land

Article

The Evaluation of the Phytoremediation Potential of the Energy Crops in Acid Soil by Sewage Sludge Fertilization

Ieva Mockevičienė [1], Gintaras Šiaudinis [1], Danutė Karčauskienė [1,*], Regina Repšienė [1], Karolina Barčauskaitė [1] and Olga Anne [2]

[1] Institute of Agriculture, Lithuanian Research Centre for Agriculture and Forestry, Vezaiciai, 96216 Klaipeda, Lithuania
[2] Engineering Department, Klaipeda University, 92295 Klaipeda, Lithuania
* Correspondence: danute.karcauskiene@lammc.lt; Tel.: +370-615-37-681

Abstract: Phytoremediation is a green technique being increasingly used worldwide for various purposes, including sewage sludge contaminated by heavy metals. Most plants proposed for this technique have high nutrient demands, and fertilization is often required to maintain soil fertility and nutrient balance. In this context, sewage sludge could be a valuable source of nutrients (especially N and P) and water for plant growth. The main aim of this study was to assess the phytoremediation potential of selected energy plants, aspects of its increase, as well as contamination risks. Three treatments were used: unfertilized soil and the application of 45 and 90 t ha^{-1} of sewage sludge. The experiment was performed in common osier and cup plant growing sites. Cr, Ni, Pb, Cu, and Zn contents in the soil tended to rise steadily when the amount of sewage sludge increased from 45 to 90 t ha^{-1}. Heavy metal concentrations in the soil were ranked as follows: Zn > Cr > Ni > Pb > Cu. Cr and Pb concentrations increased by 22.5% and 37.4% in 2020, respectively, compared to those in 2017, whereas Cu concentrations declined by 44.4%. Cu and Ni were significantly reduced by common osier while Pb and Zn were reduced by cup plant. A moderate potential ecological risk due to Cr, Ni, Cu, Pb, and Zn was observed in soils. The data can be used to estimate the suitability of the soil treated by sewage sludge for added value development in line with circular economy principles.

Keywords: heavy metals; sewage sludge; acid soil; soil quality; energy crops; ecological risk indices; bioconcentration factor

Citation: Mockevičienė, I.; Šiaudinis, G.; Karčauskienė, D.; Repšienė, R.; Barčauskaitė, K.; Anne, O. The Evaluation of the Phytoremediation Potential of the Energy Crops in Acid Soil by Sewage Sludge Fertilization. *Land* **2023**, *12*, 866. https://doi.org/10.3390/land12040866

Academic Editor: Evangelia Golia

Received: 8 March 2023
Revised: 7 April 2023
Accepted: 9 April 2023
Published: 11 April 2023

1. Introduction

Environmental pollution has become a major ecological problem around the world, with a growing public demand for the cleanest and healthiest environment. A wide range of organic and inorganic contaminants have been found to pollute the environment and pose serious health risks to living organisms. Among them, heavy metals are highly notorious pollutants due to their high abundance and non-biodegradable and persistent nature in the environment [1]. Anthropogenic influences, such as mining and processing, as well as the use of pesticides, sewage sludge, and fertilizers, are significant factors that accelerate soil contamination by metals. Anthropogenic inputs, such as mining, refinement, pesticides, sewage sludge, and fertilizer use, are major accelerators of soil pollution by metals [2,3]. Excessive pollution in the soil lowers its quality and productivity, further exposing the entire food chain [4]. Because of the high toxicity, long persistence, and bioaccumulation characteristics of heavy metals, soil contamination, particularly in agricultural soils, has become a focus of study in recent years [5].

Scientists have counted as many as 2.5 million potentially polluted sites across Europe, which need to be investigated. Of these, approximately 14% are expected to be contaminated and likely to require remediation [6]. Phytoremediation has been recognized as an emerging, low-cost, and eco-sustainable solution for heavy metal mitigation and control. It is the most suitable alternative to traditionally applied physicochemical remediation techniques, which are highly expensive and create secondary pollution, deteriorating soil fertility, thus negatively affecting the agroecosystem [7–10]. Phytoremediation as a green technique has been increasingly used worldwide for various purposes, including the treatment of municipal sewage sludge. Continually expanding areas of contaminated or degraded soil which are unsuitable for agricultural production continue to be a source of concern. Due to this reason, it is important to search for new sustainable phytoremediation varieties on such soils, i.e., energy crop cultivation with the use of sewage sludge [11]. Due to the lack of nutrients and organic matter [12] in the natural acid soil, for instance, in the case of *Retisol* in Western Lithuania, it is necessary to use soil conditioner to increase its productivity. One of them might be sewage sludge, which has a high phytoremediation potential and can successfully replace mineral fertilizers while offering extra benefits such as increased carbon sequestration. Their environmental use is closely linked to new management directions in energy recycling, as set out in Article 14 of Council Directive 91/271/EEC, which states that sewage sludge must be reused in each appropriate case, as a result of the European Commission's eco-innovation trend primarily focused on the main concept of "reduce, reuse, recycle" [13].

In recent years, several approaches to sewage sludge phytoremediation have been investigated. The use of a green approach, such as phytoremediation, to remediate (remove) heavy metals from contaminated sludge could be a valuable tool to improve sludge quality with a more economical and environmentally friendly approach. The application of sewage sludge on ornamental [14], energy crops [15,16], or forest species [17] is the most common green remediation approach, with the goal of extracting heavy metals. Only a few tests exist in the literature where phytoremediation was evaluated directly on a high concentration of sewage sludge, for example, the suitability of different plant species for sludge phytoremediation under natural conditions. Recent studies concluded that common osier (*Salix viminalis* L.), as a fast-growing species, has a high potential for bioremediation. Because of its ability to absorb and accumulate contaminants, it is suitable for detoxifying heavy metal-contaminated soils in situ [18,19]. Since common osier has few environmental needs, it can be grown in low-quality soils. Herewith, common osier is particularly recommended for soils where the growth of traditional food or feed species is restricted; they can be beneficial for the reclamation and rejuvenation of damaged areas. Their functionality in the remediation process is due to several contaminant characteristics, including high biomass yield, a large root system, a high rate of evapotranspiration, waterlogging tolerance, and easy propagation, making them ideal candidates for environmental applications. The cleanup time using energy crops depends on several factors: the concentration of contaminants, the contaminated area size and depth, plant species, and plant age.

The use of sewage sludge as an organic fertilizer for *Salix*, which is rich in a variety of nutrients, should not only speed up phytoremediation processes but also lead to significantly higher biomass productivity [20]. Cup plant (*Silphium perfoliatum* L.) is another potential, high-yielding perennial species that can be used as an energy crop. Cup plant has been recognized as a promising species for soil cleaning from heavy metals [21]. Currently, the limited studies on cup plant's accumulation ability indicate that it may be a promising species for soil remediation [22].

However, extensive research is currently underway to testify to the phytoremediation potential of hyper-accumulating plants at the field scale for the treatment and management of heavy metals-contaminated sites. The main objective of this research was:

(1) to focus on the status of heavy metals in soil after application with different sewage sludge contamination levels;
(2) to determine the potential risks to the environment that heavy metal pollution could pose;
(3) to evaluate the effects of two energy crops on the changes in the selected heavy metal concentrations in soil.

Assessment of the phytoremediation potential of selected plants, aspects of its increase, as well as contamination risks, are highlighted in this study. At both national and global scales, this study would be relevant for addressing the remediation of heavy metal-contaminated soils through green phytoremediation technology, which is a promising approach for revegetation of acid soil and closely linked to the EU's Green Deal strategies related to the prevention of soil degradation. Furthermore, phytoremediation technology allows the application of circular economy principles, where biowaste such as sewage sludge can be used as part of the fertilizer for growing energy crops, which in turn can be used as a feedstock for energy production and be considered as an added-value product.

2. Materials and Methods

2.1. Field Experiment Design

The field experiment was conducted at the Vėžaičiai Branch of the Lithuanian Research Centre for Agriculture and Forestry, located in the West Lithuania eastern side (55°43′ N, 21°27′ E) (Figure 1). The soil of the experimental site is *Bathygleyic Dystric Glossic Retisol* (texture–moraine loam (clay 13–15%)). According to the Vėžaičiai meteorological station data recorded from 1981 to 2020, the average annual amount of precipitation is about 915 mm. The maximum amount of rainfall falls in late autumn and early winter; it accelerates nutrients leaching from the upper soil layers and results in soil acidification processes.

Figure 1. The field experimental site.

Prior to the establishment of the experiment in April 2013, the following soil properties (Table 1) were evaluated.

Table 1. Chemical characteristics of the experimental site prior to its establishment in April 2013.

Parameter	Extraction Method	Average Value	
		Common Osier	*Cup Plant*
pH_{KCl}	ISO 10390:2021	4.59	4.30
mobile P_2O_5	LVP D-07:2016	88 mg kg^{-1}	85 mg kg^{-1}
mobile K_2O	Egner–Rhiem–Domingo method	191 mg kg^{-1}	185 mg kg^{-1}
mobile Al	ISO 14254:2018	33.89 mg kg^{-1}	34.28 mg kg^{-1}
total N	ISO 11261-1995	1.26 mg kg^{-1}	1.57 mg kg^{-1}
total C	ISO 10694:1995	12.5g kg^{-1}	13.9 g kg^{-1}
C/N ratio		9.92	8.85
Cr	LST EN13650:2006 LST	30.24 mg kg $^{-1}$	49.57 mg kg^{-1}
Ni	EN11885:2009	26.24 mg kg $^{-1}$	19.93 mg kg^{-1}
Pb	LST EN13650:2006	12.82 mg kg^{-1}	17.58 mg kg^{-1}
Cu	LST EN13650:2006	8.89 mg kg^{-1}	6.93 mg kg^{-1}
Zn	LST ISO 8288:2002	27.55 mg kg^{-1}	31.06 mg kg^{-1}

During the period of 2013–2020, soil acidification slightly increased (from 4.27–4.59 in 2013 to 4–4.01 in 2020). Soil acidification over the 7-year period also indicates a decrease in soil-exchangeable calcium from 461 to 172 mg kg^{-1} and increased mobile aluminum content from 67.06 to 91.16 mg kg^{-1}.

The research was performed using two energy crops: common osier (*Salix viminalis* L.) and cup plant (*Silphium perfoliatum* L.). The preceding crop before the start of the experiment was perennial meadow. Initially, in April 2013, the meadow was disced. Thereafter, the site's soil was plowed, cultivated, and harrowed. Common osier and cup plant crops were planted in 2013. Common osier was planted using 0–30 cm long cuttings on 6 May 2013. Each treatment was made up of two rows that ran parallel to each other, with a distance between the cuttings of 0.50 m, a distance between two rows of 0.75 m, and a distance between the adjacent treatments of 1.25 m. The total area of one common osier treatment was 20 m^2. On 4 June 2013, seedlings of the cup plant were planted at the 2–3-leaf stage. As in planting common osier, each treatment was made of two parallel rows. The distance between the rows was 0.90 m, and the distance between the adjacent treatments was 1.00 m. The seedlings in each row were planted at a 0.50 cm distance. The total area of one treatment was 18 m^2.

The protection against weeds was done once in July 2013.

Granulated sewage sludge was spread on the soil surface was incorporated into the soil by a tiller machine at a depth of 0–12 cm on 14 May 2014.

There were three treatments in one factorial field experiment: (1) no fertilization (control treatment), (2) 45 t ha^{-1}, and (3) 90 t ha^{-1} of granulated sewage sludge.

Three replications were used. All three replications of each treatment were arranged randomly. By selecting sewage sludge rates, the main focus was on selecting appropriate rates that could apply enough nutrients (N (nitrogen), P (phosphorus), or K (potassium)) available for *Salix viminalis* growth and biomass yield at least for two successive rotations ahead (8 or more years). The same sewage sludge rates were applied for *Silphium perfoliatum*.

2.2. Quality of Sewage Sludge

The granulated sewage sludge was taken from the joint stock company "Šilutės vandenys". After performing the main chemical characteristics, it was found that granulated sewage sludge pH was 5.57; total nitrogen was 32.8 g kg^{-1}; total phosphorus −4.99 g kg^{-1}; organic matter −65.03%. The heavy metal concentrations were the following: lead (Pb) 14.48 mg kg^{-1}; cadmium (Cd) 0.45 mg kg^{-1}; chromium (Cr) 11.53 mg kg^{-1}; copper (Cu) 47.7 mg kg^{-1}; nickel (Ni) 8.24 mg kg^{-1}; zinc (Zn) 286 mg kg^{-1}; mercury (Hg) 0.97 mg kg^{-1}. The applied sewage sludge meets the first category requirements for heavy metal contamination, according to nature protection requirements.

2.3. Soil Chemical Analysis

Soil samples for chemical analyses were collected in October 2013 (before the start of the experiment), 2017, and 2020 seasons from three replicates of the upper soil layer (0–30 cm). The sampling was performed at both the cup plant and common osier growing sites. All samples (n–27) were air-dried, with visible roots and plant debris manually removed. The samples were disaggregated and homogeneously mixed after sieving through a 2.0 mm sieve.

Characterization of soil chemical properties was performed at the Chemical Research Laboratory of the Institute of Agriculture, Lithuanian Research Centre for Agriculture and Forestry. pH was measured in 1 M KCl (according to the standard ISO 10390:2005), and mobile aluminum was measured through the Sokolov method. Soil total nitrogen was determined by the Kjeldahl method, and soil mobile and potassium content through the AL method. Organic carbon content was determined by photometric procedure at the wavelength of 590 nm using the UV–VIS spectrophotometer using the glucose as a standard after wet combustion, according to Nikitin (1999).

For the analysis of heavy metals, soil samples were homogeneously mixed and passed through a 1 mm sieve for concentration measurement. After the acidic digestion of the prepared samples, the total amounts of the examined heavy metals (Cr, Ni, Pb, Cu, and Zn) were determined. The homogeneously mixed sample (~0.3 g) was digested with 10 mL of concentrated (≥65%) nitric acid and 2 mL of concentrated (≥37%) hydrochloric acid.

The samples were submerged in an acid solution for 30 min at room temperature before digestion. For performing microwave-assisted extraction (MAE), the CEM MARS 6® was used with the required necessary conditions: microwave power of 800 W, temperature of 180 °C, pressure of 800 psi, ramp duration of 20 min, and hold duration of 20 min. After the MAE, the sample was cooled and diluted. All prepared samples were measured three times, considering that each digestion cycle contained a blank sample. Heavy metals were evaluated and validated using an inductively coupled plasma mass spectrometer (ICP-MS) in standard mode using an external multi-element calibration curve in the range of 10–500 µg L^{-1}. The same analysis was evaluated for the determination of total heavy metal concentrations in plants' above-ground biomass.

2.4. Study of Potential Ecological Risk

The contamination factor (*Cf*) is determined by dividing heavy metal content in the soil by the reference value [23,24]. Low contamination is denoted by a *Cf* 1; moderate pollution is denoted by 1 < *Cf* < 3; considerable contamination is denoted by 3 < *Cf* < 6; very high pollution is denoted by a *Cf* > 6.

$$Cf = \frac{Ci}{B} \quad (1)$$

where *Ci* is the heavy metal content in certain treatments, and *B* is the reference value of heavy metal content determined in the control (unpolluted) treatment.

Based on the toxicity of heavy metals, this index evaluates the environmental risk posed by heavy metal contamination.

$$R_I = \sum_{1}^{n} E^i \quad (2)$$

$$E^i = T_R^i \times C_f \quad (3)$$

where R_I is the summation of all risk factors posed by heavy metals contamination in soil, E^i is each possible ecological risk factor, and C_f is the contamination factor. T_R is the toxic response criterion, which indicates the toxicity of heavy metals and so defines metal pollution risk. The standardized toxic response factors for heavy metals are Zn-1, Pb-5, Cr-2, Cu-30, and Ni-5 [24].

2.5. Bioconcentration Factor

The analysis of heavy metal accumulation patterns in various plants is essential. Bioconcentration factor (BCF) is defined as a coefficient that shows what quantities of elements are able to absorb by different parts of the plant from the soil. This factor defines the ability of individual elements to accumulate in certain parts, regardless of whether the fertilizer is used at high or low concentrations. With higher BCF values, plants are more capable of accumulating heavy metals from the soils and less capable of blocking soil metal pollution [25]. Generally, the BCF is obtained as shown in Equation (4) [26].

$$BCF = \frac{C_{plant}}{C_{soil}} \quad (4)$$

where C_{plant} and C_{soil} are the concentrations of heavy metals in plant and soil, respectively.

2.6. Statistical Analysis

The analysis of variance (ANOVA) and the least significant difference (LSD) methods were employed for various treatments in the statistical software package SAS (Statistical Analysis System, 2011). The correlations between the various heavy metals were evaluated using Pearson correlation analysis.

3. Results and Discussion

3.1. Distribution of Heavy Metals in the Upper Soil Layer of Both Plants under Fertilization with Sewage Sludge

Due to their high amount of organic compounds and macro-elements, sewage sludge can be considered valuable organic fertilizer, according to long-term research. Optimal macro-element supplementation has a positive influence on soil quality and plant physiology, as well as optimal root system growth. However, sludge could also be characterized by a high concentration of heavy metals and other harmful compounds, which could move through the whole soil-plant ecosystem. These harmful aspects are two major issues limiting its usefulness as a soil and plant fertilizer/amendment [27–29].

In our study, the calculated average heavy metal values in unfertilized (control background) moraine loam *Retisol* were ranked as follows: Zn > Cr > Ni > Pb > Cu (Figure 2), showing a pattern similar to those reported in studies conducted in Brazil [30] and the United Kingdom [31].

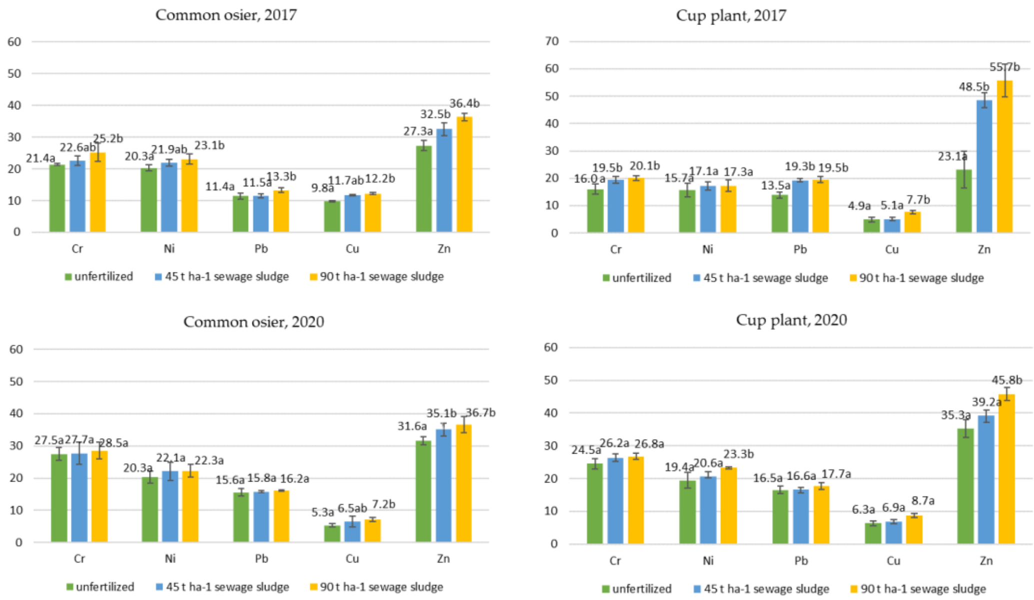

Figure 2. The content of heavy metals in the soil at different rates of an application of the sewage sludge. Different lowercase letters indicate significant differences among treatments.

Heavy metal concentrations in the naturally acidic upper soil layer tended to increase with time in this study. This could be related to the pH of the analyzed soil, which slightly decreased from 4.2–4.5 to 4.0 during the study period. In relation to those heavy metals which are more accessible at a lower pH, they may be excessively absorbed by plants. This increase in soil acidity may explain the increased heavy metal accumulation in non-fertilized soil. Furthermore, with increasing soil acidity, the mobility of Cr and Pb also increases, so migration into underlying soil layers is possible [32,33]. Ali et al. [2] and Mohamed et al. [33] reported similar findings. Metals, as natural components of soil mineral fraction, are important components of clay and minerals. Considering that the study was carried out in a crop rotation field where fertilization, in particular with phosphorus fertilizers and pesticides, was used for more than 50 years, heavy metals could be naturally found in the soil. Heavy metals are also present in the solid part of the soil; therefore, under favorable conditions, in this case, with an increase in soil acidity, heavy metals could be transferred to the soil solution.

In general, with the increasing application rate of sewage sludge from 45 to 90 t ha^{-1}, the amount of heavy metals (Zn, Cr, Ni, Pb, Cu) in the upper soil layer tended to increase gradually, compared to the unfertilized soil. In comparison to the sequence determined in unfertilized soil, where Zn ranked higher due to its larger concentration, the incorporation of sewage sludge had no effect on the sequence of the examined heavy metals. Although we did not observe a higher content of lead in the heavy metal sequence in the soil three years after the application of the sludge compared to the unfertilized soil, as other scientists did [34], we eventually found a higher content of lead in the heavy metal sequence in the soil three years after the incorporation of the sludge compared to the control treatment. Metal concentrations in the plots of both plants were revealed to be in the proper sequence: Zn > Cr > Pb > Ni > Cu.

Following application, the sludge is only apparent on the soil surface as a thin coating. Growing common osier and applying different doses of sewage sludge, significantly higher amounts of Cr, Ni, Pb, Cu, and Zn were observed after the application of 90 t ha^{-1} of sewage sludge to the soil, especially for Zn. Regarding heavy metal content, Cr, Ni, and Zn were determined to predominate in the soil fertilized with sewage sludge. Additionally, concentrations of Cu were lowest compared to other observed heavy metals growing the different energy plants. Because heavy metals, notably Cu, can be fixed by insoluble high-molecular-weight organic acids such as humic acids, thus limiting their bioavailability in soil. Plants can also absorb Cu and Zn more easily than Pb and Ni, suggesting high mobility, in particular of Zn and Cu, reflecting their ease of extraction by plants [35]. The noticeable effect in decreasing Ni, Pb, and Zn concentrations in soil was observed in these treatments where the cup plant was grown. Growing common osier significantly reduced the concentration of Cu and Ni in soil. During the study, in determining the contents of heavy metals, we observed that the total amounts of heavy metals in treated soils did not exceed the limit values set forth in the Lithuanian environmental normative document LAND-20-2005 (Regarding the Lithuanian environmental protection normative document LAND 20-2005 "Requirements for the use of sewage sludge for fertilization"/Order of the Minister of the Republic of Lithuania: 2005 11 28) (Table 2).

Table 2. The maximum permissible concentration of heavy metals (MPC) in soil according to the Lithuanian environmental normative document LAND-20-2005.

Soil Granulometric Composition	Concentration of Heavy Metals, mg/kg				
	Pb	**Cr**	**Zn**	**Cu**	**Ni**
Sand	50	50	160	50	50
Loams, clays	80	80	300	75	75

Our data also suggest that the cultivation of common osier is linked to a reduction in the harmful impact of sewage sludge. The number of heavy metals determined in soil where common osier was grown was significantly lower (by 32–40% in 2017 and by 10–20% in 2020) compared to that determined after the cultivation of cup plant (Figure 2). This could be related to the common osier root structure, which reduces heavy metal toxicity, as well as to the phytoremediation capabilities. Additionally, the concentration of Zn increased twice and Pb 1.4 times compared to the unfertilized soil. In the soil, Zn can form complexes with organic ligands and precipitate with negatively charged ions [36,37]. Cation exchange and organic ligand complexation have been proposed as the key processes for immobilizing Zn. Furthermore, a decrease in soil acidity promotes the production of Zn sediments [38]. Comparing the findings obtained in this study with the other research works for cup plants treated with sewage sludge leads to an interesting tendency: the cup plants were found to be more sensitive to contamination with sewage sludge containing high concentrations of lead, and especially zinc, and demonstrated signs of soil toxicity. This suggests that the physiological processes of cup plant require copper, which accumulates in their biomass. This statement is also supported by the differences in the concentration of copper in the soil of these plants and in the soil not fertilized with sewage sludge.

Common osier showed an initial essential affirmative impact on diminishing the phytotoxicity of two main heavy metals (Zn and Pb) in acidic soil, whereas cup plant showed a slightly weaker effect in lowering the toxicity of heavy metals in the soil ecosystem. This suggests that soil treated with sewage sludge and planted with common osier creates a more favorable rhizosphere biota habitat. According to Matyka et al. [39], the common osier root structure protects the soil from erosion and improves carbon storage in the soil, which increases carbon sequestration and reduces nitrogen leaching and heavy metal toxicity, all of which contribute to improved soil quality. This decrease could also be attributed to a variety of factors, including the phytoremediation capabilities of common osier, among others. Oleszcuk [40] investigated the remediation capabilities of common osier against sludge-derived heavy metals, reporting a 17% reduction in heavy metals after 1.5 years of cultivation.

Under the continuing periodic incorporation of sewage sludge, contaminants such as heavy metals accumulate in the soil. As a result of the findings (Table 3), the heavy metals' amount in the soil changed between the period of 2017–2020.

Table 3. Changes in the selected heavy metals concentrations in soil under different contamination with sewage sludge levels by growing different energy plants.

Change in Heavy Metals Concentrations in Soil between 2017 (=100%) and 2020										
	Common Osier					**Cup Plant**				
	Cr	**Ni**	**Pb**	**Cu**	**Zn**	**Cr**	**Ni**	**Pb**	**Cu**	**Zn**
45 t ha^{-1} sewage sludge	+22.5	+0.9	+37.4	−44.4	+8.0	+34.3	+20.4	−13.9	+35.3	−19.2
90 t ha^{-1} sewage sludge	+13.1	−3.5	+21.8	−40.9	+0.82	+33.3	+34.6	−9.2	+12.8	−17.7

Moreover, the fluctuations of Ni and Zn content in a time when growing common osier were not as clear as those of the other heavy metals; these two metals did not show any tendencies to change over time. Other heavy metal concentrations (Cr and Pb) changed between 2017 and 2020, and the rate of increase has accelerated dramatically as a result of the sludge application. In addition, after the incorporation of 45 t ha^{-1} sewage sludge, a significant increase in heavy metal content in the soil was recorded. After the incorporation of sludge, the amount of Cr and Pb in previously unaffected soil increased by 22.5% and 37.4%, respectively, compared to their concentrations in 2017, although the concentrations of Cu reduced by 44.4%. This could result in Cu bioaccumulation in plants, harming both the ecological situation and human health through the food chain [41,42]. The highest rate (90 t ha^{-1}) of sewage sludge resulted in heavy metal content in the soil, which was comparable to the lowest rate (45 t ha^{-1}). This indicates that 45 t ha^{-1} is also an amount that substantially increases the content of heavy metals in the acid soil compared with unfertilized soil. Hence, the concentration of Ni tended to decrease (−3.5%) over time. The growth of different energy plants resulted in a significant change in heavy metal concentrations over time. When the cup plant was grown, significant changes were observed related to the changes in Ni, Pb, and Zn concentrations in the soil when both doses of the sewage sludge were applied (Table 3). Ni concentration increased by 20.4% and 34.6% after applying 45 and 90 t ha^{-1} of sewage sludge to the soil where cup plant was grown, respectively, compared with the soil with common osier. Concentrations of Zn and Pb decreased annually when cup plant was grown because their concentrations in soil were much lower compared to where common osier was grown. In comparison to the sewage sludge pollution levels, the concentrations of Zn and Pb in the soil decreased by 1.5 and 4.7 times, respectively, between these two heavy metals with decreasing tendencies. The amount of Cr and Ni increased in soil treated with sludge, whereas the amount of Cu, Zn, and Pb decreased over the period from 2017 to 2020.

3.2. Relationship between the Heavy Metals in Soil

In the soil, heavy metal ions compete for surface area with other functional groups and inorganic minerals [43]. The effectiveness of heavy metal immobilization in the soil can be reduced by interactions between heavy metal ions competing for areas where they can absorb. A greater positive correlation coefficient between metals indicates that they may have common sites for sorption, mutual dependency, and transporting behavior [44].

The dependency between the heavy metals was investigated by calculating correlation coefficients (Table 4).

Table 4. Dependency between heavy metals in soil contaminated with sewage sludge.

	Growing Common Osier						Growing Cup Plant				
	Cr	**Ni**	**Pb**	**Cu**	**Zn**		**Cr**	**Ni**	**Pb**	**Cu**	**Zn**
Cr	1	0.377	0.69 **	0.56 **	0.48 *	Cr	1	0.72 **	0.41	0.14	0.17
Ni		1	−0.08	0.01	0.08	Ni		1	0.18	0.38	−0.03
Pb			1	−0.69 **	0.39	Pb			1	0.11	0.79 **
Cu				1	−0.03	Cu				1	−0.25
Zn					1	Zn					1

Note: * and ** indicate significant differences at $p < 0.05$ and $p < 0.01$ levels, respectively, based on the least significant difference (LSD) test. Strong associations between heavy metals are represented by bold values.

During the study, significant relationships between heavy metals in soil were identified. Overall, growing different energy plants resulted in unequal dependences of heavy metals in the soil. The synergistic and antagonistic effects of soil heavy metals mainly focused on Cr, Pb, Zn, and Cu. The Cr content in the soil showed a positive and significant correlation with both Pb and Cu contents in the soil when growing common osier, indicating that Pb and Cu amount in the soil can increase Cr absorption. The amount of Pb in the soil demonstrated a strong negative dependence on the amount of Cu in the soil. In particular, Cr in the soil used to have a strengthening interaction on the crop's uptake of two heavy metals, Pb and Cu, but Pb in the soil had an antagonistic effect on the Cu content in the soil.

Differently, when growing cup plant, the Cr amount in the soil showed very strong and positive dependence with Ni content, as did Pb content with Zn content, with correlation coefficients of 0.72 and 0.79, respectively. Heavy metals have complicated interacting relationships, according to Zheng et al. [45]. In soil, Cr played a strengthening role in the uptake of Ni. Similarly, Pb had a synergistic effect on Zn content. Other heavy metals in the soil also altered the concentration of Cr and Pb in the soil. There were no significant relationships between the content of Cu and Ni in the soil and the amounts of other heavy metals (Pb, Cu, and Zn).

3.3. Determination of Contamination Risk Posed by Heavy Metals in Soil

Improvement of soil quality requires assessing contamination levels and potential risks, as well as identifying potential sources of contamination. Anthropogenically affected soil pollution has been the subject of numerous studies. However, the majority of them were primarily concerned with the pollution level. Because metals in soils can be found naturally or as a consequence of anthropogenic activity, an ecological risk assessment is required to understand the contamination patterns and contributions of various sources before applying effective soil evaluation criteria. Identification of possible pollution with heavy metals in the soil, such as the contamination factor and geo-accumulation index, especially taking into account treatment with sewage sludge, is necessary. Table 4 represents the contamination indices for each treatment. A C_f greater than one suggests a level of contamination that is likely to be anthropogenic [46]. For Cr, Ni, Pb, Cu, and Zn, indexes describing possible pollution indicate low to moderate possible contamination across treatments, showing significant contamination for all metals. Cu, Zn, and Pb are the most contaminating of the five heavy metals.

Depending on the particular toxicity of each metal, the potential ecological threat presented by heavy metal pollution levels was calculated using the potential ecological risk index, as shown in Table 5. The difficulty with this assessment is that it is discretionary and ignores the cumulative resistance of multiple metals [47]. According to the data, Cu poses a major ecological risk of the five metals evaluated. It has a moderate potential ecological risk in soil after fertilization with sewage sludge, whereas Cr, Ni, Pb, and Zn pose a low potential ecological risk at all study treatments. Cu is a biotoxic heavy metal that is recognized as a significant contaminant in agroecosystems. As a result, its presence in soils at levels exceeding acceptable heavy metal concentrations. Siebielec and Stuczyski [48] and Urbaniak et al. [20] obtained similar results. The heavy metal concentration of the investigated sludge was low, according to the authors, and it might be used for agricultural purposes.

Table 5. Metal contaminant factors (Cf) and potential ecological risk index (R_I) of heavy metals in soils contaminated by sewage sludge.

		Growing Common Osier		Growing Cup Plant	
		45 t ha^{-1} Sewage Sludge	**90 t ha^{-1} Sewage Sludge**	**45 t ha^{-1} Sewage Sludge**	**90 t ha^{-1} Sewage Sludge**
Cf	*Chromium*	1.03	1.10	1.05	1.04
E^i		2.06	2.20	2.10	2.08
Cf	*Nickel*	1.09	1.11	1.04	1.03
E^i		5.44	5.54	5.19	5.16
Cf	*Lead*	1.00	1.08	1.19	1.02
E^i		5.00	5.40	5.95	5.11
Cf	*Copper*	1.07	1.16	1.17	1.06
E^i		42.2	44.7	45.17	41.76
Cf	*Zinc*	1.15	1.24	1.44	1.16
E^i		1.15	1.24	1.44	1.16
R_I		55.84	59.14	59.86	55.27

Note: $E^i < 40$ denotes low potential ecological risk; $40 < E^i < 80$ denotes moderate ecological risk; $80 < E^i < 160$ denotes considerable ecological risk; $160 < E^i < 320$ denotes high ecological risk; $E^i > 320$ denotes very high ecological risk. $R_I < 95$ represents a low potential ecological risk; $95 < R_I < 190$ - moderate ecological risk; $190 < R_I < 380$ represents a considerable ecological risk; $R_I > 380$ represents very high ecological risk [23].

On the basis of all pollution indices, samples collected from soil contaminated with 90 t ha^{-1} sewage sludge and planted with common osier were the most contaminated, and the cumulative contamination level in the soil was in the arrangement of Zn > Cr > Pb > Ni > Cu. The presence of Cr, Ni, Pb, Cu, and Zn in soil was found to pose a moderate ecological risk for all of the treatments investigated, according to the overall R_I indices.

3.4. Heavy Metals Concentration in Plant Aboveground Biomass and Bioconcentration Factor

The accumulation of heavy metals in the aboveground biomass of selected energy plants is reported in Table 6. The analysis of heavy metal concentrations in plants' aboveground biomass was conducted in 2020. According to the obtained data, it was determined that an increase in sewage sludge significantly increased the accumulation of plant aboveground biomass. By increasing the sewage sludge dose from 45 t ha^{-1} to 90 t ha^{-1}, common osier showed a significantly higher concentration rate of all heavy metals except Ni. Common osier showed the highest concentration of Zn in their aboveground biomass at both sewage sludge rates. Similarly to common osier, cup plant showed a greater accumulation ability to accumulate Cu and Zn. By contrast, cup plant showed a greater ability to accumulate Cr and Ni compared to common osier. It should be noted that intensive bioaccumulation of metals in plants aboveground part is a very important feature for plants used for phytoextraction purposes [49].

In order to evaluate the plants' potential for phytoremediation, the bioconcentration factor (BCF) was calculated. In most plant species, the bioconcentration factor for heavy metals is usually less than 1, except for the hyperaccumulators, which are always higher. The greater BCF values show a higher accumulation of heavy metals in plants. In our study, it was determined that the intensity of metal uptake and potential of phytoremediation varies and depends on the plant species. The ability of two types of energy plants (common osier and cup plant) to absorb heavy metals is expressed as BCF (Figure 3).

Table 6. Heavy metals concentration in plant aboveground biomass under different contamination with sewage sludge levels by growing different energy plants.

Heavy Metals Concentration (mg kg^{-1}) in Plant Aboveground Biomass, 2020										
	Common Osier					Cup Plant				
	Cr	Ni	Pb	Cu	Zn	Cr	Ni	Pb	Cu	Zn
45 t ha^{-1} sewage sludge	0.11 ± 0.003	0.53 ± 0.126	0.45 ± 0.091	3.11 ± 0.267	48.40 ± 2.781	0.23 ± 0.113	0.88 ± 0.384	0.29 ± 0.093	5.76 ± 0.877	21.52 ± 1.574
90 t ha^{-1} sewage sludge	0.14 ± 0.012	0.46 ± 0.221	0.55 ± 0.0104	5.15 ± 1.063	57.28 ± 3.890	0.24 ± 0.074	1.37 ± 0.260	0.38 ± 0.001	8.97 ± 1.256	27.75 ± 3.219

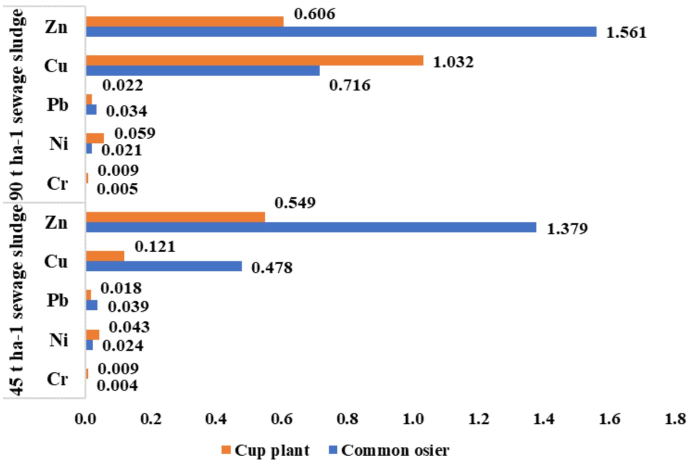

Figure 3. Bioconcentration factor of heavy metals under different rates of sewage sludge application.

The BCF for the heavy metals of plants in the soil treated with different rates of sewage sludge varied from 0.004 to 1.561. The results showed that both energy plants had a strong enrichment of copper and zinc, especially the cup plant, which showed a greater accumulation ability to accumulate this heavy metal. It was almost twice as great compared to common osier. However, the BCF for other heavy metals (chromium, nickel, lead) was relatively low, indicating that selected energy plants can only absorb but not accumulate these heavy metals. So, the varying accumulation of different heavy metals in plants determined in this study could be related to varying heavy metal bioavailability. These results could be associated with the fact that the application of sewage sludge led to higher retention of heavy metals; therefore, it positively influenced their availability toward the plan. Also, some authors considered that the content of organic matter in used sewage sludge affected the availability of heavy metals [50]. Some heavy metals like Zn are more mobile and bioavailable for plants than others. Such heavy metals can be easily taken up by plants from the soil [51]. Some heavy metals can be classified as readily bioavailable (Cd, Ni, Zn, As, Se, Cu), some as moderately bioavailable (Co, Mn, Fe), and some least available (Pb, Cr). The more readily bioavailable a heavy metal is, the greater the phytoremediation efficiency for such metal. In addition, the greater loss of some heavy metals (Cu and Zn) from the soils with growing both energy plants which was observed in this study, could be attributed to the growth of the plant providing suitable conditions for bioavailability, solubility, and removal of metals from the soil with plants than in soil without the plant.

4. Conclusions

The allocation of Cr, Ni, Pb, Cu, and Zn in the soil contaminated with various levels of sewage sludge was examined during this research. The amounts of heavy metals were rated in decreasing order in all research treatments: Zn > Cr > Ni > Pb > Cu. Cr, Ni, Pb, Cu, and Zn contents in the soil tended to rise steadily when the amount of sewage sludge increased from 45 to 90 t ha^{-1}. An increase in sewage sludge dose had no effect on the sequence of heavy metals but produced a significant increase in their concentrations in the soil. Growing different energy plants resulted in significant changes in the heavy metals concentrations over time. Throughout the time period of 2017 to 2020, Cu and Ni were significantly reduced by growing common osier, while Pb and Zn were reduced by growing cup plant. To investigate the interactions among heavy metals in the soil, the possibilities of contamination posed by heavy metals in soil were examined. Except for the accumulation of Zn, which exhibited significant potential ecological risk in the soil after fertilization with sewage sludge, the possible contamination level was mainly minimal for all experimental treatments. Based on the overall risk factors, a moderate ecological risk was identified for all studied treatments due to the presence of Cr, Ni, Pb, Cu, and Zn in soil. The study showed that all treatments had a low BCF for Cr, Ni, and Pb, which indicates that fewer heavy metals were in plant samples compared to the soil samples. Exceptionally, a very high BCF for Zn, where BCF of greater than 1 was observed in all study treatments. The obtained results point out that there is likely a risk of accumulation of Zn in the food chain, leading to health risks to humans and animals.

In conclusion, the findings revealed that sewage sludge could be used for farming, such as fertilizing degradable soil agents, increasing the cultivation of energy plants and soil restoration. The entire immobilization consequences and prospective environmental concerns of heavy metal discharge from sewage sludge must focus on future research to assure their long-term use for heavy-metal-contaminated soil restoration.

Author Contributions: Conceptualization, G.Š., D.K. and I.M.; methodology, G.Š. and I.M.; software, G.Š. and I.M.; validation, G.Š., I.M. and D.K.; formal analysis, G.Š. and R.R.; investigation, G.Š., I.M., D.K., R.R. and K.B.; resources, G.Š., I.M., and K.B.; data curation G.Š., I.M.; writing—original draft preparation, G.Š. and I.M.; writing—review and editing, G.Š., I.M., D.K., R.R., K.B. and O.A.; visualization, I.M. and D.K.; supervision G.Š. and O.A. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the EU European Regional Development Fund under the Interreg V-A South Baltic Cross-Border Co-operation Program 2014–2020 NR. STHB. 02.02.00–SE–0155/18 Baltic Phytoremediation (BARP) project (No. 2452016159).

Data Availability Statement: The data used to support the findings of this study will be available from the corresponding authors upon request.

Acknowledgments: The study was conducted in compliance with the long-term program "Plant biopotential and quality for multifunctional practice".

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

References

1. Saxena, G.; Bharagava, R.N. Organic and inorganic pollutants in industrial wastes, their ecotoxicological effects, health hazards and bioremediation approaches. In *Environmental Pollutants and Their Bioremediation Approaches*, 1st ed.; Bharagava, R.N., Ed.; CRC Press: Boca Raton, FL, USA, 2017; pp. 23–56. [CrossRef]
2. Ali, A.; Shaheen, S.M.; Guo, D.; Li, Y.; Xiao, R.; Wahid, F.; Azeem, M.; Sohail, K.; Zhang, T.; Alvarenga, P.; et al. Sewage sludge, compost, and other representative organic wastes as agricultural soil amendments: Benefits versus limiting factors. *Waste Manag.* **2020**, *40*, 44–52.
3. Wang, Y.; Zhang, L.; Wang, J.; Lu, J. Identifying quantitative sources and spatial distributions of potentially toxic elements in soil by using three receptormodels and sequential indicator simulation. *Chemosphere* **2020**, *242*, 125266. [CrossRef] [PubMed]
4. Yi, K.; Fan, W.; Chen, J.; Jiang, S.; Huang, S.; Peng, L.; Zeng, Q.; Luo, S. Annual input and output fluxes of heavy metals to paddy fields in four types of contaminated areas in Hunan Province, China. *Sci. Total Environ.* **2018**, *634*, 67–76. [CrossRef] [PubMed]
5. Jiang, X.; Zou, B.; Feng, H.; Tang, J.; Tu, Y.; Zhao, X. Spatial distribution mapping of Hg contamination in subclass agricultural soils using GIS enhanced multiple linear regression. *J. Geochem. Explor.* **2018**, *196*, 1–7. [CrossRef]
6. Payá Pérez, A.; Rodríguez Eugenio, N. *Status of Local Soil Contamination in Europe: Revision of the Indicator "Progress in the Management Contaminated Sites in Europe"*; EUR 29124 EN.; Publications Office of the European Union: Luxembourg, 2018; ISBN 9789279800726.
7. Ali, H.; Khan, E.; Sajad, M.A. Phytoremediation of heavy metals—Concepts and applications. *Chemosphere* **2013**, *91*, 869–881. [CrossRef]
8. Chandra, R.; Saxena, G.; Kumar, V. Phytoremediation of Environmental Pollutants: An Eco-Sustainable Green Technology to Environmental Management. In *Advances in Biodegradation and Bioremediation of Industrial Waste*; Chandra, R., Ed.; CRC Press: Boca Raton, FL, USA, 2015; pp. 1–29. [CrossRef]

9. Mahar, A.; Wang, P.; Ali, A.; Awasthi, M.K.; Lahori, A.H.; Wang, Q.; Li, R.; Zhang, Z. Challenges and opportunities in the phytoremediation of heavy metals contaminated soils: A review. *Ecotoxicol. Environ. Saf.* **2016**, *126*, 111–121. [CrossRef]
10. Muthusaravanan, S.; Sivarajasekar, N.; Vivek, J.S.; Paramasivan, T.; Naushad, M.; Prakashmaran, J.; Gayathri, V.; Al-Duaij, O.K. Phytoremediation of heavy metals: Mechanisms, methods and enhancements. *Environ. Chem. Lett.* **2018**, *16*, 1339–1359. [CrossRef]
11. Fijalkowski, K.; Rosikon, K.; Grobelak, A.; Hutchison, D.; Kacprzak, M.J. Modification of properties of energy crops under Polish condition as an effect of sewage sludge application onto degraded soil. *J. Environ. Manag.* **2018**, *217*, 509–519. [CrossRef]
12. Karcauskiene, D.; Repsiene, R.; Ambrazaitiene, D.; Skuodiene, R.; Jokubauskaite, I. Soil pH control, ecological and agro-nomic assessment in agroecosystem. In *Soil pH for Nutrient Availability and Crop Performance*; IntechOpen: London, UK, 2018; pp. 47–71.
13. Kacprzak, M.; Neczaj, E.; Fijałkowski, K.; Grobelak, A.; Grosser, A.; Worwag, M.; Rorat, A.; Brattebo, H.; Almås, Å.; Singh, B.R. Sewage sludge disposal strategies for sustainable development. *Environ. Res.* **2017**, *156*, 39–46. [CrossRef]
14. Chu, S.; Wu, D.; Liang, L.L.; Zhong, F.; Hu, Y.; Hu, X.; Lai, C.; Zeng, S. Municipal sewage sludge compost promotes Mangifera persiciforma tree growth with no risk of heavy metal contamination of soil. *Sci. Rep.* **2017**, *7*, 1–11. [CrossRef]
15. Antonkiewicz, J.; Kołodziej, B.; Bielińska, E.J. The use of reed canary grass and giant miscanthus in the phytoremediation of municipal sewage sludge. *Environ. Sci. Pollut. Res.* **2016**, *23*, 9505–9517. [CrossRef]
16. Wyrwicka, A.; Urbaniak, M. The biochemical response of willow plants (*Salix viminalis* L.) to the use of sewage sludge from various sizes of wastewater treatment plant. *Sci. Total Environ.* **2018**, *615*, 882–894. [CrossRef] [PubMed]
17. Grobelak, A.; Placek, A.; Grosser, A.; Singh, B.R.; Almås, R.; Napora, A.; Kacprzak, M. Effects of single sewage sludge application on soil phytoremediation. *J. Clean. Prod.* **2016**, *155*, 189–197. [CrossRef]
18. Wiesmeier, M.; Lungu, M.; Hübner, R.; Cerbari, V. Remediation of degraded arable steppe soils in Moldova using vetch as green manure. *Solid Earth* **2015**, *6*, 609–620. [CrossRef]
19. Glenn, E.P.; Jordan, F.; Waugh, W.J. Phytoremediation of a Nitrogen-Contaminated Desert Soil by Native Shrubs and Microbial Processes. *Land Degrad. Dev.* **2016**, *28*, 361–369. [CrossRef]
20. Urbaniak, M.; Wyrwicka, A.; Tołoczko, W.; Serwecińska, L.; Zieliński, M. The effect of sewage sludge application on soil properties and willow (*Salix* sp.) cultivation. *Sci. Total Environ.* **2017**, *586*, 66–75. [CrossRef]
21. von Cossel, M.; Amarysti, C.; Wilhelm, H.; Priya, N.; Winkler, B.; Hoerner, L. The replacement of maize (*Zea mays* L.) by cup plant (*Silphium perfoliatum* L.) as biogas substrate and its implications for the energy and material flows of a large biogas plant. *Biofuels Bioprod. Biorefining* **2019**, *14*, 152–179. [CrossRef]
22. Sumalan, R.L.; Muntean, C.; Kostov, A.; Kržanović, D.; Jucsor, L.; Ciulca, S.I.; Cernicova-Buca, M. The cup plant (*Silphium perfoliatum* L.)—A viable solution for bioremediating soils polluted with heavy metals. *Not Bot. Horti. Agrobot. Cluj Napoca* **2020**, *48*, 2095–2113. [CrossRef]
23. Maanan, M.; Saddik, M.; Maanan, M.; Chaibi, 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]
24. Hakanson, L. An ecological risk index for aquatic pollution control: A sediment logical approach. *Water Res.* **1980**, *14*, 975–1001. [CrossRef]
25. Jiang, F.; Ren, B.; Hursthouse, A.; Deng, R. Evaluating health risk indicators for PTE exposure in the food chain: Evidence from a thallium mine area. *Environ. Sci. Pollut. Res.* **2020**, *27*, 23686–23694. [CrossRef] [PubMed]
26. Peng, C.; Tong, H.; Shen, C.; Sun, L.; Yuan, P.; He, M.; Shi, J. Bioavailability and translocation of metal oxide nanoparticles in the soil-rice plant system. *Sci. Total Environ.* **2020**, *713*, 136662. [CrossRef] [PubMed]
27. Bai, Y.; Zang, C.; Gu, M.; Gu, C.; Shao, H.; Guan, Y.; Wang, X.; Zhou, X.; Shan, Y.; Feng, K. Sewage sludge as an initial fertility driver for rapid improvement of mudflat salt-soils. *Sci. Total Environ.* **2017**, *578*, 47–55. [CrossRef] [PubMed]
28. Herzel, 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]
29. Rigby, H.; Clarke, B.O.; Pritchard, D.L.; Meehan, B.; Beshah, F.; Smith, S.R.; Porter, N.A. A critical review of nitrogen mineralization in biosolids-amended soil, the associated fertilizer value for crop production and potential for emissions to the environment. *Sci. Total Environ.* **2016**, *541*, 1310–1338. [CrossRef]
30. Nascimento, A.L.; de Souza, A.J.; Oliveira, F.C.; Coscione, A.R.; Viana, D.G.; Regitano, J.B. Chemical attributes of sewage sludges: Relationships to sources and treatments, and implications for sludge usage in agriculture. *J. Clean. Prod.* **2020**, *258*, 120746. [CrossRef]
31. Jones, V.; Gardner, M.; Ellor, B. Concentrations of trace substances in sewage sludge from 28 wastewater treatment works in the UK. *Chemosphere* **2014**, *111*, 478–484. [CrossRef]
32. Gautam, M.; Agrawal, M. Influence of metals on essential oil content and composition of lemongrass (*Cymbopogon citratus* (DC) Stapf.) grown under different levels of red mud in sewage sludge amended soil. *Chemosphere* **2017**, *175*, 315–322. [CrossRef]
33. Mohamed, B.; Mounia, K.; Aziz, A.; Ahmed, H.; Rachid, B.; Lotfi, A. Sewage sludge used as organic manure in Moroccan sun-flower culture: Effects on certain soil properties, growth, and yield components. *Sci. Total Environ.* **2018**, *627*, 681–688. [CrossRef]
34. Jama, A.; Nowak, W. Willow (*Salix viminalis* L.) in purifying sewage sludge treated soils. *Pol. J. Agron* **2012**, *9*, 3–6.

35. Lee, M.H.; Han, S.J.; Lee, Y.K.; Ike, I.A.; Ok, Y.S.; Hur, J. Enhancing copper binding property of compost-derived humic sub-stances by biochar amendment: Further insight from two-dimensional correlation spectroscopy. *J. Hazard. Mater.* **2020**, *390*, 121–128. [CrossRef] [PubMed]
36. Lu, K.; Yang, X.; Gielen, G.; Bolan, N.; Ok, Y.S.; Niazi, N.K.; Xu, S.; Yuan, G.; Chen, X.; Zhang, X.; et al. Effect of bamboo and rice straw biochars on the mobility and redistribution of heavy metals (Cd, Cu, Pb and Zn) in contaminated soil. *J. Environ. Manag.* **2017**, *186*, 285–292. [CrossRef] [PubMed]
37. Gao, J.; Zhao, T.; Tsang, D.C.; Zhao, N.; Wei, H.; Feng, M.; Liu, K.; Zhang, W.; Qiu, R. Effects of Zn in sludge-derived biochar on Cd immobilization and biological uptake by lettuce. *Sci. Total Environ.* **2020**, *714*, 136721. [CrossRef] [PubMed]
38. Zhang, W.; Huang, X.; Jia, Y.; Rees, F.; Tsang, D.C.W.; Qiu, R.; Wang, H. Metal immobilization by sludge-derived biochar: Roles of mineral oxides and carbonized organic compartment. *Environ. Geochem. Health* **2016**, *39*, 379–389. [CrossRef] [PubMed]
39. Matyka, M. Polish agriculture and crop production for energy purposes. In *Studies and Reports IUNG—PIB*; *Monogr. Rozpr. Nauk*; IUNG—PIB: Puławy, Poland, 2009; pp. 167–174.
40. Oleszczuk, P. Phytotoxicity of municipal sewage sludges compost related to physico-chemical properties, PAHs and heavy metals. *Ecotoxicol. Environ. Saf.* **2008**, *69*, 496–505. [CrossRef]
41. Bourioug, M.; Gimbert, F.; Alaoui-Sehmer, L.; Benbrahim, M.; Aleya, L.; Alaoui-Sossem, B. Sewage sludge application in a plan-tation: Effects on trace metal transfer in soil-plant-snail continuum. *Sci. Total Environ.* **2015**, *502*, 309–314. [CrossRef]
42. Obiora, S.C.; Chukwu, A.; Chibuike, G.; Nwegbu, A.N. Potentially harmful elements and their health implications in cultivable soils and food crops around lead-zinc mines in Ishiagu, Southeastern Nigeria. *J. Geochem. Explor.* **2019**, *204*, 289–296. [CrossRef]
43. Deng, Y.; Huang, S.; Laird, D.A.; Wang, X.; Meng, Z. Adsorption behavior and mechanisms of cadmium and nickel on rice straw biochar's in single- and binary-metal systems. *Chemosphere* **2019**, *218*, 308–318. [CrossRef]
44. Suresh, G.; Ramasamy, V.; Meenakshisundaram, V.; Venkatachalapathy, R.; Ponnusamy, V. Influence of mineralogical and heavy metal composition on natural radionuclide concentrations in the river sediments. *Appl. Radiat. Isot.* **2011**, *69*, 1466–1474. [CrossRef]
45. Zheng, S.; Wang, Q.; Yuan, Y.; Sun, W. Human health risk assessment of heavy metals in soil and food crops in the Pearl River Delta urban agglomeration of China. *Food Chem.* **2020**, *316*, 126213. [CrossRef]
46. Nouri, M.; Haddioui, A.E.M. Assessment of metals contamination and ecological risk in ait Ammar abandoned iron mine soil, Morocco. *Ekologia* **2016**, *35*, 32–49. [CrossRef]
47. Morkunas, I.; Woźniak, A.; Mai, V.C.; Rucińska-Sobkowiak, R.; Jeandet, P. The Role of Heavy Metals in Plant Response to Biotic Stress. *Molecules* **2018**, *23*, 2320. [CrossRef] [PubMed]
48. Siebielec, G.; Stuczyński, T. Trace metals in municipal sewage sludge produced in Poland. *Proc. ECOpole* **2008**, *2*, 479–484.
49. Ghazaryan, K.A.; Movsesyan, H.S.; Minkina, T.M.; Nevidomskaya, D.G.; Rajput, V.D. Phytoremediation of cop-per-contaminated soil by Artemisia absinthium: Comparative effect of chelating agents. *Environ. Geochem. Health* **2022**, *44*, 1203–1215. [CrossRef]
50. del Mar Delgado, M.; de Imperial, R.M.; González, I.; Lobo, C.; Plaza, A.; Martínez, S.; Martín, J.V. Phytoremediation potential of thistle (*Cynara Cardunculus* L.) and its ability to remove heavy metals from polluted soils with high rates of sewage sludge. *Pol. J. Environ. Stud.* **2017**, *26*, 1935–1941. [CrossRef]
51. Pam, A.A.; Sha'Ato, R.; Offem, J.O. Evaluation of heavy metals in soils around auto mechanic workshop clusters in Gboko and Makurdi, Central Nigeria. *J. Environ. Chem. Ecotoxicol.* **2013**, *5*, 298–306.