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The Effect of Sludge-Ash Granulates on the Content and Uptake of Heavy Metals by Winter Rape Seeds and Triticale

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Abstract: Four granulates were prepared from waste, including lignite ash, industrial sludge, sawdust, ammonium nitrate and potassium salt (60% K_2O). The produced granulates were chemically tested. They contained significant Ca and C organic contents and slightly less S, P, K and Mg. The concentration of Cd, Cr, Cu, Ni, Pb and Zn did not exceed the applicable standards. Then, they were tested in a experiment with 2 plants: spring rape, *Larissa* cv., and spring triticale, *Milikaro* cv. The content of the tested heavy metals in rape seed and triticale grain largely depended on the chemical properties and the amount of components used to produce granulates. As a rule, a higher share of industrial sludge and a lower share of lignite ash (granulates II with industrial sludge 40% and IV with industrial sludge 50%) in the granulates increased the content of heavy metals in the test plants. Applying the 2nd and 3rd doses of granulates increased the contents of cadmium, copper, chromium, nickel, lead, and zinc. Increasing doses of granulates significantly increased the uptake of heavy metals by rape seed and triticale grain. Under the influence of applied fertilizer granulates, the content of heavy metals in rape seeds and triticale grain was significantly positively correlated with their uptake.

Keywords: fertilization; granulates from waste; content and uptake of heavy metals; cultivate species; correlations

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1. Introduction

The threats resulting from environmental pollution make it necessary to regularly monitor the content of heavy metals and toxic substances in plants, soil, water, and air [1,2]. Due to rapidly developing civilization and thus chemicalization, the ecological balance in nature and the economy has been disturbed. The dynamic development of industry and irrational use of fertilising waste in agriculture, e.g., industrial and municipal sewage sediment and coal combustion ashes, contribute to the excessive accumulation of heavy metals in plants and soils, threatening humans and animals [2–7].

Plants intended for consumption are a include natural source of heavy metals. Therefore, they are a threat to the health quality of agricultural produce [8,9]. The source of contamination with heavy metals in cultivated plants is the soil, and their concentration depends on the content of these elements in the parent rock and the course of soil-forming processes. Most heavy metal compounds are readily soluble in the soil solution and therefore are easily absorbed by plants [10]. Agricultural soils may become contaminated with heavy metals through excessive and inappropriate use of mineral and organic fertilizers, liming, composts made from waste or fertilizers obtained, for example, from industrial sludge leachate, which, apart from nutrients and organic matter, also contains metals that quickly accumulate in the soil [6]. Increasing the amount of organic matter in mineral soils limits crop plant uptake of heavy metals. Therefore, it is advisable to successfully supplement soils with organic matter from, for example, waste, organic-mineral or organic fertilizers produced with their participation. Applying phosphorus to the soil reduces the uptake of heavy metals by plants because, with a higher content of its easily soluble forms, sparingly soluble zinc, cadmium, lead, and copper phosphates may precipitate. However, using potassium fertilisation can increase the availability of heavy metals for plants [11,12].

Among crops, rape seed is currently the second most frequently produced oilseed. The main producers are China, India, Canada and the European Union. The increase in rape seed cultivation area results from the increase in the consumption of vegetable oils by people and the demand for feed protein. In addition, the attractiveness of rape seed cultivation is influenced by its high profitability [13,14]. Cereal cultivation also increases. The coronavirus pandemic affected the economy, as a greater demand for cereal products was shown [15,16]. Currently cereal cultivation is carried out in the world on 728 million ha including triticale on 3,809,192 ha [17].

Fertilizers are critical to agricultural production, according to the IMF, and global demand for them increased by 6.3% in 2021, which, combined with supply disruptions, pushed prices up by 78.6% [18,19], that's why it began acquisition of new sources of organic matter and nutrients for plants. On the other hand, the intensive development of technological processes to produce innovative human goods generates much waste. This waste should be reused or disposed of following legal provisions. Thermal utilisation is expensive, so attempts are made to manage or process raw waste. Many wastes are characterised by a reasonably high content of organic matter and essential nutrients for plants. They may also contain excessive amounts of heavy metals and other chemical compounds that may harm the environment. Therefore, various wastes, preparations, or substances of fertilising importance are tested to determine their impact on soil fertility indices, the size and quality of plant yields and their impact on the environment [20–27].

The research was carried out to verify the hypothesis that the accumulation of heavy metals by the two tested crops is related to the presence of industrial sewage sludge. It was assumed that as a result of the research, the knowledge about the impact of selected fertilizer granulates on the development of two basic crops and the uptake of toxic metals by them will be enriched. The experiment aimed to test four sediment-ash granulates applied in three doses on spring rape and spring triticale produced from waste. Was a utilitarian goal heavy metal content was determined, the heavy metal uptake by rape seed and triticale grain was calculated, and the correlation between the content and uptake was determined. In the presented work, comprehensive research was carried out for the first time in an experiment covering the effect of four types of granulates produced from waste on the content and uptake of heavy metals by two basic species of crops.

The pot experiment showed that the granulates produced from waste had a positive effect on the growth and qualitative characteristics of cultivated plants. The waste used to produce granulates was a source of macronutrients and heavy metals. Chemical analysis of industrial sewage sludge, lignite ash and sawdust showed that the content of heavy metals does not exceed the permissible values, which allows for their soil application and use in agriculture. Therefore, a strict field experiment should be carried out on two types of soil (light and heavy) with several groups of crops. Such an experiment will provide practical knowledge for farmers and the production of granulates from waste on a larger scale.

2. Materials and Methods

2.1. Experimental Part

Considering the chemical properties of the various waste, recipes for the material composition of four granulates with the participation of industrial sludge, lignite ash, sawdust, ammonium nitrate and potassium salt (60% K_2O) were developed. For the production of sludge-ash granulates, the following were selected: industrial from the sewage treatment plant of the Chemical Plant Grupa "Azoty" in Police (53°34′26″ N, 14°32′42″ E in West Pomeranian Voivodeship, in Poland), ash from the combustion of lignite in a power plant "Adamów" S.A located in Konin (52°18′04.5″ N, 18°14′02.8″ E in Wielkopolska Voivodeship, in Poland) and a 1:1 mixture of sawdust from hardwood and coniferous trees from the sawmill in Pucice (53°27′13.107″ N, 14°44′39.194″ E in West

Pomeranian Voivodeship, in Poland). The material composition of fertilizer granulates is given below:

I granules—30% industrial sewage sludge, 30% ash, 10% sawdust, 15% ammonia phosphate, 15% potassium salt;

II granules—40% industrial sewage sludge, 20% ash, 10% sawdust, 15% ammonia phosphate, 15% potassium salt;

III granules—20% industrial sewage sludge, 40% ash, 10% sawdust, 15% ammonia phosphate, 15% potassium salt;

IV granules—50% industrial sewage sludge, 20% ash, 10% sawdust, 10% ammonia phosphate, 10% potassium salt.

The produced sediment-ash granulates were used for experiments. The plants tested were spring rape, *Larisa* cv., and spring triticale, *Milikaro* cv.

The chemical analysis carried out indicates that the industrial sewage sludge had an alkaline reaction (8.60) and contained 28% dry matter (DM). It had little organic carbon content (2.10%) and nitrogen (2.40 g·kg^{-1} DM). The ash from the combustion of lignite was characterized by a strongly alkaline reaction (11.8) and a significant content of dry matter (98.0%). It did not contain organic carbon and nitrogen. Total contents of calcium (14.5 g·kg^{-1} DM), magnesium (1.75 g·kg^{-1} DM) and sulfur (4.20 g·kg^{-1} DM) in relation to the content of phosphorus (6.70 g·kg^{-1} DM) and potassium (1.20 g·kg^{-1} DM) were considerable. The mixture of sawdust from deciduous and coniferous trees contained significant amounts of dry matter, organic carbon and nitrogen (5.90 g·kg^{-1} DM), and little phosphorus (0.39 g·kg^{-1} DM), potassium (0.45 g·kg^{-1} DM), calcium (0.90 g·kg^{-1} DM) and magnesium (0.96 g·kg^{-1} DM). The content of heavy metals in the waste used for the production of granulates is given in the Table 1.

Table 1. Content of heavy metals in waste used for the production of fertilizer granulates.

Metal	Waste		
	Industrial Sewage Sludge	**Brown Coal Ash**	**Sawdust Mixture**
	Total Content in mg·kg^{-1} DM		
Cd	0.82	1.95	0.16
Cu	22.0	25.6	4.25
Cr	8.85	12.5	1.60
Ni	13.8	12.0	0.80
Pb	52.0	14.2	2.30
Zn	120.0	220	38.4

The content of heavy metals in the waste used to produce fertilizer granulates was low. The concentration level of these elements was below the permissible levels. Table 2 presents the content of heavy metals in the produced granulates. Whereas in Table 3, the doses of applied granulates to the soil are presented.

Table 2. The content of heavy metals in the produced sludge-ash granulates.

Metal	Fertilizer Granulates			
	I	**II**	**III**	**IV**
	Total Content in mg·kg^{-1} DM			
Cd	0.83	0.72	0.95	0.80
Cr	6.50	6.12	6.85	7.02
Cu	14.5	14.1	14.9	16.4
Ni	7.77	7.92	7.18	9.28
Pb	19.9	23.5	16.0	28.8
Zn	105	95	115	107

Table 3. Doses of applied granulates introduced in g/pot.

Type of Granulates (G*)	Doses (D**)		
	1	2	3
I	14	28	42
II	15	30	45
III	14	28	42
IV	20	40	60

G*—type of granulates, D**—doses of granulates.

The soil material with the granulometric composition of firm loamy sand classified as good rye complex, valuation class IVb, was used for the plants research. The soil material used for the study was slightly acidic (pH_{KCl} 6.0). The chemical properties of the soil are given in Table 4. The content of forms available for plants of phosphorus, potassium, and magnesium was average. The total content of heavy metals of cadmium, copper, chromium, nickel, lead, and zinc tested in the soil it was not over-standard for plant cultivation the contained in the Regulation of the Minister of the Environment [28].

Table 4. Indicators of soil fertility before setting up the experiment [29].

pH_{KCl}	C_{org} $g \cdot kg^{-1}$ DM	Total Content of Heavy Metals $mg \cdot kg^{-1}$ DM						C:N	The Content of the Assimilable Forms $mg \cdot kg^{-1}$ DM		
		Cd	Cr	Cu	Ni	Pb	Zn		P	K	Mg
6.0	9.63	0.22	8.80	8.60	7.12	12.8	35.7	11.2	60.9	121.0	42.5

Two factors were considered in the scheme of experiments. The first factor was the types of fertilizer granulates (4), and the second was their increasing doses (3). Each experimental subject was carried out in four replicates.

The soil material collected for testing was sieved through a sieve with a mesh size of 5 mm to remove more significant impurities. Then, 9 kg soil was transferred to the vases. The doses of granulates were determined based on their nitrogen content. Single, doubled and tripled doses were 0.24 g N·pot, 0.48 g N·pot and 0.72 g N·pot, which corresponded to 80 kg $N \cdot ha^{-1}$, 160 kg $N \cdot ha^{-1}$ and 240 kg $N \cdot ha^{-1}$.

In spring, the calculated doses of granulates were introduced into vases with soil and mixed to a depth of 3–4 cm. Seeds of spring rape *Larissa* cv. and grains of spring triticale *Milikaro* cv. were sown in 20 pieces each. Pots with soil and test plants were sprinkled with distilled water while maintaining soil moisture at 60% of the total water capacity. After rape seed and triticale reached a height of 10 cm, the selection was made, leaving 5 plants in vases.

For top dressing in all pots, both test plants were fertilized with N (nitrogen) in the form of CH_4N_2O (urea) five weeks after the emergence of rape seed and triticale during the shoot-out period. The nitrogen dose per 1 ha was 92 kg N, i.e., 200 $kg \cdot ha^{-1}$ urea. It was calculated per 1 pot with a value of 0.276 g nitrogen. Nitrogen fertilizer was used in the form of a water solution.

2.2. Analysis Methods

After reaching production maturity, the test plants were collected, and samples were taken for laboratory tests. Then, rape seeds and triticale grain were subjected to chemical analyses in two repetitions.

The total content of heavy metals (Cd, Cr, Cu, Zn, Ni, Pb) in plants and fertilizer granulates was determined by mineralizing them in a mixture of 70% $HClO_4$ and 65% NHO_3 acids and analyzing the filtrates using a PerkinElmer AAS 300 atomic emission spectrometer (Scientific Instruments, Athens, Greece) [30]. Spectral purity reagents and standard Aldrich solutions were used for chemical analyses. The determinations in each of the analyzed samples were made in duplicate. The accuracy of the analytical methods was verified based on certified reference materials and standard solutions: IAEA-V-10-Hay Powder (International Atomic Energy Agency, Vienna, Austria). Heavy metal intake was calculated by multiplying the yield by the content of a given heavy metal. The correlations between heavy metal content and uptake in both test plants were calculated.

Statistical elaboration of the test results was performed with a two-factor analysis of variance in the randomised blok system. To arrangements the importance of differences, Tukey's confidence half-intervals were used for the level of p = 0.05, using the FR-ANALWAR program, according to Rudnicki. In addition, between the content of heavy metals and their uptake in rape seed and triticale grain, the Pearson linear correlation coefficient r was calculated. The significance of the correlation was calculated with the participation of the Student's T test.

3. Results and Discussion

The quality of plant yields depends, among others, on the heavy metals (Cd, Cu, Cr, Ni, Pb, Zn). The effects of sediment-ash granulates on the content and uptake of heavy metals by rape seeds and triticale grains are presented in Tables 5 and 6.

Table 5. Content of Cd, Cu, Cr, Ni, Pb and Zn in rape seeds (in mg·kg^{-1} DM) to pot under the effect of sludge-ash granulates.

Type of Granulates (G*)	Cd				Cu			
	Dose (D)							
	1	2	3	Mean	1	2	3	Mean
I	0.025	0.027	0.030	0.027	4.28	4.36	4.63	4.42
II	0.033	0.035	0.037	0.035	4.78	5.08	5.29	5.05
III	0.028	0.029	0.029	0.029	4.60	4.78	4.93	4.77
IV	0.036	0.035	0.039	0.035	5.00	5.30	5.65	5.32
Mean	0.030	0.032	0.034	0.032	4.66	4.88	5.12	4.89
Control	0.021				3.43			
	$LSD_{0.05}$ G—0.002; D—0.001; G × D—0.003				$LSD_{0.05}$ G—0.099; D—0.077; G × D—0.172			
	Cr				Ni			
I	21.7	25.6	25.7	24.3	0.27	0.29	0.33	0.30
II	22.4	26.7	29.6	26.2	0.30	0.40	0.47	0.39
III	22.7	26.2	29.6	26.2	0.33	0.39	0.39	0.37
IV	24.0	31.6	33.5	29.7	0.58	0.61	0.69	0.63
Mean	22.7	27.5	29.6	26.6	0.37	0.42	0.47	0.42
Control	20.00				0.21			
	$LSD_{0.05}$ G—0.685; D—0.532; G × D—1.186				$LSD_{0.05}$ G—0.048; D—0.037; G × D—n.s.			
	Pb				Zn			
I	0.62	0.73	0.88	0.74	21.8	23.9	24.5	23.4
II	0.67	0.78	0.87	0.77	22.1	24.1	24.6	23.6
III	0.64	0.70	0.73	0.69	23.0	23.9	24.8	23.9
IV	0.74	0.81	0.88	0.81	24.8	26.6	27.2	26.2
Mean	0.67	0.75	0.84	0.75	22.9	24.6	25.3	24.3
Control	0.39				18.70			
	$LSD_{0.05}$ G—0.029; D—0.023; G × D—0.051				$LSD_{0.05}$ G—0.629; D—0.489; G × D—n.s.			

* Full material composition of fertilizer granulates is given in Sections 2 and 2.1. n.s.—insignificant difference.

Table 6. Content of Cd, Cu, Cr, Ni, Pb and Zn in triticale (in mg·kg^{-1} DM) to pot under effect of sludge-ash granulates.

Type of Granulates (G*)	Cd				Cu			
	Dose (D)							
	1	2	3	Mean	1	2	3	Mean
I	0.031	0.034	0.036	0.034	4.34	4.58	4.96	4.63
II	0.032	0.037	0.038	0.036	4.26	4.68	4.78	4.57
III	0.033	0.036	0.039	0.036	4.27	4.44	4.49	4.40
IV	0.039	0.042	0.043	0.041	4.42	4.66	4.83	4.64
Mean	0.034	0.037	0.039	0.037	4.32	4.59	4.76	4.56
Control	0.029				3.98			
$LSD_{0.05}$ G—0.004; D—0.003; G × D—n.s.					$LSD_{0.05}$ G—0.090; D—0.070; G × D—0.156			
	Cr				Ni			
I	13.45	16.30	17.05	15.60	0.27	0.29	0.33	0.30
II	15.20	16.85	17.30	16.45	0.38	0.43	0.49	0.43
III	14.60	15.10	15.30	15.00	0.29	0.32	0.35	0.32
IV	16.40	17.10	18.10	17.20	0.29	0.32	0.35	0.32
Mean	14.91	16.34	16.94	16.06	0.39	0.48	0.51	0.36
Control	13.15				0.26			
$LSD_{0.05}$ G—0.344; D—0.267; G × D—0.596					$LSD_{0.05}$ G—0.042; D—0.033; G × D—n.s.			
	Pb				Zn			
I	0.71	0.76	0.79	0.75	36.20	37.75	38.40	37.45
II	0.79	0.87	0.88	0.85	39.05	40.55	41.85	40.48
III	0.66	0.73	0.77	0.72	35.45	37.30	38.05	36.93
IV	0.84	0.88	0.97	0.90	39.75	41.05	42.40	41.07
Mean	0.75	0.81	0.85	0.80	37.61	39.16	40.17	38.98
Control	0.37				30.00			
$LSD_{0.05}$ G—0.037; D—0.029; G × D—n.s.					$LSD_{0.05}$ G—0.597; D—0.464, G × D—n.s.			

* Full material composition of fertilizer granulates is given in Sections 2 and 2.1. n.s—insignificant difference.

Rape seeds from the objects where granulate II with 40% industrial sludge and 20% ash and fertilizer granulate IV with 50% industrial sludge and 20% ash were used contained more heavy metals compared to the objects where granulate I with 30% industrial sludge and 30% ash, granulate III with 20% industrial sludge and 40% ash and compared to the control (Table 5). Differences in the effect of fertilizers I (30% industrial sludge), II (40% industrial sludge), III (20% industrial sludge) and IV (50% industrial sludge) on the content of copper, chromium, nickel, lead and zinc in rape seeds were significant. On the other hand, the highest amount of cadmium in rape seeds was found as a result of using granulates II and IV compared to granulates I and III. Increasing doses of granulates did not differentiate the cadmium content in the test plant.

Increasing doses of granulates significantly increased the contents of cadmium, copper, chromium, nickel, lead, and zinc in the seeds of the test plant. The difference in the effect between the 1st and 2nd doses of granulates on the content of cadmium and nickel in the seeds of the test plant was insignificant (Table 5). The applied third dose of granulates significantly increased the content of the metals tested in spring rape.

The applied granulates in the experience increased the average content of Cr, Cu, Ni, Pb, Zn and Cd, in rape seeds compared to the control by 33.0%, 42.6%, 52.4%, 92.3%, 98.7% and 100%, respectively. The most significant increase in the content of cadmium, lead, and nickel was found between the 1st and 3rd doses of applied granulate I (30% industrial sludge) by 20%, 41.9% and 12.4%, respectively. The applied granulate II (40% industrial sludge) contributed to the increase between the 1st and 3rd doses of copper by 10.7% and nickel by 56.7%. Fertilizer granulate IV (50% industrial sludge) had the greatest impact on the increase in chromium content in rape seeds between the 1st and 3rd dose by 39.6%. Analysing the effect of the applied granulates on the concentration of the tested heavy metals in rape seeds, it was found that the second dose of granulate II (40% industrial sludge) caused an increase in the content of copper, nickel, and lead by 6.27%, 19.2% and 16.4%, respectively, compared to the first dose hey. On the other hand, granulate IV (50% industrial sludge) had a significant effect between the 1st and 2nd applied doses on the increase in the content of chromium by 31.7% and zinc by 7.25%.

Triticale grain from objects where granulate II with 40% of industrial sludge and 20% of ash and fertilizer granulate IV with 50% of industrial sludge and 20% of ash was used contained more cadmium, chromium, nickel, lead, and zinc compared to objects where granulate I with 30% industrial sludge and 30% ash was used, granulate III with 20% industrial sludge and 40% ash and in relation to the control object (Table 6). However, the copper content in the triticale grain was significantly higher in the object with granulates I and IV than in granulates II and III and in the control.

Differences in influence the effect of granulates I (30% industrial sludge), II (40% industrial sludge), III (20% industrial sludge) and IV (50% industrial sludge) on the content ofcadmium, copper, chromium, nickel, lead, and zinc in triticale grain were significant. On the other hand, the highest amounts of cadmium, copper, chromium, lead, and zinc in triticale grain were found when granulate IV was used compared to granulates I, II and III. Fertilizer granulate II (40% industrial sludge) contributed to the highest increase of nickel content in triticale grain in comparison with other granules.

Increasing doses of granulates had a significant effect on the increased the contents of cadmium, copper, chromium, nickel, lead, and zinc in the grain of the test plant.The difference in the effect between the 1st and 2nd doses of granulates on the content of cadmium, nickel and lead in triticale grain was insignificant. The applied third dose of granulates significantly increased the content of the tested metals in the test plant.

Fertilizer granulates applied I (30% industrial sludge), II (40% industrial sludge), III (20% industrial sludge) and IV (50% industrial sludge) increased the contents of copper, chromium, cadmium, zinc, nickel and lead in triticale grain compared to the control by 14.6%, 22.1%, 27.6%, 29.9%, 38.46% and 116.2%, respectively. The highest increase in the content of copper and chromium was obtained between the 1st and 3rd doses of granulate I, by 14.3% and 26.8%, respectively. The applied granulate II contributed to the increase between the 1st and 3rd doses of nickel by 28.9%, zinc by 7.17%, and between the 1st and 2nd doses of cadmium by 15.6%. On the other hand, granulate IV had the most important impact on the extension in lead content by 15.5% in the seed of the test plant between the 1st and 3rd doses. Analysing the effect of the applied granulates on the concentration of the tested heavy metals in triticale grain, it was found that the second dose of granulate II caused an increase in the content of copper, nickel, and lead by 9.86%, 13.2% and 4.76%, respectively, compared to the first dose hey. On the other hand, granulate I had a significant effect between the 1st and 2nd doses applied to increase the chromium content by 21.2%, and granulate III caused an increase in the zinc content by 5.21%.

Crops contain 7.5 mg of Cd, 17.5 mg of Cu, 17.5 mg of Cr, 55 mg of Ni, 165 mg of Pb and 250 mg of Zn in one kilogram of dry matter. Comparing your own results, we found that cadmium, copper, nickel, lead, and zinc content in rape seeds and triticale grain in all fertilisation objects was lower than average [31]. On the other hand, the content of chromium in the seeds of the test plant obtained under the influence of the applied fertilization was higher than average, but it was in the range of 5–30 mg·kg^{-1} DM [31]. A similar relationship was found in the case of triticale grain. Based on the literature data, the level of heavy metal content in the tested plants can be considered satisfactory. The contents of cadmium, nickel, and zinc in rape seeds were lower, and copper, chromium, and lead were higher compared to the results obtained by Krzywy and Możdżer [32], who tested fertilizer granulates with municipal sewage sediment and other waste. Analysing the content of heavy metals under the influence of the applied granulates in triticale grain, it was found that there was less cadmium and zinc, more chromium and lead, and copper and nickel in similar amounts concerning the content given in the literature [32]. It has also been proven that fertilisation of minerals with phosphorus, depending on the source of phosphorites and apatites used for their production, may contain heavy metals and thus contribute to an increase in cadmium content in the soil and, thus, in crop plants [12,33,34].

The lowest amount of heavy metals was taken up by spring rape seeds as a result of the application of III fertilizer granulate (20% share of industrial sludge and 40% share of ash). The uptake of heavy metals by the seeds of the test plant on this object was significantly lower compared to the other fertilisation objects of the experiment.

Increasing doses of fertilizer granulates significantly increased the uptake of cadmium, copper, chromium, nickel, lead, and zinc by the seeds of the test plant (Table 7). The second dose of granulate I (30% industrial sludge) did not cause a significant change in nickel uptake by spring rape seeds analysed in relation to the first. The third dose of granulate III (20% industrial sludge) did not cause a significant increase in the intake of copper, chromium, cadmium, nickel and lead, and the dose of granulate IV (50% industrial sludge) significantly reduced the intake of heavy metals compared to the second dose. The highest uptake of cadmium, copper, nickel, chromium, nickel and lead was found between the 1st and 3rd doses of granulate II used: 46.1%, 53.8%, 55.5%, 73.7%, 84.1% and 114.3%, respectively.

Table 7. Uptake of Cd, Cu, Cr, Ni, Pb and Zn in rape seeds (in mg·kg^{-1} DM) to pot under the effect of sludge-ash granulates.

Type of Granulates (G*)	Cd				Cu			
	Dose (D)							
	1	2	3	Mean	1	2	3	Mean
I	0.26	0.29	0.38	0.31	0.045	0.047	0.059	0.050
II	0.27	0.32	0.42	0.34	0.039	0.047	0.060	0.049
III	0.22	0.28	0.27	0.26	0.037	0.046	0.046	0.043
IV	0.29	0.46	0.38	0.38	0.041	0.064	0.055	0.053
Mean	0.26	0.34	0.36	0.32	0.040	0.051	0.055	0.049
Control	0.11				0.018			
	$LSD_{0.05}$ G—0.023; D—0.017; G × D—0.039				$LSD_{0.05}$ G—0.001; D—0.001; G × D—n.s.			
	Cr				Ni			
I	0.23	0.27	0.33	0.28	2.80	3.10	4.10	3.30
II	0.19	0.24	0.33	0.25	2.45	3.70	5.25	3.80
III	0.18	0.25	0.27	0.23	2.60	3.65	3.70	3.32
IV	0.20	0.38	0.32	0.30	4.70	7.30	6.60	6.20
Mean	0.20	0.29	0.31	0.27	3.14	4.44	4.90	4.16
Control	0.10				1.05			
	$LSD_{0.05}$ G—0.008; D—0.006; G × D—0.014				$LSD_{0.05}$ G—0.426; D—0.331; G × D—0.738			
	Pb				Zn			
I	6.50	7.80	10.95	8.42	0.23	0.26	0.31	0.27
II	5.35	7.20	9.85	7.47	0.18	0.22	0.28	0.23
III	5.05	6.70	6.70	6.15	0.19	0.23	0.24	0.22
IV	6.00	9.70	8.45	8.05	0.20	0.32	0.26	0.26
Mean	5.73	7.85	8.99	7.52	0.20	0.26	0.27	0.24
Control	2.00				0.10			
	$LSD_{0.05}$ G—0.361; D—0.281; G × D—0.625				$LSD_{0.05}$ G—0.008; D—0.006; G × D—0.014			

* Full material composition of fertilizer granulates is given in Sections 2 and 2.1. n.s.—insignificant difference.

A seeds took up significantly more heavy metals from objects fertilised with granulates compared to the control (Table 8). As a rule, granulates II and IV, with a higher share of industrial sludge (respectively 40% and 50%), caused a significantly higher uptake of heavy metals by the grain of the test plant than granulates I (30% industrial sludge) and III (20% industrial sludge), with a higher share of ash. The differentiation of the effect of granulated fertilizers II and IV on the uptake of chromium and zinc by spring triticale grain were significant. Similarly, granulates I and III significantly differed in the uptake of cadmium, copper, chromium, nickel, lead, and zinc by the grain of the analysed plants.

Table 8. Uptake of Cd, Cu, Cr, Ni, Pb and Zn in triticale (in mg·kg^{-1} DM) to pot under the effect of sludge-ash granulates.

Type of Granulates (G*)	Cd				Cu			
	Dose (D)							
	1	2	3	Mean	1	2	3	Mean
I	0.41	0.55	0.61	0.52	0.06	0.07	0.08	0.07
II	0.46	0.72	0.73	0.63	0.06	0.09	0.09	0.08
III	0.26	0.27	0.44	0.32	0.03	0.03	0.05	0.04
IV	0.60	0.69	0.74	0.67	0.07	0.08	0.08	0.08
Mean	0.43	0.56	0.63	0.54	0.05	0.07	0.08	0.07
Control	0.19				0.03			
	$LSD_{0.05}$ G—0.053; D—0.041; G × D—0.091				$LSD_{0.05}$ G—0.002; D—0.001; G × D—n.s.			
	Cr				Ni			
I	0.18	0.26	0.29	0.24	3.43	4.63	5.45	4.50
II	0.21	0.32	0.33	0.29	5.30	8.31	9.36	7.66
III	0.11	0.11	0.17	0.13	2.26	2.28	3.85	2.79
IV	0.24	0.28	0.31	0.28	5.87	7.85	8.81	7.51
Mean	0.19	0.24	0.28	0.24	4.21	5.77	6.87	5.62
Control	0.09				1.69			
	$LSD_{0.05}$ G—0.008; D—0.006; G × D—0.014				$LSD_{0.05}$ G—0.726; D—0.564; G × D—1.257			
	Pb				Zn			
I	9.15	12.13	13.26	11.51	0.47	0.60	0.64	0.57
II	11.16	16.82	16.72	14.90	0.55	0.79	0.80	0.71
III	5.10	5.24	8.99	6.31	0.28	0.27	0.42	0.32
IV	12.57	14.39	16.76	14.57	0.60	0.68	0.73	0.67
Mean	9.49	12.14	13.83	11.82	0.48	0.59	0.65	0.57
Control	2.41				0.20			
	$LSD_{0.05}$ G—0.619; D—0.481; G × D—1.072				$LSD_{0.05}$ G—0.010; D—0.008; G × D—0.018			

* Full material composition of fertilizer granulates is given in Sections 2 and 2.1. n.s.—insignificant difference.

The increase in granulates doses significantly increased the uptake of cadmium, copper, chromium, nickel, lead and zinc by spring triticale grain (Table 8). The second dose of granulate III did not cause significant changes in the intake of heavy metals. The third dose of granulate II did not cause a significant increase in the uptake of copper, cadmium and lead by triticale grain and of copper granulate IV in comparison to the second dose applied.

The highest uptake of zinc, copper, lead, chromium, cadmium, nickel, and by triticale grain was obtained between the 1st and 3rd doses of granulate II (40% industrial sludge) applied, with values of 45.4%, 49.8%, 50.0%, 57.1%, 58.6% and 76.6%, respectively. The application of granulate I (30% industrial sludge) between the 1st and 2nd doses resulted in higher cadmium intake by 34.0%, copper intake by 16.6%, chromium intake by 44.4%, nickel intake by 34.9%, lead intake by 32.5%, and zinc intake by 27.6%. On the other hand, granulate III (20% industrial sludge) had no significant effect on the test plant's uptake of the tested heavy metals. Granulate IV (50% industrial sludge) between the 1st and 2nd doses had the most significant impact on nickel uptake by 33.7% and zinc uptake by 21.6%.

The research results indicate that the uptake of heavy metals by rape seeds was arranged in the following series of decreasing values: Pb > Ni > Cd > Cr > Zn > Cu, and by triticale grain Pb > Ni > Zn > Cd > Cr > Cu. Moreno [35] found that the amount of heavy metals taken up by crop plants, i.e., barley grain can be represented as a series: Zn > Cu > Cd > Ni. This confirms the thesis that the content and uptake of nutrients and heavy metals in crops depend primarily on the species and even the cultivar of the plant [36].

Fertilizer granulates I (30% industrial sludge), II (40% industrial sludge), III (20% industrial sludge) and IV (50% industrial sludge) made from waste and applied significantly increased the content of heavy metals in rape and triticale grain compared to the control object. The level of heavy metal content in the test plants was lower than the toxic concentration of these elements for cultivated plants [31]. The results of research on the effect of granulates from industrial sludge on the quality of rape seeds and triticale grains indicate that their effects depend on the amount and chemical properties of individual components. The research showed that the greater the share of industrial sludge and the smaller the share of lignite ash in the granulates, the more heavy metals the test plants contained (granulates II and IV). These results are confirmed by research conducted by [25,37]. Among many wastes used in agriculture on the European Union (EU) the sludges introduced more stringent requirements in comparison with the directive, currently regulated only by the limits of heavy metals (Cd, Cu, Hg, Ni, Pb and Zn) listed in Council Directive 86/278/EEC [38].

The test results showed a relationship (significant at $p < 0.05$) between the test plant content and uptake of heavy metals. Under the influence of fertilizer granulates, the content of heavy metals in rape seeds and triticale grain was significantly positively correlated (r) with their uptake (Table 9). The correlation analysis showed a very high degree of correlation between the content of heavy metals in spring rape obtained under the impact of fertilizer granulates and the uptake of nickel, a high degree of correlation between the content and uptake of lead and chromium, and an average between the content and uptake of copper, zinc, and cadmium by rape seeds. The value of the correlation coefficients ranged from $r = 0.507$ to $r = 0.906$. The highest correlation coefficient value was found in rape seeds between the content and uptake of nickel ($r = 0.906$)—Figures 1 and 2.

The correlation analysis showed a high degree of interdependence between the content of heavy metals in triticale grains obtained under the influence of fertilizer granulates and the uptake of cadmium, nickel and copper, as well as a very high degree of interdependence between the content and uptake of zinc. The value of the correlation coefficients ranged from $r = 0.491$ to $r = 0.849$. The highest value of the correlation coefficient was found in the triticale grain between the content and uptake of lead, chromium, and zinc (0.829; 0.840; 0.849). It was found that the relationship between the content and uptake of heavy metals by test plants increased under the influence of increasing doses of applied fertilizer granulates. Statistical analysis of the obtained test results confirmed significant relationships between the content and uptake of heavy metals by rape seed and triticale grain. The literature also pointed out the relationship between the content of micronutrients in plants and the activity of enzymes in the soil [39–41].

Table 9. Correlation between the content and uptake of heavy metals by test plants.

Metal	Correlation between the Content and Intake of Heavy Metals			
	Rape Seed		Triticale Grain	
	p	*r*	*p*	*r*
Cd	0.026	0.653	0.104	0.491
Cu	0.092	0.507	0.007	0.726
Cr	0.002	0.798	0.001	0.840
Ni	0.002	0.906	0.016	0.673
Pb	0.001	0.806	0.002	0.829
Zn	0.036	0.607	0.002	0.849

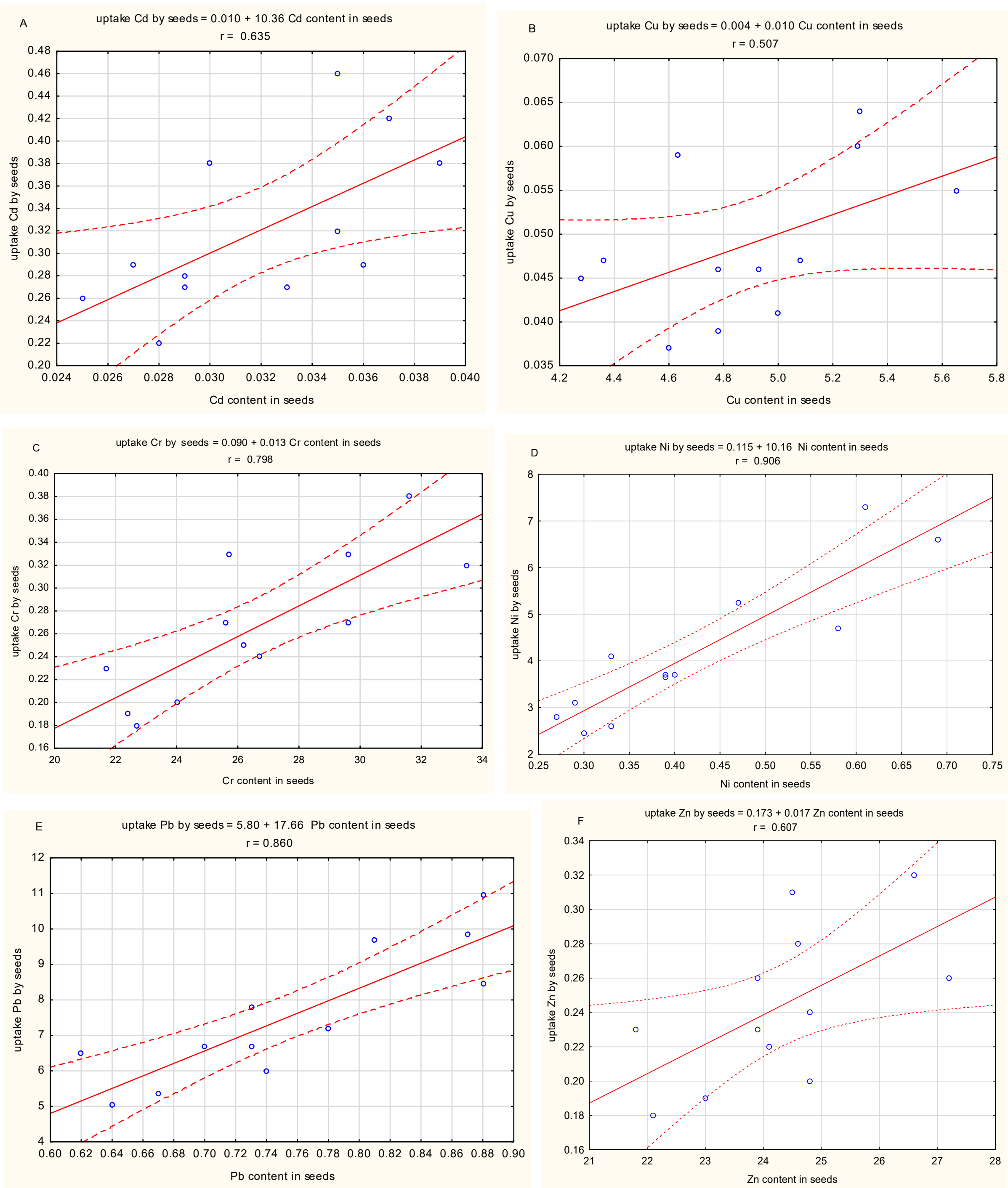

Figure 1. Rectilinear relationship between the content and uptake of heavy metals by rape seeds under the influence of applied fertilizer granulates in mg·kg^{-1} DM.

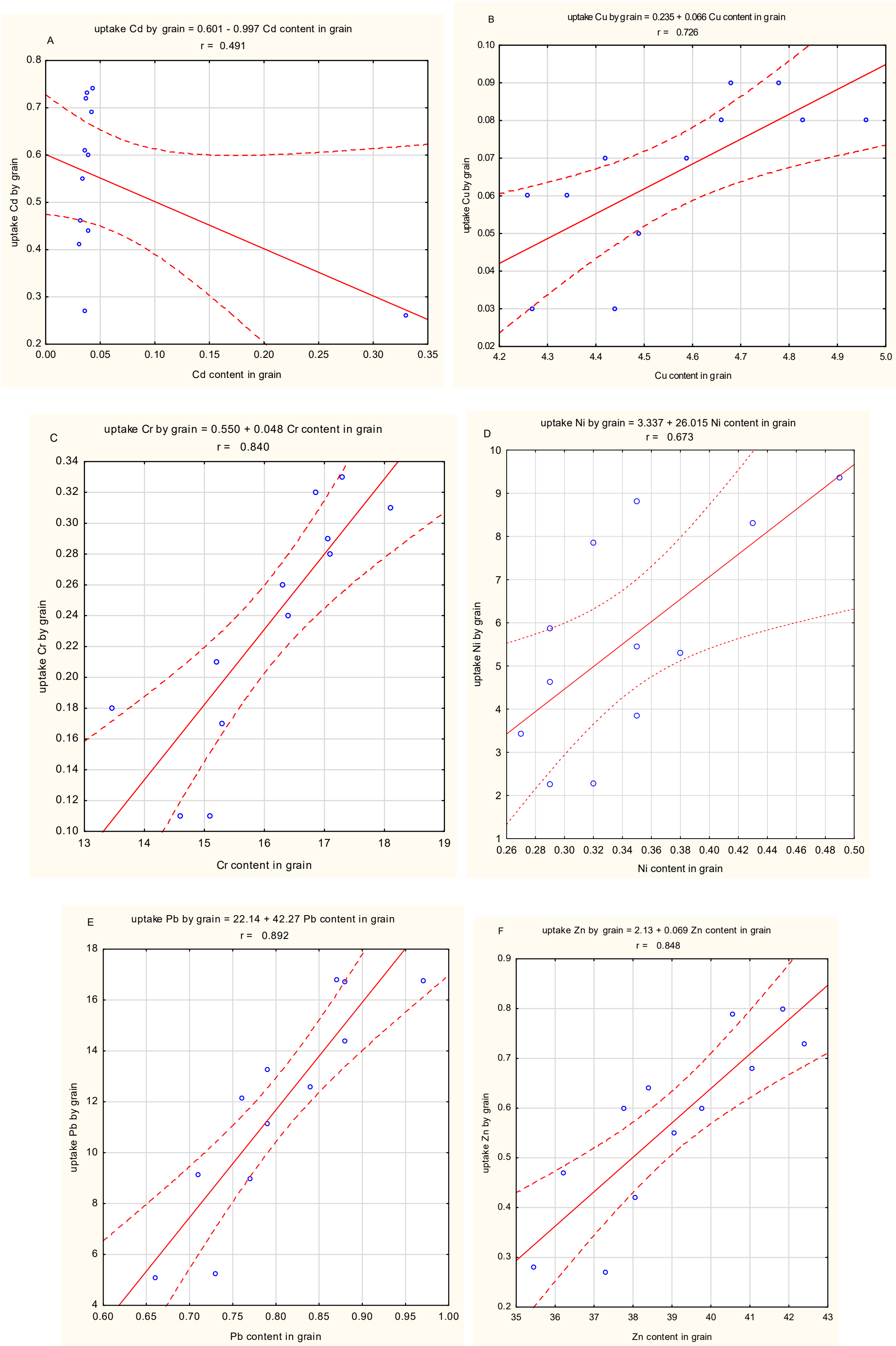

Figure 2. Rectilinear relationship between the content and uptake of heavy metals by triticale grain under the influence of applied fertilizer granulates in mg·kg^{-1} DM.

4. Conclusions

The experiment carried out indicate that fertilizer granulates increased the content of heavy metals in the test plants. The hypothesis of an increased accumulation of heavy metals in rape seed and triticale grain in the presence of granulate with the highest % share of industrial sewage sludge (granulate IV—50%) was confirmed. Increasing doses of granulates increased the content of heavy metals in the test plants, but the differences were not always significant. The tested granulates I—30%, II—40%, and III—20% significantly increased the content of heavy metals in rape seeds and triticale grains compared to the control. The studies showed that rape seed and triticale grain from the objects fertilised with granulate IV contained the highest amount of heavy metals and the least in the test plants fertilised with granulate I and III. The size of the applied dose significantly affected the concentration of heavy metals in the test plants. The applied granulate II significantly increased the uptake of the tested metals by both test plants. The applied doses of fertilizer granulates significantly increased the uptake of cadmium, copper, chromium, nickel, lead, and zinc by rape seed and triticale grain. There is a correlation between the content and uptake of heavy metals by rape seed and triticale grain as a result of the applied fertilization. The pot experiment showed that the granules produced from waste had a positive effect on the growth and qualitative characteristics of cultivated plants. The waste used to produce granulates was a source of macronutrients and heavy metals. Chemical analysis of industrial sewage sludge, lignite ash and sawdust showed that the content of heavy metals does not exceed the permissible values, which allows for their soil application and use in agriculture. Therefore, a strict field experiment should be carried out on two types of soil (light and heavy) with several groups of crops. Such an experiment will provide practical knowledge for farmers and the production of granulates from waste on a larger scale.

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References

1. Chen, Y.-G.; He, X.-L.-S.; Huang, J.-H.; Luo, R.; Ge, H.-Z.; Wołowicz, A.; Wawrzkiewicz, M.; Gładysz-Płaska, A.; Li, B.; Yu, Q.-X.; et al. Impacts of heavy metals and medicinal crops on ecological systems, environmental pollution, cultivation, and production processes in China. *Ecotoxicol. Environ. Saf.* **2021**, *219*, 112336. [CrossRef] [PubMed]
2. Xiang, M.; Li, Y.; Yang, J.; Lei, K.; Li, Y.; Li, F.; Zheng, D.; Fang, X.; Cao, Y. Heavy metal contamination risk assessment and correlation analysis of heavy metal contents in soil and crops. *Environ. Pollut.* **2021**, *278*, 116911. [CrossRef] [PubMed]
3. Chen, Y.; Ma, J.; Miao, C.; Ruan, X. Occurrence and environmental impact of industrial agglomeration on regional soil heavy metalloid accumulation: A case study of the Zhengzhou Economic and Technological Development Zone (ZETZ), China. *J. Clean. Prod.* **2020**, *245*, 118676. [CrossRef]
4. Yang, G.-H.; Zhu, G.-Y.; Li, H.-L.; Han, X.-M.; Li, J.-M.; Ma, Y.-B. Accumulation and bioavailability of heavy metals in a soil-wheat/maize system with long-term sewage sludge amendments. *J. Integr. Agric.* **2018**, *17*, 1861–1870. [CrossRef]
5. Antonkiewicz, J.; Kowalewska, A.; Mikołajczak, S.; Kołodziej, B.; Bryk, M.; Spychaj-Fabisiak, E.; Koliopoulos, T.; Babula, J. Phytoextraction of heavy metals after application of bottom ash and municipal sewage sludge considering the risk of environmental pollution. *J. Environ. Manag.* **2022**, *306*, 114517. [CrossRef]

6. Mishra, S.; Bharagava, R.N.; More, N.; Yadav, A.; Zainith, S.; Mani, S.; Chowdhary, P. Heavy metal contamination: An alarming threat to environment and human health. In *Environmental Biotechnology: For Sustainable Future*; Sobti, R., Arora, N., Kothari, R., Eds.; Springer: Singapore, 2019; pp. 103–125. Available online: https://link.springer.com/chapter/10.1007/978-981-10-7284-0_5 (accessed on 10 November 2022).
7. Ahmad, W.; Alharthy, R.D.; Zubair, M.; Ahmed, M.; Hameed, A.; Rafique, S. Toxic and heavy metals contamination assessment in soil and water to evaluate human health risk. *Sci. Rep.* **2021**, *11*, 17006. [CrossRef]
8. 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]
9. Hembrom, S.; Singh, B.; Gupta, S.K.; Nema, A.K. A comprehensive evaluation of heavy metal contamination in foodstuff and associated human health risk: A global perspective. In *Contemporary Environmental Issues and Challenges in Era of Climate Change*; Singh, P., Singh, R., Srivastava, V., Eds.; Springer: Singapore, 2020; pp. 33–64. [CrossRef]
10. Uchimiya, M.; Bannon, D.; Nakanishi, H.; McBride, M.B.; Williams, M.A.; Yoshihara, T. Chemical speciation, plant uptake, and toxicity of heavy metals in agricultural soils. *J. Agric. Food Chem.* **2020**, *68*, 12856–12869. [CrossRef]
11. Pogrzeba, M.; Rusinowski, S.; Krzyżak, J. Macroelements and heavy metals content in energy crops cultivated on contaminated soil under different fertilization—Case studies on autumn harvest. *Environ. Sci. Pollut. Res.* **2018**, *25*, 12096–12106. [CrossRef]
12. Qaswar, M.; Yiren, L.; Jing, H.; Liu, K.; Mudasir, M.; Zhenzhen, L.; Hongqian, H.; Xianjin, L.; Jianhua, J.; Ahmed, W.; et al. Soil nutrients and heavy metal availability under long-term combined application of swine manure and synthetic fertilizers in acidic paddy soil. *J. Soils Sediments* **2020**, *20*, 2093–2106. [CrossRef]
13. Carré, P.; Pouzet, A. Rape seed market, worldwide and in Europe. *Oilseeds Fats, Crops Lipids* **2014**, *21*, D102. [CrossRef]
14. Woźniak, E.; Waszkowska, E.; Zimny, T.; Sowa, S.; Twardowski, T. The rape seed potential in Poland and Germany in the context of production, legislation, and intellectual property rights. *Front. Plant Sci. Sec. Plant Breed.* **2019**, *10*, 1423. [CrossRef] [PubMed]
15. Küçüközdemir, Ü. Tritikale, breeding and cultivation, Chapter 12. In *Theoretical and Practical New Approaches in Cereal Science and Technology*; Karaman, M., Ed.; Iksad Publishing House: Ankara, Turkey, 2021; pp. 321–365. Available online: https://www.researchgate.net/profile/Mehmet-Duezguen/publication/353737691_Determination_and_Evaluation_of_Quality_Parameters_in_Cool_Climate_Cereals/links/61248c510c2bfa282a66bfde/Determination-and-Evaluation-of-Quality-Parameters-in-Cool-Climate-Cereals.pdf#page=328 (accessed on 5 November 2022).
16. Uçar, Ö. Chapter 15—The situation of cereals cultivation in the world and Turkey. In *New Approaches and Applications in Agriculture*; Baran, M.F., Ed.; Iksad Publishing House: Ankara, Turkey, 2020; pp. 328–344. Available online: https://www.researchgate.net/profile/Oezge-Ucar-3/publication/351619381_THE_SITUATION_OF_CEREALS_CULTIVATION_IN_THE_WORLD_AND_TURKEY/links/60a18bd4a6fdcccacb5d1c76/THE-SITUATION-OF-CEREALS-CULTIVATION-IN-THE-WORLD-AND-TURKEY.pdf (accessed on 5 November 2022).
17. FAO. Annual population 2020. Available online: https://www.fao.org/faostat/en/#data/OA (accessed on 4 November 2022).
18. Oxford Analytica. Fertilizer and Food Prices Could be High for Years. Emerald Expert Briefings 2022. ISSN: 2633-304X. Available online: https://dailybrief.oxan.com/Analysis/DB268415/Fertiliser-and-food-prices-could-be-high-for-years (accessed on 3 January 2023).
19. Ritchie, H.; Roser, M.; Rosado, P. Fertilizers. Published Online at OurWorldInData.org. 2022. Available online: https://ourworldindata.org/fertilizers (accessed on 5 November 2022).
20. Dwibedi, S.K.; Sahu, S.K.; Pandey, V.C.; Rout, K.K.; Behera, M. Seedling growth and physicochemical transformations of rice nursery soil under varying levels of coal fly ash and vermicompost amendment. *Environ. Geochem. Health* **2021**, *45*, 319–332. [CrossRef] [PubMed]
21. Gamrat, R.; Tomaszewicz, T.; Chudecka, J.; Stankowski, S.; Wróbel, M.; Nowak, G. Plant communities in the lysimeter experiment of ash reclamation in the Dolna Odra Power Station in Nowy Czarnów. *Pol. J. Soil Sci.* **2018**, *7*, 271–282. [CrossRef]
22. Gamrat, R.; Tomaszewicz, T.; Hury, G.; Wysocka, G. Study on the content of heavy metals in plants which occupy active ash settling ponds of the Dolna Odra Power Plant. *J. Elem.* **2018**, *23*, 217–229. [CrossRef]
23. Swati, Y.; Pandey, V.C.; Kumar, M.; Singh, L. Plant diversity and ecological potential of naturally colonizing vegetation for ecorestoration of fly ash disposal area. *Ecol. Engin.* **2022**, *176*, 106533. [CrossRef]
24. Pawelec, K.; Siwek, H.; Włodarczyk, M.; Kitczak, T. Fertilization with municipal wastewater phosphorus adsorbed to alginate beads: Results from a pot experiment with italian ryegrass. *Agronomy* **2021**, *11*, 2142. [CrossRef]
25. Krzywy, E.; Ciubak, J.; Cydzik, E.; Możdżer, E.; Kucharska, M. The use of municipal sewage sludge and lignite coal fly ashes in the production of fertilizer granulates. *Chemik* **2012**, *11*, 1163–1168. Available online: https://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-article-BPP4-0001-0173/ (accessed on 5 November 2022).
26. Krzywy, E.; Możdżer, E.; Wołoszyk, C. Use of industrial wastes to produce fertilizer blends. *Przem. Chem.* **2013**, *92*, 1261–1263.
27. Varshney, A.; Dahiya, P.; Sharma, A.; Pandey, R.; Mohan, S. Fly ash application in soil for sustainable agriculture: An Indian overview. *Energ. Ecol. Environ.* **2022**, *7*, 340–357. [CrossRef]
28. Regulation of the Minister of Natural Environment on How to Conduct Land Surface Pollution Assessment Dated 1 September 2016. Official Journal of 1365 of 2016. Available online: https://www.infor.pl/akt-prawny/DZU.2016.173.0001395,rozporzadzenie-ministra-srodowiska-w-sprawie-sposobu-prowadzenia-oceny-zanieczyszczenia-powierzchni-ziemi.html (accessed on 4 November 2022). (In Polish)

29. Możdżer, E.; Jałoszyński, S.; Jarnuszewski, G. The impact of sludge-ash granulates produced with the use of industrial waste on the yield and quality characteristics of test plants. *Fresenius Environ. Bull.* **2020**, *29*, 4886–4895.
30. Jones, J.B., Jr.; Case, V.V. Sampling, handling, and analyzing plant tissue samples. In *Soil Testing and Plant Analysis*, 3rd ed.; SSSA Book Series, 3; Westerman, R.L., Ed.; Soil Science Society of America: Madison, WI, USA, 1990; pp. 389–427.
31. Kabata-Pendiasa, A. Trace elements in soils and plants, 4th edition. *Expl. Agric.* **2011**, *47*, 548. [CrossRef]
32. Krzywy, E.; Możdżer, E. The effect of granular fertilizers produced from industrial and municipal wastes on the content of some heavy metals in test plants. *Chemik* **2013**, *67*, 628–635. (In Polish)
33. Mwstefa, S.B.; Ahmed, I.T. Effect of phosphorus fertilization on phytoremediation efficacy of heavy metals by wheat and bean plants. *ZANCO J. Pure Appl. Sci. Off. Sci. J. Salahaddin Univ.-Erbil* **2019**, *31*, 18–27.
34. Pradika, V.; Masykuri, M.; Supriyadi, S. Farmer awareness to the dangers of heavy metal Cadmium (Cd) pollution due to over-fertilization in Sragen Regency Central Java. *Caraka Tani J. Sustain. Agric.* **2019**, *34*, 76–85. [CrossRef]
35. Moreno, J.L.; Garcia, C.; Hernandez, T.; Pascual, J.A. Transference of heavy metals from a calcareous soil amended with sewage sludge compost to barley plants. *Bioresour. Technol.* **1997**, *3*, 251–258. [CrossRef]
36. Jiwan, S.; Ajay, S.K. Effects of heavy metals on soil, plants, human health and aquatic life. *Int. J. Res. Chem. Environ.* **2011**, *1*, 15–21. Available online: http://www.ijrce.org/index.php/ijrce/article/view/78 (accessed on 5 November 2022).
37. Łabętowicz, J.; Stępień, W.; Kobiałak, M. Innovative waste treatment technologies for agroecological utility fertilizers. *Ecol. Eng.* **2019**, *20*, 13–23. [CrossRef]
38. Hudcová, H.; Vymazal, J.; Rozkošný, M. Present restrictions of sewage sludge application in agriculture within the European Union. *Soil Water Res.* **2019**, *14*, 104–120. [CrossRef]
39. Styrczula, P.; Możdżer, E. Effect of multi-component mineral fertilizers and organic fertilization on the NPK content and uptake by perennial rye-grass biomass. *Chemik* **2013**, *67*, 604–615. (In Polish)
40. Różyło, K.; Bohacz, J. Microbial and enzyme analysis of soil after the agricultural utilization of biogas digestate and mineral mining waste. *Int. J. Environ. Sci. Technol.* **2020**, *17*, 1051–1062. [CrossRef]
41. Sharma, S.; Dhaliwal, S.S. Effect of sewage sludge and rice straw compost on yield, micronutrient availability and soil quality under rice–wheat system. *Commun. Soil Sci. Plant Anal.* **2019**, *50*, 1943–1954. [CrossRef]