

Article

The Effect of Different Doses of Sewage Sludge and Liming on Total Cobalt Content and its Speciation in Soil

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Received: 25 August 2020; Accepted: 8 October 2020; Published: 11 October 2020



Abstract: The aim of this paper is to evaluate the effect of liming and various doses of municipal sewage sludge (5, 10, and 15% of the weight of the soil) on cobalt total content and its speciation. The incubation experiment lasted 420 days and was conducted in controlled laboratory conditions. Soil was sampled after 30, 60, 90, and 120 days and then, with a break of 180 days, after 360 and 420 days. In all samples, cobalt total content was determined by means of ICP-AES (emission spectrophotometer), and fractions of this metal were measured with the seven-step Zeien and Brümmer method, with seven of them separated: F1–easily soluble, F2–exchangeable, F3–bound to MnOx, F4–bound to organic matter, F5–bound to amorphous FeOx, F6–bound to crystalline FeOx, and F7–residual. Compared to the control, the average content of total cobalt in the soil increased more than two times in experimental units with higher doses of sewage sludge (10% and 15% of the weight of the soil). The metal was mainly bound to the residual fraction, where it constituted 40% of its total content, while in the organic fraction, its share was 20%. In the soil incubated with sludge, cobalt in mobile fractions constituted a small percentage of its total content. Liming limited the release of this metal.

Keywords: cobalt; sludge; soil sequential analysis; the Zeien–Brümmer method

1. Introduction

Due to the intensive development of wastewater treatment plants in Poland, the problem of municipal sewage sludge disposal is constantly increasing [1]. Sewage sludge, in addition to food scraps, sand, and fat, is the main by-product of wastewater treatment processes, accounting for the largest share of the suspended solids (66.7% of the volume of wastewater). In accordance with Chapter 2 of Article 3 Point 4 of the Polish Waste Act [2], municipal sewage sludge is defined as the material from fermentation chambers of wastewater treatment plants and other urban wastewater treatment facilities. This waste is a rich source of nutrients [3–5] but also a serious source of mineral and organic pollutants [6–9]. The chemical composition of municipal sewage sludge varies greatly, due to different types of wastewater fed into the treatment plant, different shares of industrial wastewater, and different treatment processes. Heavy metals found in municipal sewage sludge may come from water for domestic purposes, rainwater, or meltwater entering sewerage systems from urban, industrial, and storage areas and, in particular, from transport bases and roads and from car parks with a paved surface [10]. Of the heavy metals present in municipal sewage sludge, cobalt deserves special attention due to its toxicity and the complexity of its soil sorption. There are few reports in the literature on its speciation.

Cobalt activity is dependent on soil conditions and its speciation is most heavily affected by soil pH, texture, redox potential, and mineral and organic colloids [11,12]. It has been found [13,14] that

liming treatment increasing pH in the soil is often the main factor affecting its C to N ratio and the process of organic matter decomposition. In the natural environment, cobalt occurs most often in the form of Co^{2+} , Co^{3+} , and $\text{Co}(\text{OH})^{3-}$ ions [15,16].

Adversely affecting soil biological activity, excessive amounts of cobalt, and other heavy metals all have a negative impact on the growth and development of crops and on animals feeding on them; consequently, the quantity and quality of agricultural products is also lowered [17–19].

The total content of heavy metals in the environment is not a sufficient criterion for their toxicity assessment as the degree of their mobility also has to be determined [20]. It is most commonly done using sequential chemical extraction [21–26]. This is a method of isolating mobile fractions of a given metal and its stable forms that are not available to plants.

Sequential chemical extraction is increasingly used for testing soil contaminated either with heavy metals or with waste, containing their elevated amounts [22–26]. According to many authors [15,27,28], in favorable soil condition, plant roots may affect the complexation or dissolution of heavy metals by secreting a variety of substances. That is why, to eliminate the impact of roots on heavy metal speciation, the present incubation experiment was conducted without plants, with CaCO_3 , and with different doses of sewage sludge applied to soil in containers.

The aim of the experiment was to evaluate the effect of liming and different doses of sewage sludge on total content and speciation of cobalt in soil.

2. Materials and Methods

The incubation experiment with three replications was carried out for 420 days in laboratory conditions. The experiment was conducted in a laboratory of the University of Natural Sciences and Humanities in Siedlce, Poland, between 2014 and 2015. The containers were filled with 3 kg of soil taken from the humus layer, with the granulometric composition of light sandy clay loam (Polish Society of Soil Science, Poland), with a pH_{KCl} value of 4.30. The determination of the soil reaction was made using the potentiometric method, measuring the pH of the soil suspension in 1 M KCl. The share of individual mineral particles (mm) ranged as follows: from 1 to 0.1—60%; from 0.1 to 0.05—7%; from 0.05 to 0.02—17%; from 0.02 to 0.06—10%; from 0.06 to 0.002—6%. The soil was collected from fields of local farmers. Total content of heavy metals in the soil before the experiment started was as follows (mg kg^{-1}): Pb—6.03; Cd—1.02; Cr—2.09; Cu—2.21; Zn—19.95; Ni—1.56. The above quantities were lower than the limits set by the Regulation of Ministry of the Environment [29] for light soil treated with sewage sludge. The carbon content of organic compounds in the soil was 10.1 g kg^{-1} dry matter (DM) with 1.58 g kg^{-1} DM of calcium.

Before filling the containers, the soil was strained through a 0.20 mm sieve and divided into two parts, one without liming, while the other was limed with CaCO_3 , according to the hydrolytic acidity, Kappen method. Reagent-grade calcium carbonate (CaCO_3) at a dose of 3 g per pot was applied. It was pure anhydrous calcium carbonate, the distributor of which was TechlandLab Ltd., Tarnobrzeg, Poland. Next, the soil was left for 1 month until it reached 50–60% of its maximum water holding capacity. Two series were obtained this way: without liming (soil not limed) and with liming (limed soil). The sludge came from the municipal mechanical-biological wastewater treatment plant in Siedlce, Poland. It was applied in quantities of 5, 10, and 15% of the weight of the soil, with 150, 300, or 450 g of sludge applied to one container, and the contents were mixed thoroughly. Fresh sewage sludge was mixed with soil by hand so that the mixture was homogeneous. The content of selected heavy metals (Table 1) did not exceed the standards provided by the regulation of the Minister of the Environment [30]. However, there were high amounts of total nitrogen and total organic carbon in the sewage sludge.

Table 1. Concentration of chemical elements and pH of the sludge.

pH	DM %	Organic	Total Nitrogen	C:N	Co	Pb	Cd	Cr	Cu	Zn	Ni
		Carbon C _{org}	N _{tot}								
		g kg ⁻¹			mg kg ⁻¹						
6.8	25.0	345	40	8.6:1	3.80	50.23	0.165	19.85	85.0	1120	50.14

In the experiment, there were two control units: one without sludge and without liming and the other without sludge but with CaCO₃ applied. During the experiment, soil moisture was maintained at 50–60% of the maximum water holding capacity and air temperature varied from 20 to 22 °C. Soil samples were collected every 30 days (after 30, 60, 90, and 120 days). There was then a 180-day break, while the soil moisture and air temperature were maintained at the same level as before. Next, the soil was sampled twice with an interval of 60 days, i.e., on the 360th and 420th days of the experiment. Soil samples were collected from each pot using a gouge auger. A representative sample was obtained by mixing 3 individual subsamples collected from the same pot. In all soil samples, cobalt content was determined after dry mineralization at a temperature of 450 °C by means of the emission spectrophotometer (ICP-AES) method. The fractions of this metal were established using the seven-step Zeien and Brümmer method [31] (Table 2).

Table 2. Sequential extraction of heavy metals with the Zeien-Brümmer method.

Fraction	Name	Extraction Reagent	Extraction Time	pH
F1	easily soluble	1 mol NH ₄ NO ₃ dm ⁻³	24 h	neutral
F2	exchangeable	1 mol CH ₃ COONH ₄ dm ⁻³	24 h	6.0
F3	bound to MnO _x	1 mol NH ₂ OH HCl dm ⁻³ + 1 mol CH ₃ COONH ₄ dm ⁻³	0.5 h	6.0
F4	bound to organic matter	0.025 mol C ₁₀ H ₂₂ N ₄ O ₈ dm ⁻³	1.5 h	4.6
F5	bound to amorphous FeO _x	0.2 mol (NH ₄) ₂ C ₂ O ₄ dm ⁻³ + 0.2 mol H ₂ C ₂ O ₄ dm ⁻³	4 h	3.25
F6	bound to crystalline FeO _x	0.2 mol (NH ₄) ₂ C ₂ O ₄ dm ⁻³ + 0.2 mol H ₂ C ₂ O ₄ dm ⁻³ + 0.1 mol C ₆ H ₈ O ₆ dm ⁻³	0.5 h	3.25
F7	residual	Calculated as the difference between the total content of cobalt and the sum of the above determined fractions	-	-

The proportion of soil to solution—1 g: 10 cm³.

Statistical Analysis

The results were statistically processed. Analysis of variance was used to determine whether differences between mean values were significant. In the case of significant differences, Tukey's test was applied (LSD_{0.05}) to compare the means. Additionally, the Statistica program, Version 10.0 StatSoft [32], was used. Finally, linear correlation coefficients between pH and total cobalt content and cobalt fractions in the soil were calculated.

3. Results and Discussion

The overall cobalt content of the sewage sludge was quite low, at 3.80 mg kg⁻¹ DM (Table 1). Bojakowska et al. [33] reported similar content of this metal in municipal sewage sludge, ranging from 1 to 7 mg kg⁻¹ DM. Because cobalt content of the sewage sludge is low, there are few scientific reports, unlike in the case of other heavy metals, on its speciation in this residual material, as well as in the soil environment.

Cobalt sequential analysis indicated that, in municipal sewage sludge, the percentage of its fractions varied widely (Figure 1). It was found that most cobalt (over 40%) was in the least available residual fraction (F7). Additionally, cobalt bound to organic matter constituted more than 20% of its overall content. In municipal sludge, metalorganic compounds usually constitute a big percentage of the total content [34,35]. The formation of metalorganic compounds in sewage sludge is the result of direct metal–carbon bonding. Such bonds are polarized covalent bonds [36]. In the easy soluble (F1) and exchangeable (F2) fractions, only a small share of cobalt was found (2.3%). According to Bożym and Rajmund [37], the amount of cobalt soluble forms in test material depends on the type and concentration of the solvent. Wang et al. [38] found varied content of each of the heavy metals in the residual fraction using the Community Bureau of Reference-BCR method. It was also found [39–41] that cobalt is easily sorbed by organic substances and forms organic chelates, which increase its mobility and affect its movement in the soil profile, increasing its uptake by plants. In a reducing environment, cobalt was easily soluble and available to plants.

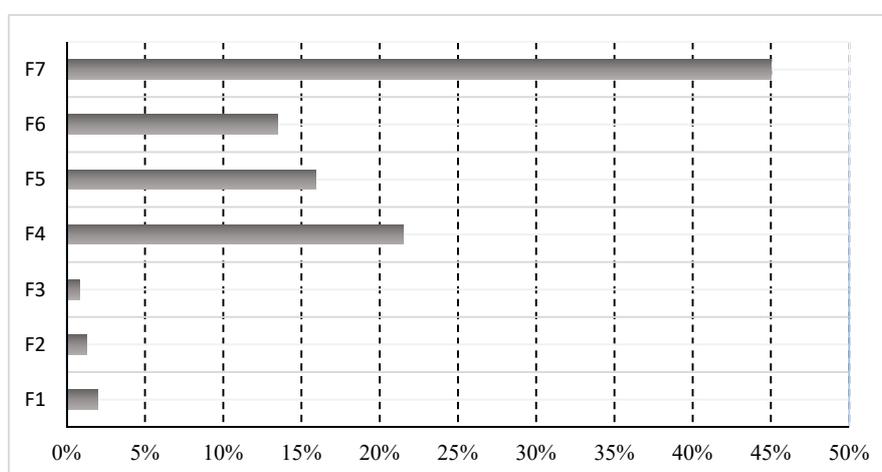


Figure 1. The percentage of cobalt fractions in sewage sludge. F1 = easily soluble; F2 = exchangeable; F3 = bound to MnO_x ; F4 = bound to organic matter; F5 = bound to amorphous FeO_x ; F6 = bound to crystalline FeO_x ; F7 = residual.

In the present incubation experiment, varied doses of sewage sludge and liming had a significant effect on the overall content of cobalt in the soil (Table 3). Throughout, the content of this metal in soil treated with different doses of sewage sludge was low and ranged from 0.949 to 2.87 $mg\ kg^{-1}$ soil. The average content in the surface layer of Polish sandy soil is 2.63 $mg\ kg^{-1}$, with 7.23 $mg\ kg^{-1}$ in clay soil and luvisols and 3.0 $mg\ kg^{-1}$ in organic soil [15,42].

Table 3. Total content of cobalt ($mg\ kg^{-1}$) in soil in the incubation experiment.

Days	Without Liming					Liming				
	0	5%	10%	15%	Mean	0	5%	10%	15%	Mean
30	1.02	1.68	2.33	2.76	1.95	0.999	1.52	2.41	2.87	1.95
60	1.11	1.55	2.52	2.71	1.97	1.04	1.45	2.36	2.69	1.89
90	1.03	1.69	2.74	2.87	2.08	1.10	1.36	2.71	2.59	1.94
120	0.998	1.76	2.81	2.78	2.09	0.949	1.69	2.51	2.55	1.93
360	0.987	1.74	2.68	2.71	2.03	0.955	1.54	2.66	2.78	1.98
420	1.02	1.63	2.60	2.66	1.98	1.00	1.50	2.58	2.81	1.97
mean	1.03	1.68	2.61	2.75	2.02	1.01	1.51	2.54	2.72	1.94

LSD_{0.05} for: A = 0.12; B = 0.065; C = n.s.; A/B = n.s.; B/A = n.s.; A/C = n.s.; C/A = n.s.; B/C = n.s.; C/B = n.s.

n.s. = not significant difference; 0 = control unit, 5%, 10%, 15% of sewage sludge to soil dry mass; A = sewage dose; B = liming; C = days; A/B, B/A, A/C, C/A, B/C, C/B = interaction.

On average, compared to the control, total content of cobalt in the soil increased more than two times in response to the two higher doses of sewage sludge (10 and 15% of the weight of the soil). In the non-limed soil, it was, respectively, 2.61 and 2.75 mg kg⁻¹ and 2.54 and 2.72 mg kg⁻¹ in the limed soil. A similar trend of zinc accumulation in the soil treated with different doses of sewage sludge was noted by Kalembasa and Malinowska [43] and by Malinowska [33]. In a four-year experiment, Speir et al. [44] found increased concentration of Cu, Ni, and Zn in the soil with sewage sludge.

Seven step sequential analysis was used 30 days after sewage sludge application, and a small percentage of cobalt in the mobile fraction in the soil was found. Its amount increased with doses of sewage sludge, and it was significantly greater in the non-limed soil than in limed soil (Tables 4 and 5). Soil acidity has a significant impact on the transformation of heavy metals, in particular on their mobilization and immobilization and the resulting circulation of chemical elements in the environment, and thus on the productivity of agricultural ecosystems [39,45]. In the non-limed soil, treated with the largest dose of sludge (15%), the sum of the easy soluble (F1) and exchangeable (F2) fractions accounted for 2.63% of cobalt, while in the limed soil it was 3.30%. An upward trend was found in samples collected later. Thus, after 90 days, the share of mobile fractions of cobalt had increased almost twice.

Table 4. Percentage share of cobalt fractions in total content in soil in the incubation experiment.

Fertilization Object	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇	pH *
30 days								
without liming								
control	1.82	1.10	2.36	25.45	19.05	20.21	30.01	4.30
5%	1.81	0.991	1.35	28.00	20.03	15.01	32.81	4.55
10%	1.98	1.20	1.31	35.04	11.00	14.38	35.09	5.05
15%	2.09	1.21	1.34	37.01	10.60	10.80	37.01	5.17
mean	1.93	1.13	1.59	31.38	15.17	15.10	33.73	
liming								
control	1.08	0.981	0.301	25.05	16.32	20.26	36.01	6.30
5%	1.40	0.995	0.309	32.01	18.94	14.51	31.84	6.32
10%	1.52	1.00	0.321	29.09	18.12	13.44	36.51	6.35
15%	1.55	1.08	0.311	28.95	19.37	10.70	38.04	6.48
mean	1.39	1.01	0.311	28.78	18.19	14.73	35.60	
60 days								
without liming								
control	1.05	1.70	2.20	20.16	17.23	22.61	35.05	4.38
5%	2.59	1.95	2.93	25.11	17.96	20.72	28.84	4.80
10%	1.90	0.991	1.31	24.75	18.04	13.00	40.11	5.02
15%	1.52	1.02	2.31	27.04	17.00	10.05	41.08	5.00
mean	1.77	1.42	2.19	24.27	17.56	16.60	36.27	
liming								
control	1.11	1.58	1.25	23.85	19.01	20.05	33.17	6.25
5%	1.38	0.709	1.39	30.49	18.88	17.20	29.95	6.30
10%	1.45	0.985	1.14	35.45	14.56	11.96	34.48	6.25
15%	1.80	0.846	1.85	36.21	12.15	11.08	36.08	6.50
mean	1.44	1.03	1.41	31.50	16.15	15.07	33.42	

Table 4. Cont.

Fertilization Object	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇	pH *
90 days								
without liming								
control	2.60	2.05	1.21	21.05	14.02	29.07	30.01	4.26
5%	2.51	3.70	1.19	25.29	13.26	22.54	31.51	5.15
10%	2.85	3.00	2.24	25.06	18.45	19.41	29.00	5.10
15%	3.13	2.78	2.24	24.08	18.14	19.00	30.63	5.12
mean	2.77	2.88	1.72	23.87	15.97	22.51	30.29	
liming								
control	2.21	1.55	1.22	22.50	15.20	28.90	28.42	6.25
5%	1.74	2.70	1.19	21.91	14.19	28.35	29.91	6.34
10%	2.11	2.69	2.05	28.08	17.36	18.96	28.72	6.40
15%	2.99	2.68	2.22	27.04	17.21	14.81	33.05	6.45
mean	2.26	2.41	1.67	24.88	15.99	22.76	30.03	
120 days								
without liming								
control	1.75	1.30	0.918	23.00	14.01	30.11	29.01	4.30
5%	1.76	2.39	1.20	26.00	16.12	25.60	27.02	5.17
10%	2.80	2.70	3.19	21.56	18.23	24.72	26.80	5.20
15%	2.84	2.66	3.16	24.01	17.98	12.63	36.72	5.21
mean	2.29	2.26	2.12	23.64	16.59	23.27	29.89	
liming								
control	1.50	1.49	1.11	25.00	20.41	19.99	30.50	6.31
5%	1.57	1.96	1.60	28.90	16.58	17.39	32.00	6.40
10%	1.70	1.60	1.18	25.42	16.01	23.05	31.04	6.45
15%	1.79	2.62	1.19	23.08	17.02	15.17	38.95	6.37
mean	1.64	1.92	1.27	25.60	17.55	18.90	33.12	

F₁—LSD_{0.05} for: A = 0.357; B = 0.191; C = 0.357; A/B = 0.504; B/A = 0.387; C/A = n.s.; A/C = n.s.; C/B = n.s.; B/C = n.s.;
 F₂—LSD_{0.05} for: A = 0.284; B = 0.152; C = 0.284; A/B = 0.402; B/A = 0.304; C/A = n.s.; A/C = n.s.; C/B = n.s.; B/C = n.s.;
 F₃—LSD_{0.05} for: A = 0.157; B = 0.084; C = 0.157; A/B = 0.222; B/A = 0.168; C/A = 0.222; A/C = 0.222; C/B = 0.222;
 B/C = 0.168; F₄—LSD_{0.05} for: A = 0.304; B = 0.164; C = 0.304; A/B = 0.430; B/A = 0.326; C/A = 0.430; A/C = 0.430;
 C/B = 0.430; B/C = 0.326; F₅—LSD_{0.05} for: A = 0.260; B = 0.139; C = 0.260; A/B = 0.368; B/A = 0.279; C/A = 0.368;
 A/C = 0.368; C/B = 0.368; B/C = 0.279; F₆—LSD_{0.05} for: A = 0.310; B = 0.166; C = 0.310; A/B = 0.438; B/A = 0.332;
 C/A = 0.438; A/C = 0.438; C/B = 0.438; B/C = 0.332; F₇—LSD_{0.05} for: A = 0.282; B = 0.151; C = 0.282; A/B = 0.398;
 B/A = 0.302; C/A = 0.398; A/C = 0.398; C/B = 0.398; B/C = 0.302. A = sewage dose; B = liming; C = days; A/B,
 B/A, A/C, C/A, B/C, C/B = interaction; n.s. = not significant difference; F1 = easily soluble, F2 = exchangeable,
 F3 = bound to MnO_x, F4 = bound to organic matter, F5 = bound to amorphous FeO_x, F6 = bound to crystalline
 FeO_x, F7 = residual; 5%, 10%, 15% of sewage sludge to dry mass of soil. * Malinowska [46].

Table 5. Percentage share of cobalt fractions in total content in soil in the incubation experiment.

Fertilization Objects	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇	pH *
360 days								
without liming								
control	2.50	2.30	2.19	18.80	12.96	39.45	21.79	4.40
5%	1.60	1.38	1.11	24.20	10.25	31.57	29.89	4.80
10%	1.63	1.40	0.325	28.91	13.69	23.05	31.00	5.15
15%	1.68	1.50	0.500	30.42	13.44	18.47	34.05	5.05
mean	1.85	1.65	1.04	25.58	12.59	28.14	29.18	

Table 5. Cont.

Fertilization Objects	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇	pH *
liming								
control	1.45	0.800	0.118	24.70	13.01	38.40	21.52	6.10
5%	1.45	1.311	0.310	27.00	12.69	28.24	29.00	6.25
10%	1.59	1.40	0.545	30.56	14.52	25.74	25.65	6.28
15%	1.60	1.41	0.630	32.86	14.03	25.47	24.00	6.35
mean	1.52	1.23	0.401	28.78	13.56	29.46	25.04	
420 days								
without liming								
control	1.35	1.14	0.101	23.00	11.23	43.13	20.05	4.35
5%	1.40	1.20	0.341	20.50	12.03	37.53	27.00	4.90
10%	1.45	1.24	0.552	29.00	12.45	34.60	20.71	5.20
15%	2.47	2.20	0.450	29.42	11.56	22.84	31.06	5.08
mean	1.57	1.45	0.361	25.48	11.82	34.53	24.71	
liming								
control	1.20	0.901	0.100	25.00	11.02	40.78	21.00	6.00
5%	1.33	1.19	0.250	35.09	14.11	27.94	20.09	6.30
10%	1.39	1.20	0.356	30.01	12.36	29.61	25.07	6.18
15%	1.89	1.82	0.273	45.68	13.02	9.27	28.05	6.28
mean	1.45	1.28	0.245	33.95	12.63	26.90	23.55	

F₁—LSD_{0.05} for: A = 0.204; B = 0.108; C = 0.108; A/B = 0.288; B/A = 0.216; C/A = 0.216; A/C = 0.288; C/B = n.s.; B/C = n.s.; F₂—LSD_{0.05} for: A = 0.284; B = 0.151; C = 0.151; A/B = 0.407; B/A = 0.302; C/A = 0.302; A/C = 0.407; C/B = n.s.; B/C = n.s.; F₃—LSD_{0.05} for: A = 0.050; B = 0.027; C = 0.027; A/B = 0.071; B/A = 0.053; C/A = 0.053; A/C = 0.071; C/B = 0.038; B/C = 0.038; F₄—LSD_{0.05} for: A = 0.628; B = 0.334; C = 0.334; A/B = 0.889; B/A = 0.668; C/A = 0.668; A/C = 0.889; C/B = 0.473; B/C = 0.473; F₅—LSD_{0.05} for: A = 0.228; B = 0.121; C = 0.121; A/B = 0.322; B/A = 0.224; C/A = 0.242; A/C = 0.322; C/B = n.s.; B/C = n.s.; F₆—LSD_{0.05} for: A = 0.319; B = 0.170; C = 0.170; A/B = 0.451; B/A = 0.339; C/A = 0.339; A/C = 0.451; C/B = 0.240; B/C = 0.240; F₇—LSD_{0.05} for: A = 0.620; B = 0.330; C = 0.330; A/B = 0.877; B/A = 0.660; C/A = 0.660; A/C = 0.877; C/B = 0.467; B/C = 0.467. A = sewage dose; B = liming; C: days; A/B, B/A, A/C, C/A, B/C, C/B = interaction; n.s. = not significant difference; F₁ = easily soluble, F₂ = exchangeable, F₃ = bound to MnO_x, F₄ = bound to organic matter, F₅ = bound to amorphous FeO_x, F₆ = bound to crystalline FeO_x, F₇ = residual; 5%, 10%, 15% of sewage sludge to dry mass of soil. * Malinowska [46].

Throughout the experiment, the largest percentage of this metal in the soil was recorded in the residual (F₇) and organic (F₄) fractions. Within 120 days, the percentage of cobalt in the residual fraction was dominant and represented more than 30% almost in all units. In the subsequent periods of the research, this participation was reduced. The amount of cobalt bound to organic matter was greater in limed soil than in the soil without liming, with the exception of samples collected after 30 days. The relationship between soil pH and the amount of metals bound to organic matter was confirmed by the research of Domańska [47] and Malinowska [46]. On the 420th day, the percentage of cobalt in the organic fraction increased, compared to the start of the experiment. At the end of the experiment, there was also a marked increase in the amount of cobalt bound to organic matter as a response to increasing doses of sewage sludge. Bhattacharyya et al. [39] found that the amounts of cobalt in alluvial soils decreased in the following order: organic-bound; Fe and Mn oxide-bound; residual; exchangeable; carbonate-bound; soluble in water. Zhai et al. [48] reported the dominance of Fe and Mn oxide-bound cobalt in soil, accounting for 23–35%, while 4–20% was organic bound.

According to many authors [45,49], acidity is one of the most important properties of the soil, determining the course of many of its processes. It affects organic metabolism, the assimilation of heavy metals, and the development of microorganisms, affecting the yield of plants.

In turn, the average percentage of cobalt bound to crystalline iron oxides (F₆) in the soil collected in different periods was higher in non-limed than in limed soil, as opposed to cobalt bound to amorphous FeO_x (F₅), the content of which was higher in limed soil. Starting with the 90th day, there was a

statistically significant higher increase in the share of cobalt bound to crystalline FeOx than that bound to amorphous FeOx. At the end of the experiment, after 420 days, there was a several fold decrease in the percentage of cobalt bound to manganese oxides (F3), compared to the soil collected after 30 days. Based on statistical analysis of non-limed soil, it was found that there was a positive correlation (Table 6) between soil pH, total content of cobalt, and the amount of this metal bound to organic matter (F4) and a significant negative correlation between pH, total cobalt content, and the amount of this metal bound to crystalline FeOx (F6). In non-limed soil, there was also a significant positive correlation between total content of cobalt and the content of this metal in the residual fraction (F7).

Table 6. Linear correlation coefficient between soil pH, total cobalt content, and its content in fractions.

Fraction	pH		Co	
	−Ca	+Ca	−Ca	+Ca
F1	0.279	0.460 *	0.304	0.432 *
F2	−0.223	0.374	−0.236	0.251
F3	0.037	0.564 *	0.100	0.201
F4	0.489 *	0.138	0.535 *	0.503 *
F5	−0.037	0.453 *	0.081	−0.072
F6	−0.425 *	−0.719 *	−0.568 *	−0.513 *
F7	0.257	0.634 *	0.405 *	0.265

$p \leq 0.05$; −Ca = without liming; +Ca = liming; * = significant difference; F1 = easily soluble; F2 = exchangeable; F3 = bound to MnO_x; F4 = bound to organic matter; F5 = bound to amorphous FeO_x; F6 = bound to crystalline FeO_x; F7 = residual.

In the limed soil, there was a statistically significant positive correlation between pH and the content of cobalt bound to MnOx (F3) between pH and the amount of cobalt bound to amorphous FeOx (F5) and between pH and the amount of the metal bound to the residual (F7) fraction. Additionally, there was a negative correlation between pH and the amount of cobalt bound to crystalline FeOx (F6). Total content of cobalt was significantly positively correlated with its amount in the organic fraction (F4) and negatively with the crystalline FeOx fraction (F6). According to Kalembsa and Malinowska [43] and Laudicina et al. [50], liming and the type and amount of organic substance had a significant impact on forms of heavy metals in the soil. It was confirmed by high values of linear correlation coefficients. In their research, Bakkaus et al. [51] found no relationship between exchangeable cobalt content and total Mn and Fe content in soil.

On the basis of detailed 420 days of the studies, with various doses of sewage sludge added to the soil, it was found that residual (F7) and iron oxide-bound (F5 and F6) cobalt was dominant, indicating the possibility of agricultural and natural use of this waste. According to McLaren et al. [41], cobalt bound to oxides is low in bioavailability (sorption is strong). Pinkerton and Brown [52] reported that, even after cobalt salts were introduced into the soil, there was no increase in its accumulation by plants.

4. Conclusions

1. Percentage of cobalt fractions in municipal sewage sludge can be arranged in a series of increasing percentages: F3(0.80) < F2(1.30) < F1(2.00) < F6(13.5) < F5(15.9) < F4 (21.50) < F7(45.0).
2. In the incubation experiment, varied sewage sludge doses had a significant effect on total content of cobalt in the soil. Its amounts increased with higher doses of sewage sludge.
3. The percentage of cobalt in separate fractions in the soils of different experimental units was dependent on the dose of sewage sludge and liming. On average, compared to the control, cobalt content increased more than two times as a response to higher doses of sewage sludge (10 and 15% of the weight of the soil).
4. Compared to the beginning of the experiment, increasing doses of sewage sludge increased the percentage of cobalt in the organic fraction (F4) after 420 days of soil incubation, while, at the same

time, the percentage share of this chemical element bound to manganese oxides (F3) decreased a few times.

- Based on the experiment, it was concluded that the chemical speciation of cobalt is not a permanent phenomenon and that it can be redistributed between the fractions, depending on pH of the soil and its organic matter content.

Author Contributions: Conceptualization, K.J.; methodology, E.M.; writing—original draft preparation, K.J.; writing—review and editing, E.M. All authors have read and agreed to the published version of the manuscript. All authors have equally contributed to this article.

Funding: The results of the research carried out under the research theme No.40/B/20 were financed from the science grant, granted by the Ministry of Science and Higher Education.

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

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