd	20	20–40	5	20	39	40	1.25	20	5
Ni	300	300–400	100	200	420	420	30	300	200
Cr	500	-	600	1000	-	1200	75	-	800
Pb	750	750–1200	300	1000	300	300	100	750	500
Cu	1000	1000–1750	250	500	1500	1500	75	1000	800
Zn	2500	2500–4000	500	1000	2800	2800	300	2500	2000

An essential consideration regarding heavy metals involves the capacity of living organisms to accumulate these substances within their bodily tissues. Within this context, two distinct processes, bioaccumulation and biomagnification, emerge. Bioaccumulation commences at the base of the food chain, where pollutant concentrations gradually increase from the environment to the initial consumer, such as from plankton to a primary consumer organism in the ecosystem [22]. Conversely, biomagnification entails the progressive elevation of pollutant concentrations at each food chain level, culminating in the highest concentration within organisms situated at the chain's end.

For biomagnification, toxins must possess specific attributes like longevity, mobility, fat solubility, and biological activity. In sufficiently high doses, these harmful substances can lead to severe health issues in marine life and humans [23].

Heavy metals fall into two distinct groups. The first group includes cadmium, lead, and mercury, known for their high toxicity to humans and animals, although their impact on plant growth and development is relatively lower. The second group comprises copper, nickel, and zinc, which become more toxic to plants when present in increased quantities. Elevated concentrations of heavy metals can adversely affect soil biological properties, disrupt the food chain, harm plant health, and cause groundwater contamination [12,24,25]. Exceeding the permissible level of heavy metal content can reduce soil fertility, inhibit soil enzymatic activity, and alter soil acidity [26].

This study analyzed the heavy metal content in sewage sludge obtained from four wastewater treatment plants using different technologies and the soils at their potential application sites. The objective was establishing a reliable indicator to assess the potential risk of heavy metal contamination associated with introducing sewage sludge. Two indicators were explored: those based solely on total metal content and those incorporating heavy metal mobility. The sampling locations for the tests are shown in Figure 2 and the characteristics of the wastewater treatment plant in Table 2.

Table 2. Description of sludge sampling sites.

Object	WWTP1	WWTP2	WWTP3	WWTP4
Location	Swieta Katarzyna	Sobkow	Pacanow	Opatow
Wastewater treatment plant type	MBR	SBR	EvU-Perl	Activated sludge
Form of sludge treatment	Oxygen stabilization of sludge	System Draimad	Oxygen stabilization of sludge	Fermentation
Equivalent number of inhabitants p.e. *	2626	3725	1446	15,355

Note(s): * population equivalents.

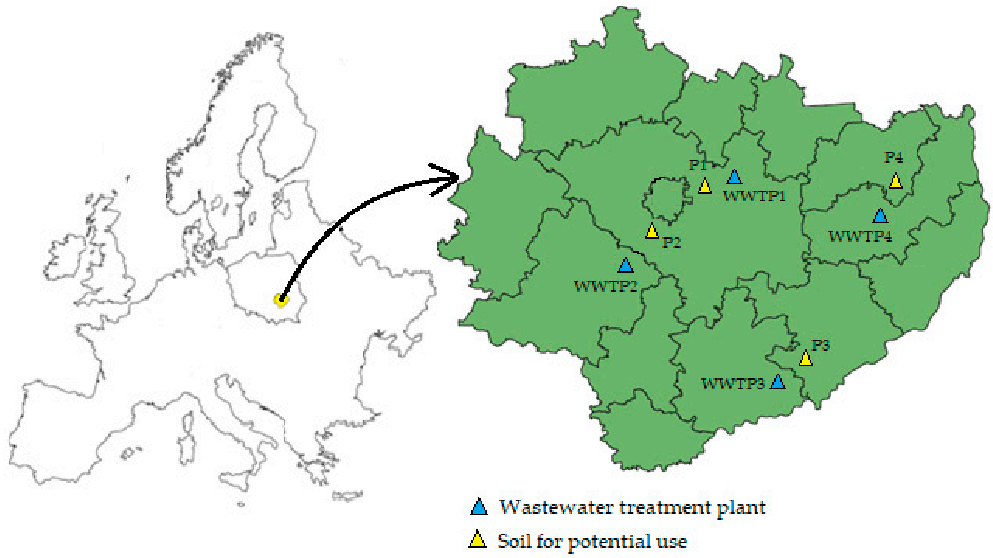

Figure 2. Map of the locations of wastewater treatment plants and the potential areas for agricultural use of sludge (own study).

Samples of soil were gathered using an Egner's stick from locations identified for the possible agricultural use of sludge, with depths reaching up to 0.3 m. These soils have a various glanurometric composition, consisting of medium to heavy compacted textures, sometimes experiencing prolonged periods of moisture in some cases persisting throughout the year. Despite their potential fertility and nutrient richness, akin to soils suitable for wheat and notably suitable for rye, these soils do exhibit certain deficiencies. For a detailed account of these soils, please refer to Table 3.

Table 3. Description of soil sampling sites.

Location	Distance from WWTP	Soil Taxonomy	pH (KCl)	Organic Matter Content	Organic Carbon	Nitrogen Total	C/N Ratio	Absorbable Phosphorus	Calcium Content	Soil Sorption Capacity
-	km	-	pH	%	%	%	-	mg $P_2O_5 \times$ 100 g^{-1}	$C_{mol} \times kg^{-1}$	$C_{mol} \times kg^{-1}$
Wola Kopcowa—P1	15.2	Spodosols	5.8	3.28	1.83	0.08	20.84	6	1.3	6.83
Dyminy—P2	25.4	Spodosols	6.5	3.19	1.86	0.13	15.43	1.7	5.2	11.82
Niedzialki—P3	17.3	Inceptisols	7.6	0.76	0.52	0.07	4.15	10	0.13	45.31
Cmielow—P4	13.8	Dystric Eutrudepts	5.3	2.64	1.54	0.14	10.5	5.3	5.1	10.12

2. Heavy Metals in the Human Environment

2.1. Sources of Heavy Metals

Sewage sludge originates from a blend of household and industrial wastewater, encompassing chemicals found in household products like detergents, cleaning agents, and cosmetics, as well as substances from industrial processes. Agricultural wastewater commonly carries pesticides, fertilizers, and other chemicals applied to crops, which can enter sludge through soil flushing from rainfall or irrigation. Healthcare facilities contribute to the mix with chemicals used in treatment, disinfection, or laboratory testing potentially finding their way into wastewater and subsequently into sludge. The unlawful disposal of municipal and industrial waste in improper landfills can also introduce contaminants into sewage systems, contributing to sludge pollution [27–29].

Presently, the most significant environmental exposure to toxic heavy metals results from human activities. Anthropogenic sources of heavy metal contamination in the environment include various industrial sectors, transportation, municipal management, energy production, fertilizer use, and waste disposal. Table 4 outlines the origins of heavy metal pollution [30,31].

Table 4. Sources of heavy metal pollution caused by human activity [28,29,31].

Heavy Metal	Sources of Metals in Sewage Sludge
Cadmium (Cd)	Electroplating plants, production of dyes, batteries, accumulators, paints and plastics, polymer stabilizers, chemical industry, production of plant protection products, graphic arts, printing industries
Lead (Pb)	Production of dyes, batteries, fertilizers, automotive, energy industry, plant protection products, electrochemical
Chromium (Cr)	Electroplating industry, tanning industry, wood impregnation, textile, dye and plastic production, printing and graphic arts industries
Copper (Cu)	Metallurgical industry, dye industry, textile industry, production of plant protection products and fertilizers
Mercury (Hg)	Production of batteries, phosphoric acid, caustic soda, pulp mills, production of plant protection products and mercury, metallic mercury
Nickel (Ni)	Electroplating industry, paper industry, refineries, steel plants, fertilizer plants
Zinc (Zn)	Battery manufacture, paints, textile industry, plastics, polymer stabilizers, printing and graphic arts industries, printing and graphic arts

Disparities in soil characteristics, such as permeability and depth to groundwater, play a pivotal role in determining the risk of water contamination by leached metals after the application of sludge as a fertilizer. In soils with high permeability, water effortlessly infiltrates through the layers, facilitating the rapid transport of metals to deeper soil layers or groundwater [32]. This situation escalates the potential for groundwater contamination, especially when metals are not adequately retained and bound within the soil layer. Soils with low permeability hinder water movement, slowing down the transport of metals into the deeper soil. However, during conditions of excessive irrigation or heavy rainfall, there remains a risk of metals entering groundwater, even in low-permeability soils [33].

The soil type, whether sandy, loamy, or clay, influences the soil's capacity to retain metals. For instance, clay soils may exhibit higher metal-retention capabilities than sandy soils, impacting the availability and mobility of metals. The presence of soil organic matter is crucial for metal fixation, with organic-rich soils acting as 'traps' for metals, diminishing their mobility and the risk of entering groundwater. Proximity to the groundwater surface increases the risk of metals entering groundwater. Shallow groundwater creates a direct connection between applied sludge and water resources, heightening the potential for contamination [32,34]. In soils with substantial depth between the surface and groundwater, the processes of metal leaching may be limited, reducing the risk of groundwater contamination. Nevertheless, even in deep soil layers, the intensive use of sludge can influence the chemical composition of groundwater over time [35].

2.2. Impact of Wastewater Treatment Technology on the Heavy Metal Content of Sewage Sludge

Distinct wastewater treatment technologies have a significant impact on the metal composition of sludge, influencing both the quantity of metals and their chemical forms. Biological processes, encompassing both aerobic and anaerobic methods, exert their influence through the activities of microorganisms. Certain bacteria have the capability to reduce or oxidize metals, thereby modifying their chemical speciation and solubility. Specific microorganisms can adsorb metals or form complexes, extracting them from the aqueous phase [36,37]. Phytoremediation, a biological process utilizing plants to absorb metals from soil or sludge, is among the techniques employed. The phosphorisation process, designed for phosphorus removal from water, can also impact heavy metals. Apatite phosphate, a byproduct of phosphorisation, can form complexes with certain metals, diminishing their mobility. Coagulation and flocculation techniques, employed for the removal of suspended solids and colloidal substances from wastewater, may concurrently lead to the accumulation of heavy metals [38]. The coagulants used in these processes can contribute to the formation of sludge-containing metals. The settling process in settling tanks aids in segregating sludge containing heavy metals. Different types of settling tanks, such as gravity or floating tanks, can influence the chemical composition of the resulting sludge. Filtration processes, both conventional and advanced, prove effective in eliminating suspended solids and heavy metals from wastewater. The choice of suitable filters plays a crucial role in determining the efficacy of metal removal [38,39]. Within wastewater treatment, membrane technologies like ultrafiltration and reverse osmosis effectively retain particles, including heavy metals. Advanced oxidation processes, such as ozonation or Fenton oxidation, can alter the chemical forms of metals, enhancing their removability from wastewater. In certain instances, modern treatment technologies enable the recovery of metals from sludge, offering potential benefits from a raw material recovery standpoint [40].

Various wastewater treatment technologies influence the metal content of sludge through a combination of biological, chemical, and physical processes, as well as advanced treatment methods. It is important to note that the effectiveness of metal removal is contingent on several factors, including the type of metal, environmental conditions, and the specifics of the treatment technology employed [41].

2.3. Heavy Metal Speciation

The best results for sewage sludge samples were obtained using a four-step procedure developed by the European Community Bureau of Reference, abbreviated BCR [42,43]. Initially, classical BCR was a three-step process. Nowadays, after modifying the method by introducing royal water mineralization, four fractions of heavy metals can be separated: ion-exchangeable (carbonate), bound to iron and manganese oxides (reducible), bound to organic matter (oxidizable), and residual matter [44–46]. The BCR method has been applied in many studies on the quality of sewage sludge and heavy metal-contaminated soils. The technique makes it possible to assess the mobility of metals in the studied matrix and estimate the risk of spreading contaminants into the environment [47]. The course of the BCR procedure is shown in Figure 3. Digestion with aqua regia ($HCl + HNO_3$) was used in the soil samples to determine the total heavy metal content.

2.4. Heavy Metal Accumulation Risk Indicators

By evaluating the presence of heavy metals in relation to established threshold values documented in the existing literature, it provides only generalized estimations of metal content within the soil, potentially limiting a comprehensive understanding of soil quality. Employing pollution indicators becomes imperative to gauge the extent of heavy metal contamination within soil efficiently. Early indices pioneered by Muller [48] and Hakanson [49] laid the groundwork in this field. These pollution indices are increasingly recognized as essential tools for the geochemical evaluations of soil environments. Furthermore, these contaminant indices are crucial in monitoring soil quality, particularly within agroecosystems. Their utilization provides a more nuanced understanding of the soil's health and potential risks associated with heavy metal contamination.

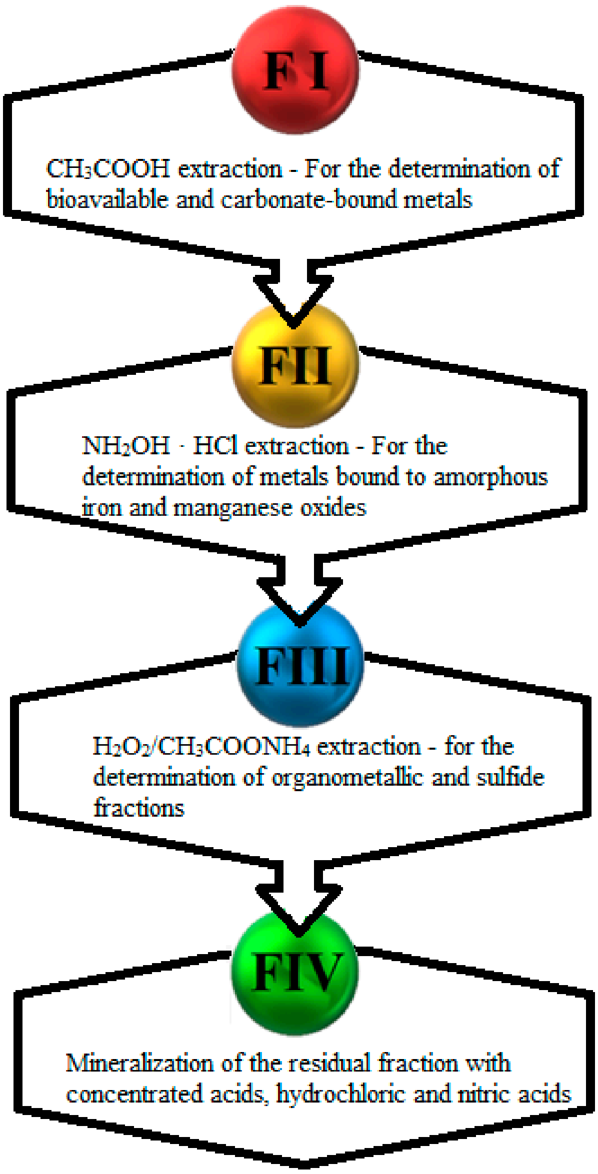

Figure 3. Sequence diagram of heavy metal speciation analysis by BCR method. (own study).

2.4.1. Geoaccumulation Index of Heavy Metal in Soil (I_{geo})

The method introduced by Muller [48] makes it possible to determine and classify the state of contamination of sediment and soil at five levels, from uncontaminated to highly contaminated. The geoaccumulation index (I_{geo}) depends mainly on the heavy metal content of the soil substrate at the site of potential introduction of the polluting agent. I_{geo} is defined by the following equation [50]:

$$I_{geo} = log_2 \frac{C_n}{1.5 \cdot B_n} \quad (1)$$

where:

C_n—the concentration of individual heavy metals, [mg/kg d.m.]

B_n—geochemical background value, [mg/kg d.m.]

The heavy metals' geoaccumulation index and risk assessment code are presented in Table 5.

Table 5. I_{geo} index categorization [48,49].

I_{geo}	Contamination Value
$I_{geo} \leq 0$	Lack of pollution
$0 < I_{geo} \leq 1$	Low pollution
$1 < I_{geo} \leq 3$	Average pollution
$3 < I_{geo} \leq 5$	High pollution
$5 < I_{geo}$	Extreme pollution

2.4.2. Nemerow Pollution Index ($PI_{Nemerow}$)

By considering the content of all analyzed heavy metals, the Nemerov pollution index ($PI_{Nemerow}$) evaluates the overall degree of soil contamination [51,52]. Compared to the I_{geo} index, the Nemerov method is a more comprehensive approach to assessing soil quality, which emphasizes the most polluting factors while taking into account the contribution of other factors in the evaluation system [53]. It determines the soil/sediment quality category by calculating a pollution index, which is a weighted multifactor index of environmental quality that accounts for extreme values or highlights maximum values [39]. It is calculated in the following way:

$$PI_{Nemerow} = \sqrt{\frac{\left(\frac{1}{n}\sum_{i-1}^{n} PI\right)^2 + PI_{max}^2}{n}} \quad (2)$$

where:

PI—calculated values for the single pollution index,

PI_{max}—maximum value for the single pollution index of all heavy metals and

n—the number of heavy metals.

The single pollution index (PI) is described below [48].

$$PI = \frac{C_n}{B_n} \quad (3)$$

where:

C_n—the concentration of individual heavy metals,

B_n—the value of the geochemical background.

2.4.3. Risk Assessment Code (RAC)

By considering both the total metal concentration and chemical speciation, the risk assessment code (RAC) offers a quantitative approach to evaluate the degree of bioavailability of heavy metals. The indicator was introduced by Perin and co-authors in 1985 [54]; it was assumed that the FI fraction, associated with carbonates, which are the most mobile compounds and result in the highest risk of heavy metal contamination of the ground. This indicator only partially reflects the actual risk of migration of metals in the soil matrix, due to the fact that heavy metals found in the reducible and oxidizable fraction also tend to migrate in the soil medium. The risk assessment code is calculated using the following formula:

$$RAC = \frac{FI}{HM} \cdot 100\% \quad (4)$$

where:

FI—metals' content in fraction I, [mg/kg d.m.]

HM—overall concentration of heavy metals, [mg/kg d.m.]

2.4.4. Environmental Risk Determinant (ERD)

The ERD index considers the unique tendency of each fraction to release heavy metals into the soil environment and assigns a weight between 0 and 1 to each fraction. The authors of this study introduced the ERD index as it takes into account the individual scale of each fraction, which is not addressed by any of the indices that consider the mobility issue [43]. The scales used were derived from the evaluation of other indices. The ERD index is determined using the following equation [43,49]:

$$ERD = F_{p1} + F_{p2} + F_{p3} \quad (5)$$

where:

$F_{p1} = F_1$; F_1—Metal load in the FI fraction, measured on a scale ranging from 0 to 1,
$F_{p2} = F_2{}^2$; F_2—Metal load in the FI fraction, measured on a scale ranging from 0 to 1,
$F_{p3} = F_3{}^3$; F_3—Metal load in the FI fraction, measured on a scale ranging from 0 to 1.
The risk level is classified into 4 categories as shown in Table 6.

Table 6. Classification of the Nemerov index [52,53].

Nemerow Pollution Index ($PI_{Nemerow}$)	Pollution Value
$0 < PI_{Nemerow} \leq 35$	low risk
$35 < PI_{Nemerow} \leq 100$	medium risk
$100 < PI_{Nemerow}$	High risk

2.4.5. Indicator of Ecological Risk of Metal Mobility (EMR)

By taking into account the mobility of heavy metals, it becomes apparent that solely fraction IV remains entirely stable within the soil. In contrast, the FI and FII fractions are the most mobile, while the FIII fraction may become mobile under some circumstances, i.e., when organic matter in the soil is treated by microorganisms or fungi, and rainwater may contain dissolved ozone as a result of lightning. The EMR determines the content of heavy metal group elements according to their content in four fractions. Each fraction is assigned an appropriate weight. The authors of this study proposed the following index to fully capture the essence of the issue of heavy metal mobility in risk analysis. It wis represented by the following formula:

$$\mathrm{EMR} = \frac{FI + 0.7 \cdot FII + 0.3 \cdot FIII}{\sum FI \div FIV} \quad (6)$$

3. Results

Table 7 summarizes the results of heavy metal speciation in sewage sludge, as well as the total metal content of the soil.

Table 7. ERD and EMR indicator classification [43,49].

EMR	ERD	Risk Value
$0 < EMR \leq 0.3$	$0 < ERD \leq 0.35$	low risk
$0.3 < EMR \leq 0.5$	$0.35 < ERD \leq 0.6$	medium risk
$0.5 < EMR$	$0.6 < ERD$	High risk

Table 8 shows the results of heavy metal content in soil and sewage sludge.

Table 8. Content of heavy metals (HMs) in sewage sludge (Ss) and soil (s) [mg/kg s.m.].

	Heavy Metal Content [mg/kg s.m.]					
Fraction	**Cu**	**Cr**	**Cd**	**Ni**	**Pb**	**Zn**
Sewage sludge—Ss1						
F I	7.51 ± 0.1	0.42 ± 0.1	1.22 ± 0.1	4.61 ± 0.1	8.03 ± 0.4	26.28 ± 0.6
F II	0.52 ± 0.1	0.21 ± 0.1	0.21 ± 0.1	0.33 ± 0.1	0.81 ± 0.1	8.44 ± 0.3
F III	101.95 ± 5.5	17.83 ± 0.1	3.54 ± 0.1	10.31 ± 0.1	17.02 ± 0.6	795.91 ± 23
F IV	15.11 ± 0.6	82.21 ± 0.6	33.56 ± 0.1	25.01 ± 0.2	62.24 ± 0.9	176.13 ± 8
ΣFI ÷ IV	125.03 ± 5.5	100.62 ± 0.6	38.42 ± 0.2	40.21 ± 0.3	88.02 ± 1.2	1006.61 ± 24.4
Sewage sludge—Ss2						
F I	1.52 ± 0.1	0.31 ± 0.2	0.00 ± 0.1	2.01 ± 0.1	5.71 ± 0.5	111.61 ± 2.0
F II	1.01 ± 0.1	0.01 ± 0.0	0.24 ± 0.1	1.45 ± 0.1	4.62 ± 0.6	215.24 ± 3.5
F III	79.54 ± 0.4	11.23 ± 0.2	1.06 ± 0.1	2.74 ± 0.1	4.33 ± 0.2	556.65 ± 4.8
F IV	23.03 ± 0.2	17.18 ± 0.4	1.54 ± 0.2	3.13 ± 0.1	49.84 ± 0.5	457.93 ± 4.0
ΣFI ÷ IV	105.04 ± 0.3	28.64 ± 0.5	2.81 ± 0.3	9.25 ± 0.2	64.41 ± 1.3	1341.22 ± 7.4
Sewage sludge—Ss3						
F I	1.51 ± 0.1	0.04 ± 0.1	0.01 ± 0.1	2.63 ± 0.1	3.77 ± 0.4	328.91 ± 0.9
F II	25.63 ± 0.2	24.13 ± 0.2	4.24 ± 0.1	19.62 ± 0.3	14.04 ± 2.3	743.25 ± 2.3
F III	551.44 ± 0.9	45.11 ± 0.3	5.15 ± 0.1	57.01 ± 0.6	6.01 ± 0.7	152.32 ± 0.9
F IV	4.72 ± 0.1	4.73 ± 0.1	0.83 ± 0.1	4.38 ± 0.2	26.74 ± 3.1	3.14 ± 0.1
ΣFI ÷ IV	583.31 ± 0.9	74.03 ± 0.6	10.11 ± 0.2	83.53 ± 0.7	50.23 ± 3.6	1228.01 ± 2.6
Sewage sludge—Ss4						
F I	3.36 ± 0.2	2.01 ± 0.3	0.32 ± 0.1	3.51 ± 0.1	5.21 ± 0.3	79.44 ± 0.9
F II	1.82 ± 0.1	1.15 ± 0.2	0.37 ± 0.1	1.44 ± 0.4	0.57 ± 0.3	122.82 ± 1.3
F III	57.13 ± 1.5	16.13 ± 0.4	1.92 ± 0.2	5.96 ± 0.2	7.82 ± 0.8	323.82 ± 3.1
F IV	22.84 ± 0.8	22.06 ± 0.6	1.13 ± 0.6	9.22 ± 0.2	54.74 ± 8.5	170.81 ± 3.7
ΣFI ÷ IV	85.02 ± 1.7	41.27± 0.8	3.61± 0.6	20.01 ± 0.3	68.22 ± 8.2	696.85 ± 4.3
Soil—s1						
ΣHM	3.81 ± 0.1	8.01 ± 0.2	0.5 ± 0.1	4.39 ± 0.1	16.73 ± 0.2	27.71 ± 0.3
Soil—s2						
ΣHM	5.59 ± 0.1	9.67 ± 0.3	0.64 ± 0.1	7.77 ± 0.2	36.52 ± 0.3	65.01 ± 0.3
Soil—s3						
ΣHM	2.01 ± 0.1	3.41 ± 0.1	0.55 ± 0.1	2.74 ± 0.1	5.85 ± 0.1	11.22 ± 0.2
Soil—s4						
ΣHM	6.84 ± 0.2	13.3 ± 0.2	0.5 ± 0.1	9.32 ± 0.1	54.4 ± 0.3	33.31 ± 0.2

The concentration of heavy metals at the potential site significantly influences the I_{geo} index. In the case of sludge extracted from WWTP1 and WWTP3, the I_{geo} index indicated notably high levels of contamination, particularly for copper, zinc, cadmium (in WWTP1), and nickel (in WWTP3). Conversely, for WWTP2 and WWTP4, lead and nickel were the only heavy metals that did not contribute to contamination (as depicted in Figure 4). Notably, the I_{geo} values for nickel from WWTP2 and lead from WWTP4 registered as negative, indicating that the sewage sludge metal content was lower than that found at the intended site of use. This underscores the difference in metal concentrations, emphasizing lower levels within the sediments than expected at the site of potential application.

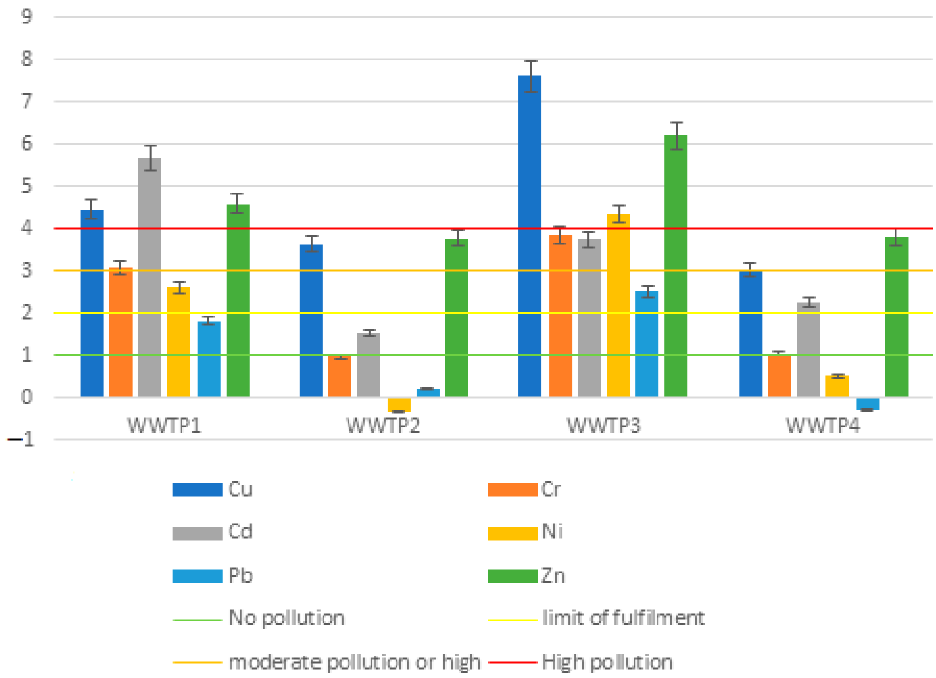

Figure 4. I_{geo} indicator of heavy metals in sewage sludge and soil.

The Nemerov index scrutinized the risk associated with the cumulative heavy metal value by juxtaposing it with the metallic content present in the soil. Notably, the most substantial contamination risk was observed, akin to the findings of the I_{geo} index, at WWTP3 (as indicated in Figure 5). This heightened risk is primarily attributed to the specific site (Ss3) designated for potential sewage sludge utilization, which exhibits an exceptionally low heavy metal content in the soil. Conversely, other scenarios did not present a pronounced risk of soil contamination upon introducing sewage sludge.

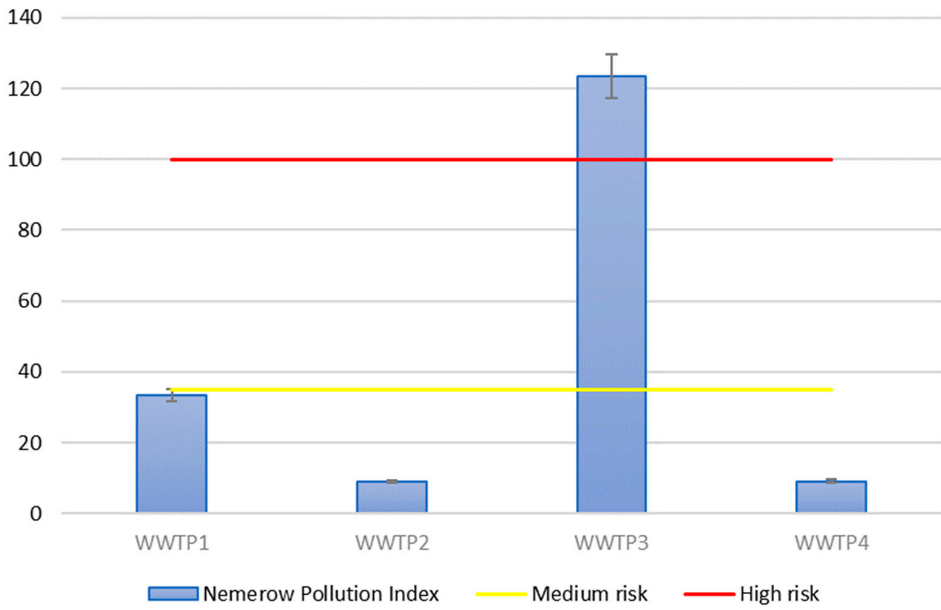

Figure 5. Nemerov pollution index for the analysis of the introduction of sewage sludge into the soil.

The RAC index is the first indicator that considers the speciation of heavy metals, but it only considers the content in the FI fraction and the total content of the element in question. RAC reached a medium risk value for nickel in all cases and for zinc in cases of sludge taken from WWTP3 and WWTP4 (Figure 6). None of the heavy metals reached a high risk of pollution due to the low concentration of metals within the FI fraction.

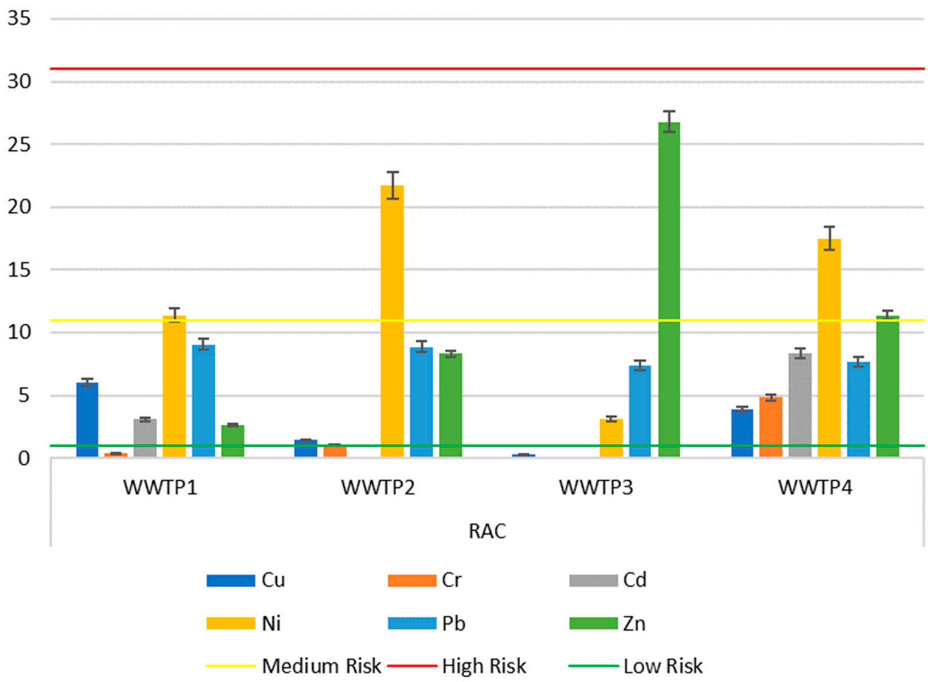

Figure 6. RAC of heavy metals in sewage sludge.

In contrast to RAC, the ERD and EMR indices consider the mobility of metals in fraction I and fractions II and III. Among these indices, the ERD index emerged as a more comprehensive assessment of the analyzed sewage sludge. Specifically, the ERD index highlighted a notable risk of contamination primarily associated with copper (at WWTP1 and WWTP3) and zinc (at WWTP3) (as depicted in Figure 7). Conversely, according to the EMR index, the high-risk threshold was surpassed solely by zinc in the sewage sludge obtained from WWTP3 (as illustrated in Figure 8).

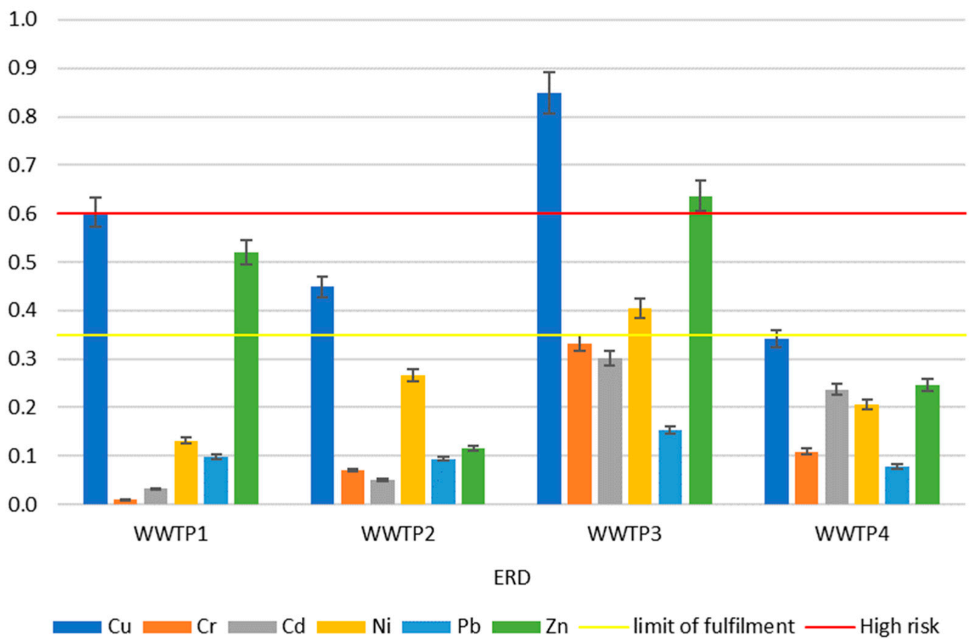

Figure 7. The ERD indicator of heavy metals in sewage sludge.

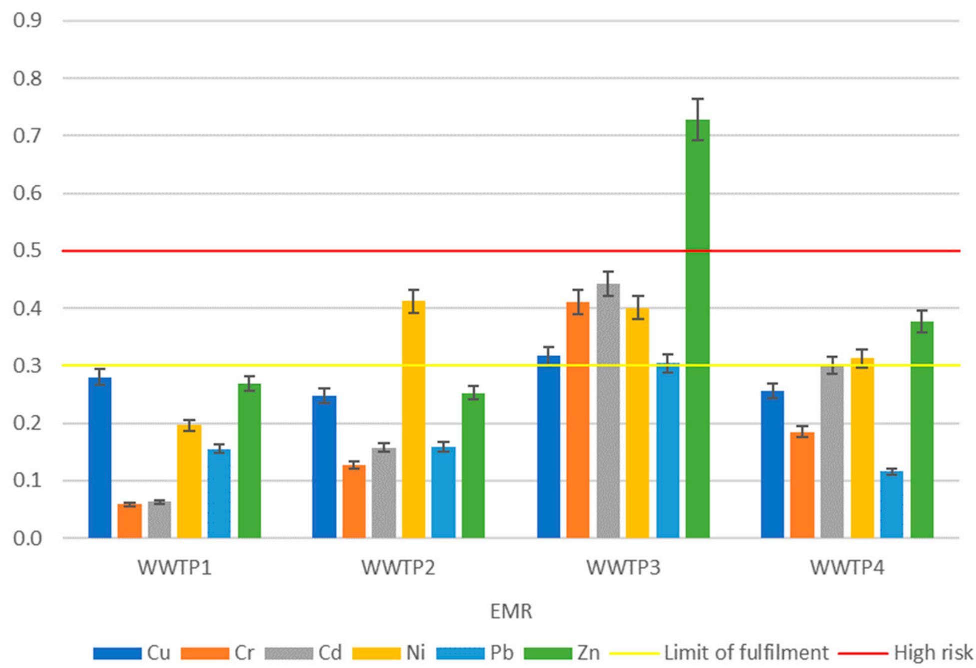

Figure 8. The EMR indicator of heavy metals in sewage sludge.

Table 9 indicating non-fulfillment of the heavy metal toxicity criteria was prepared for all the risk analysis indicators. The heavy metals mentioned in the table failed to satisfy the criteria needed to consider the sludge for potential environmental use based on the analyzed indicators.

Table 9. Schedule of non-fulfillment of the heavy metal toxicity criteria for all four contamination indices.

WWTP	I_{geo}	RAC	ERD	EMR
1	Cu, Zn, Cd, Cr	Ni	Cu, Zn	—
2	Cu, Zn	Ni	Cu	Ni
3	Cr, Cu, Cd, Zn, Ni	Zn	Cu, Ni, Zn	Cu, Cr, Cd, Ni, Zn
4	Cu, Zn	Ni, Zn	—	Ni, Zn

The requirements placed on sewage sludge are related to the content of heavy metals and parasite eggs. Heavy metals are released from wastewater during wastewater treatment processes and then accumulate in sewage sludge. Differences in treatment technologies can affect the total content of heavy metals in sewage sludge. However, more information on the total content of metals is needed to determine the risks associated with their use. The toxicity of heavy metals depends on their speciation form. They can exist in four different forms of mobility, depending on their tendency to migrate deep into the geochemical substrate. All regulations on sediment use worldwide focus only on the total amount of heavy metals found in sediments. This paper shows that the total heavy metal content, when assessing risk, is not an objective criterion. Many research teams have conducted risk analyses on the use of sewage sludge for natural purposes using various indicators. An extensive review of the available indicators of heavy metal contamination was conducted. However, although most considered the concept of heavy metal mobility, none provided accurate information on their tendency to migrate. The total heavy metal content did not exceed the legislative limits for all sampled sludge, except for cadmium at WWTP1, which was 38.42 mg/kg. The I_{geo} index based only on total metal content showed high risk for most metals, with only nickel and lead showing low risk.

The Nemerov index, on the other hand, showed high risk only at WWTP3, which was the smallest WWTP with a p.e. of 1400. Nickel and zinc were the metals that showed the highest risk level for the RAC index, suggesting the high concentration of these elements in the FI fraction. The ERD and EMR indices showed different results even though they accounted for the mobility of each fraction identically. For ERD, copper and zinc were the heavy metals that could cause the highest migration risk, while for EMR, zinc and nickel were the heavy metals that could cause the highest migration risk. For both indicators, the sludge taken from WWTP4 had the lowest aggregate mobility while the highest was from WWTP3. The critical fact here is that WWTP3 was a small treatment plant serving a small rural agglomeration, while WWTP4 was a large treatment plant receiving wastewater from the entire city. Another important fact is that cadmium, which in the case of WWTP1 exceeded the maximum permissible value to qualify for environmental use, showed low risk for all indicators considering the issue of heavy metal mobility.

For most of the available indicators, treated equally, the FI ÷ FIII fractions are considered mobile. This is a flawed approach because while the metals associated with the FI fraction have the highest propensity to move, those in the conditionally mobile FIII fraction only become mobile under certain conditions, such as in the presence of ozone created by lightning. Some indicators did not use information on the metal content of the FIII fraction in determining the risk of contamination, while the RAC indicator only considered the FI fraction. Two new indicators based on mobility, ERD and ERM, have been proposed. These indices are based on the metal content of the FI ÷ FIII fractions and introduce weight steps for each of these fractions. In this way, FIII is not entirely ignored, but at the same time, it is not treated equally to the FI and FII fractions.

4. Conclusions

This study shows that in risk assessment, the total content of heavy metals is not an objective criterion. The I_{geo} index, which only analyzes heavy metals using their total content in the soil, proved to be the most rigorous. However, this index can be a questionable indicator because metals in stable combinations do not tend to migrate through the soil and do not pose an ecological threat; rather, they only enrich the soil with valuable compounds such as nitrogen or phosphorus. The Nemerov index analyzed the total value of heavy metals in the sediments. Only sludge removed from wastewater treatment plant 3 was excluded based on the Nemerov index, mainly due to the low content of heavy metals in the soil for potential use. The RAC index only considered the heavy metal content of the FI fraction, which has a greater tendency to migrate in the soil. Zinc and nickel metals did not meet the RAC index criteria. The ERD and EMR indices were the most accurate because they considered the heavy metal content in all fractions except the FIV fraction, which is very stable in the soil. According to these indicators, sewage sludge from the Pacanow wastewater treatment plant, which operates with biobed technology, presented the most significant risk. Thus, these results indicate that sewage treatment plants operating with this type of technology generate sewage sludge containing more significant amounts of heavy metals in mobile forms compared to other technologies.

Considering the mobility of heavy metals is extremely important in the context of the natural application of sewage sludge, demanding its inclusion in the legal regulations that govern its use. Future research could improve risk assessment models such as the I_{geo} index, Nemerov index, RAC index, ERD, and EMR. These models can be refined to consider specific environmental conditions, incorporating the interaction between different fractions of heavy metals and resulting in greater accuracy in predicting environmental risks.

Author Contributions: Conceptualization, A.J. and R.K.; methodology, L'.K. and M.K.; software, N.J.; validation, A.J., R.K. and A.F.d.S.; formal analysis, A.F.d.S.; investigation, A.J., L'.K. and M.K.; resources, N.J., L'.K. and M.K.; data curation, A.F.d.S.; writing—original draft preparation, A.J. and R.K.; writing—review and editing, R.K. and A.J.; visualization, A.F.d.S. and R.K; supervision, R.K.; project administration, A.J. and R.K.; funding acquisition, A.J. All authors have read and agreed to the published version of the manuscript.

Funding: The APC were funded by the program 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 the contract no. 025/RID/2018/19 of 28 December 2018. The amount of funding is 12 million PLN.

Data Availability Statement: Data are contained within the article.

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

References

1. Miksch, K.; Sikora, J. *Biotechnologia Ścieków*; WN PWN: Warszawa, Poland, 2012.
2. Lasaridi, K.-E.; Manios, T.; Stamatiadis, S.; Chroni, C.; Kyriacou, A. The Evaluation of Hazards to Man and the Environment during the Composting of Sewage Sludge. *Sustainability* **2018**, *10*, 2618. [CrossRef]
3. Jasińska, A. The importance of heavy metal speciation in the aspect of natural management of sewage sludge. *Eng. Environ. Prot.* **2018**, *21*, 239–250. [CrossRef]
4. Latosińska, J. Risk assessment of soil contamination with heavy metals from sewage sludge and ash after its incineration. *De-Salin Water Treat* **2020**, *199*, 297–306. [CrossRef]
5. Ministry of Environment. *Strategy for Treatment of Municipal Sewage Sludge in 2019–2022*; Ministry of Environment: Warsaw, Poland, 2018; In polish: Strategia postępowania z komunalnymi osadami ściekowymi na lata 2019–2022. Minister Środowiska, 18 listopada 2018 r. Warszawa. Available online: https://www.gov.pl/attachment/2846e2b3-68c7-46eb-b36e-7643e81efd9a (accessed on 6 September 2023). (In Polish)
6. Bień, J.; Neczaj, E.; Worwąg, M.; Grosser, A.; Nowak, D.; Milczarek, M.; Janik, M. Directions of sludge management in Poland after 2013. *Eng. Environ. Prot.* **2011**, *14*, 375–384.
7. Sobolewska-Mikulska, K.; Cienciała, A. Legal-Surveying Documentation in the Registration of Rights to Properties of the Treasury and of Territorial Self-government Units–Case Study of Poland. *Real Estate Manag. Valuat.* **2020**, *28*, 76–88. [CrossRef]
8. Minister of the Environment. *Regulation of the Minister of the Environment of 6 February 2015 on the Municipal Sewage Sludge (J. L. 2015, No. 0, item. 257)*; Minister of the Environment: Warsaw, Poland, 2015.
9. McBride, M.B. Toxic metals in sewage suldge-amended soils: Has promotion of beneficial use discounted the risks? *Adv. Environ. Res.* **2003**, *8*, 5–19. [CrossRef]
10. Maddocks, G.; Lin, C.; McConchie, D. Effect of Bauxsol (TM) and biosolids on soil conditions of acid-generating mine spoil for plant growth. *Environ. Pollut.* **2004**, *127*, 157–167. [CrossRef] [PubMed]
11. Nartowska, E. The effects of potentially toxic metals (copper and zinc) on selected physical and physico-chemical properties of bentonites. *Heliyon* **2019**, *5*, e02563. [CrossRef]
12. Szopińska, K.; Cienciała, A.; Bieda, A.; Kwiecień, J.; Kulesza, Ł.; Parzych, P. Verification of the Perception of the Local Community concerning Air Quality Using ADMS-Roads Modeling. *Int. J. Environ. Res. Public Health* **2022**, *19*, 10908. [CrossRef]
13. Janaszek, A.; Kowalik, R. Analysis of Heavy Metal Contaminants and Mobility in Sewage sludge-soil Mixtures for Sustainable Agricultural Practices. *Water* **2023**, *15*, 3992. [CrossRef]
14. Available online: https://ec.europa.eu/eurostat/databrowser/view/ten00030/default/bar?lang=en (accessed on 6 December 2022).
15. European Commission. *Council Directive of 12 June 1986 on the Protection of the Environment, and in Particular of the Soil, When Sewage Sludge Is Used in Agriculture (86/278/EEC)*; European Commission: Brussels, Belgium, 1986.
16. Ministry of Environmental Protection of the People's Republic of China. *Discharge Standard of Pollutants for Municipal Wastewater Treatment Plant*; Ministry of Environmental Protection of the People's Republic of China: Beijing, China, 2002.
17. Code of Federal Regulations. *Protection of Environment. Chapter I—Environmental Protection Agency (Continued), Subchapter O—Sewage Sludge, Part 503—Standards for The Use Or Disposal Of Sewage Sludge, Subpart B—Land Application, Section 503.13—Pollutant limits. July 1, 2010*; Office of the Federal Register (United States): Washington, DC, USA, 2010.
18. Water Research Commission. *Guidelines for the Utilisation and Disposal of Wastewater Sludge. Vol. 2. Requirements for the Agri-cultural Use of Wastewater Sludge*; WRC Report no: TT 262/06; WRC: Pretoria, South Africa, 2009.
19. Government of the Netherlands. Decree on quality and use of other organic fertilisers. In *Manual of Environmental Policy*; BOOM: Rijswijk, The Netherlands, 2008; Available online: https://wetten.overheid.nl/BWBR0009360/2006-01-01 (accessed on 6 September 2023). (In Dutch)
20. The Sludge (Use in Agriculture) Regulations (Northern Ireland) 1990 Implement Council Directive 86/278/EEC on the Protec-tion of Public Health. Available online: https://www.daera-ni.gov.uk/articles/sewage-sludge (accessed on 5 September 2023).
21. Government of Malta. Legal Notice 212 of 28 June 2002 on Sludge (Use in Agriculture) Regulations. Available online: http://www.justiceservices.gov.mt/DownloadDocument.aspx?app=lom&itemid=11496&l=1 (accessed on 8 September 2023).
22. Bolan, N.; Kunhikrishan, A.; Thangarajan, R.; Kumpiene, J. Remediation of heavy metal(loid)s contaminated soils—To mobilize or to immobilize? *J. Hazard. Mater.* **2014**, *266*, 141–166. [CrossRef] [PubMed]
23. Haraguchi, K.; Hisamichi, Y.; Endo, T. Accumulation and mother-to-calf transfer of anthropogenic and natural organohalo-gens in killer whales (Orcinus orca) stranded on the Pacific coast of Japan. *Sci. Total Environ.* **2009**, *407*, 2853–2859. [CrossRef] [PubMed]
24. Szeląg, B.; Cienciała, A.; Sobura, S.; Studziński, J.; García, J.T. Urbanization and Management of the Catchment Retention in the Aspect of Operation of Storm Overflow: A Probabilistic Approach. *Sustainability* **2019**, *11*, 3651. [CrossRef]

25. Tytła, M.; Widziewicz, K.; Zielewicz, E. Heavy metals and its chemical speciation in sewage sludge at different stages of processing. *Environ. Technol.* **2016**, *37*, 899–908. [CrossRef] [PubMed]
26. Tytła, M.; Widziewicz-Rzońca, K.; Kernert, J.; Bernaś, Z.; Słaby, K. First Comprehensive Analysis of Potential Ecological Risk and Factors Influencing Heavy Metals Binding in Sewage Sludge from WWTPs Using the Ultrasonic Disintegration Process. *Water* **2023**, *15*, 666. [CrossRef]
27. Witkowska, D.; Słowik, J.; Chilicka, K. Heavy Metals and Human Health: Possible Exposure Pathways and the Competition for Protein Binding Sites. *Molecules* **2021**, *26*, 6060. [CrossRef]
28. Pourret, O.; Hursthouse, A. It's time to replace the term "heavy metals" with "potentially toxic elements" when reporting environmental research. *Int. J. Environ. Res. Public Health* **2019**, *16*, 4446. [CrossRef]
29. Latosińska, J.; Miłek, D.; Komór, A.; Kowalik, R. Selective Collection of Municipal Waste in a Residential District with Multi-Family Buildings—Case Study from Poland. *Resources* **2021**, *10*, 83. [CrossRef]
30. Kim, H.S.; Kim, Y.J.; Seo, Y.R. An overview of carcinogenic heavy metal: Molecular toxicity mechanism and prevention. *J. Cancer Prev.* **2015**, *20*, 232–240. [CrossRef]
31. Abd Elnabi, M.K.; Elkaliny, N.E.; Elyazied, M.M.; Azab, S.H.; Elkhalifa, S.A.; Elmasry, S.; Mouhamed, M.S.; Shalamesh, E.M.; Alhorieny, N.A.; Abd Elaty, A.E.; et al. Toxicity of Heavy Metals and Recent Advances in Their Removal: A Review. *Toxics* **2023**, *11*, 580. [CrossRef]
32. Tchounwou, P.B.; Yedjou, C.G.; Patlolla, A.K.; Sutton, D.J. Heavy Metal Toxicity and the Environment. *Exp. Suppl.* **2012**, *101*, 133–164.
33. Shao, T.; Wang, R.; Xu, Z.; Wei, P.; Zhao, J.; Niu, J.; Song, D. Permeability and Groundwater Enrichment Characteristics of the Loess-Paleosol Sequence in the Southern Chinese Loess Plateau. *Water* **2020**, *12*, 870. [CrossRef]
34. Wojnowska-Heciak, M.; Heciak, J.; Kłak, A. Concrete Paving Slabs for Comfort of Movement of Mobility-Impaired Pedestrians—A Survey. *Int. J. Environ. Res. Public Health* **2022**, *19*, 3183. [CrossRef]
35. Laonamsai, J.; Pawana, V.; Chipthamlong, P.; Chomcheawchan, P.; Kamdee, K.; Kimmany, B.; Jul-phunthong, P. Groundwater Quality Variations in Multiple Aquifers: A Comprehensive Evaluation for Public Health and Agricultural Use. *Geosciences* **2023**, *13*, 195. [CrossRef]
36. Arya, S.; Kumar, V.; Sharma, S. Analysis of water quality parameters of groundwater in and around Diamond Cement Industry, Jhansi, Central India. *Int. J. Curr. Res.* **2012**, *4*, 75–77.
37. Rajakaruna, R.M.A.S.D.; Sewwandi, B.G.N.; Najim, M.M.M.; Baig, M.B.; Alotaibi, B.A.; Traore, A. Sus-tainable Approaches for Wastewater Treatment: An Analysis of Sludge-Based Materials for Heavy Metal Removal from Wastewater by Adsorption. *Sustainability* **2023**, *15*, 14937. [CrossRef]
38. Hegazi, H.A. Removal of Heavy Metals from Wastewater Using Agricultural and Industrial Wastes as Adsorbents. *HBRC J.* **2013**, *9*, 276–282. [CrossRef]
39. Rathi, B.S.; Kumar, P.S. Application of Adsorption Process for Effective Removal of Emerging Contami-nants from Water and Wastewater. *Environ. Pollut.* **2021**, *280*, 116995. [CrossRef]
40. Soliman, N.K.; Moustafa, A.F. Industrial Solid Waste for Heavy Metals Adsorption Features and Chal-lenges; a Review. *J. Mater. Res. Technol.* **2020**, *9*, 10235–10253. [CrossRef]
41. Ahmaruzzaman, M. Industrial Wastes as Low-Cost Potential Adsorbents for the Treatment of Wastewater Laden with Heavy Metals. *Adv. Colloid Interface Sci.* **2011**, *166*, 36–59. [CrossRef]
42. Kowalik, R.; Gawdzik, J.; Bąk-Patyna, P.; Ramiączek, P.; Jurišević, N. Risk Analysis of Heavy Metals Migration from Sewage Sludge of Wastewater Treatment Plants. *Int. J. Environ. Res. Public Health* **2022**, *19*, 11829. [CrossRef]
43. Kowalik, R.; Latosińska, J.; Metryka-Telka, M.; Porowski, R.; Gawdzik, J. Comparison of the Possibilities of Environmental Usage of Sewage Sludge from Treatment Plants Operating with MBR and SBR Technology. *Membranes* **2021**, *11*, 722. [CrossRef]
44. Jeske, A.; Gworek, B. Review of methods for determination of bioavailability and mobility of heavy metals in soils. *Environ. Nat. Resour. Prot.* **2011**, *49*, 209–218.
45. Szumska, M.; Gworek, B. Methods for the determination of heavy metal fractions in sewage sludge. *Environ. Prot. Nat. Resour.* **2009**, *41*, 42–63.
46. Zimmerman, A.J.; Weindorf, D.C. Heavy metal and trace metal analysis in soil by sequential extraction: A review of procedures. *Int. J. Anal. Chem.* **2010**, *2010*, 387803. [CrossRef] [PubMed]
47. Kabala, C. Comparison of single and sequential iron extraction in podzolic soils of the Sudetes. *Soil Sci. Yearb. Suppl.* **2001**, *52*, 191–197.
48. Muller, G. Index of geoaccumulation in sediments of the Rhine River. *GeoJournal* **1969**, *2*, 108–118.
49. Hakanson, L. An ecological risk index for aquatic pollution control: A sedimentological approach. *Water Res.* **1980**, *14*, 975–1001. [CrossRef]
50. Karaouzas, I.; Kapetanaki, N.; Mentzafou, A.; Kanellopoulos, T.D.; Skoulikidis, N. Heavy metal contamination status in Greek surface waters: A review with application and evaluation of pollution indices. *Chemosphere* **2021**, *263*, 128192. [CrossRef]
51. Gong, Q.; Deng, J.; Xiang, Y.; Wang, Q.; Yang, L. Calculating pollution indices by heavy metals in eco-logical geochemistry assessment and a case study in parks of Beijing. *J. Earth Sci.* **2008**, *19*, 230–241.
52. Varol, M. Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. *J. Hazard. Mater.* **2011**, *195*, 355–364. [CrossRef] [PubMed]

53. Inengite, A.K.; Abasi, C.Y.; Walter, C. Application of pollution indices for the assessment of heavy metal pollution in flood impacted soil. *Int. Res. J. Pure Appl. Chem.* **2015**, *8*, 175–189. [CrossRef]
54. Perin, G.; Craboledda, L.; Lucchese, M.; Cirillo, R.; Dotta, L.; Zanetta, M.L.; Oro, A.A. Heavy metal speciation in the sediments of northern Adriatic Sea. A new approach for environmental toxicity determination. In *Heavy Metals in the Environment*; Lakkas, T.D., Ed.; CEP Consultants: Edinburgh, UK, 1985; Volume 2, pp. 454–456.