

Influence of Mineral Fertilization on Lead, Cadmium, and Chromium Fraction Contents in Soil

Adam Łukowski*, Józefa Wiater

Department of Technology in Engineering and Environmental Protection, Technical University of Białystok, Wiejska 45A, 15-351 Białystok, Poland

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Abstract

The aim of our study was to estimate the influence of mineral fertilization on the contents of various lead, cadmium, and chromium forms in the soil. It was based on a field experiment of ten plots. In average soil samples taken in 2002-04, the pseudo-total lead, cadmium, and chromium content was determined. Chemical forms of these metals, by modified BCR method, were also determined.

The lead content in particular fractions can be arranged quantitatively (average values) in order as follows: F2 (26%)>F3 (16%)>F1 (2%), in the case of cadmium: F2 (27%)>F1 (17%)>F3 (5%), and in the case of chromium: F3 (5%)>F2 (3%)>F1 (0.2%). The accumulation of lead, cadmium, and chromium in the soil during the experiment was observed. After the third year of experiment the most mobile cadmium and chromium forms (soluble + exchangeable fraction) increased, while in the case of lead they generally decreased.

Keywords: cadmium, nickel, chromium, organic fertilizers, metal fractions, soil

Introduction

Heavy metal contamination of arable land is mainly related to atmospheric deposition of industrial dust [1, 2], as well as the application of biosolids and mineral fertilizers (especially containing phosphorus) [3-5]. Fertilization can lead to heavy metal accumulation and fractional composition changes in the soil. The influence of fertilization with mixed fertilizers on fractional composition of heavy metals in the soil, including lead, cadmium, and chromium, is examined to a small degree.

Lead and cadmium belong to a group of toxic elements for plants. Chromium was never recognized as an essential element for plant growth, but some of its stimulative effects were reported [6]. In the case of Cr only Cr(VI) compounds are toxic [7]. The plant uptake of these elements is usually directly proportional to the concentration in the soil.

Excess Pb causes a number of toxicity symptoms in plants, e.g. stunted growth, chlorosis, and blackening of root systems. Lead inhibits photosynthesis, upsets mineral nutrition and water balance, changes hormonal status, and affects membrane structure and permeability [8]. The accumulation of lead in plants, as compared to other heavy metals, occurs slowly.

Cadmium can alter the synthesis of RNA (inhibit ribonuclease activity), and reduce the absorption of nitrate and its transport from roots to shoots by inhibiting the nitrate reductase activity in the shoots. It interacts with water balance and damages photosynthetic apparatus. Cd inhibits oxidative mitochondrial phosphorylation, reduces activity of plasma membrane ATPase and strongly affects the activity of several enzymes (e.g. isocitrate dehydrogenase and Rubisco) [9].

Chromium toxicity in plants is observed at multiple levels, from reduced yield, through effects on leaf and root growth, to inhibition on enzymatic activities and mutagenesis [10].

*e-mail: adamus@pb.edu.pl

The aim of our study was to evaluate changes (after application of mineral fertilization) in lead, cadmium, and chromium contents in fractions in the soil during the three years of the experiment.

Experimental Procedures

Study was based on a field experiment at the Agricultural Technical High School in Białystok. It was set in 2001 on typical brown soil (clay content 26%) developed on the light loam, low phosphorus (43.5 mg P·kg⁻¹), and potassium (102.3 mg K·kg⁻¹) content and pH=7.51 (in 1 mol·dm⁻³ KCl). The experiment consisted of 10 objects (in split-plot system):

1. control
2. urea (65 kg·ha⁻¹) + 64 kg·ha⁻¹ P₂O₅ (binary fertilizer Agrecol) + 94 kg·ha⁻¹ K₂O (Agrecol)
3. Polifoska 6 (500 kg·ha⁻¹)
4. Polifoska 8 (375 kg·ha⁻¹)
5. Polifoska B (375 kg·ha⁻¹)
6. Polimag 305 (600 kg·ha⁻¹)
7. Polimag 405 (600 kg·ha⁻¹)
8. calcium sulfate tetraurea (112 kg·ha⁻¹) + 64 kg·ha⁻¹ P₂O₅ (Agrecol) + 94 kg·ha⁻¹ K₂O (Agrecol)
9. fertilizer made from sewage sludge, further as granulate (430 kg·ha⁻¹) + 84 kg·ha⁻¹ K₂O (chloride potassium salt)
10. phosphogypsum (3,500 kg·ha⁻¹) + 30 kg·ha⁻¹ N (Salmag) + 96 kg·ha⁻¹ K₂O (chloride potassium salt) + 40 kg·ha⁻¹ P₂O₅ (triple superphosphate)

The urea, Polifoska 6, Polifoska 8, Polifoska B, Polimag 305, Polimag 405, chloride potassium salt, triple superphosphate, and phosphogypsum came from ZCh Police S.A. chemical plant. The Salmag came from Nitrogen Works Kędzierzyn (Zakłady Azotowe Kędzierzyn S.A.) and Agrecol from AGRECOL Sp. z o. o. in Wieruszów. The granulate was produced by the Institute for Chemical Processing of Coal (Instytut Chemicznej Przeróbki Węgla) in Zabrze. It consisted of about 70% sewage sludge and about 30% potassium nitrate (KNO₃). The calcium sulphate tetraurea was produced by Fertilizers Research Institute (Instytut Nawozów Sztucznych) in Puławy. It was prepared by grinding a stoichiometric mixture of urea and calcium sulfate.

The above-presented fertilization was applied once before sowing at the end of August 2001. The following additional fertilization was applied to all experimental objects: 2002) after sowing under rapeseed – 100 kg N·ha⁻¹ (57.5 kg N·ha⁻¹ in a form of urea and 42.5 kg N·ha⁻¹ in the form of ammonium nitrate); 2003) before sowing under cereal mixture (1/3 of spring wheat, 1/3 of barley, 1/3 of oats) – 72 kg N·ha⁻¹ (8 kg N·ha⁻¹ as Polimag 305 and 64 kg N·ha⁻¹ in the form of urea) and after sowing 1.5 kg N·ha⁻¹ (as leaf fertilizer Ekolist Standard); 2004) before winter triticale sowing – 11.1 kg N·ha⁻¹ in a form of Lubofos 10, and after crop 38.2 kg N·ha⁻¹ in a form of urea. Phosphorus and potassium were applied in a dose of polimag and lubofos.

Every object had three replications and the area of a single plot was 40 m². Table 1 lists the contents of general nutrients and some heavy metals in mineral fertilizers applied.

Soil samples were taken from the ploughing layer (1-20 cm) in 2002-04 after plant harvest. Pseudo-total lead, cadmium and chromium content was determined in mean samples (after previous digestion at 30% H₂O₂ with 1:1 HCl addition). Modified BCR method [11] was used to describe fractional composition of the studied metals in each sample. Extraction included three stages: 1 g of the soil was weighed and placed in a centrifuging tube, then subjected to sequential extraction according to the scheme:

- F1 – soluble + exchangeable fractions using 0.11 mol·dm⁻³ CH₃COOH in a ratio of 1:40 (m/V)
- F2 – metals bonded to iron and manganese oxides using 0.5 mol·dm⁻³ NH₂OH·HCl at a ratio of 1:40 (m/V), pH 2
- F3 – metals bonded to organic matter applying 8.8 mol·dm⁻³ H₂O₂ at a ratio of 1:10 (m/V), and then (after evaporation) using 1 mol·dm⁻³ CH₃COONH₄ at a ratio of 1:50 (m/V), pH 2

The mixture was centrifuged after every stage and extracts were stored until analysis at 4°C. All determinations in fractions were made by means of GFAAS technique using Varian AA100 apparatus. The pseudo-total metal content was determined by means of FAAS. Certified Reference Material (CRM023-050, Sandy Loam) from the Resource Technology Corporation was used for the validation of pseudo-total metal content. The content in residual fraction was calculated (pseudo-total minus sum of extractable fractions).

Lead, cadmium, and chromium contents in fractions were statistically processed, applying three-factor variance analysis, and differences were evaluated by Tukey's test. Sorption capacity was evaluated by means of Kappen's method, pH in 1 mol·dm⁻³ KCl – potentiometrically and organic carbon content – using ThermoEuroglas TOC 1200 apparatus.

Table 1 lists the contents of general nutrients and some heavy metals in mineral fertilizers applied.

Results and Discussion

In all objects, pseudo-total lead, cadmium, and chromium contents (Table 2) were within the range for agricultural soils [12]. In the soil of all objects the accumulation (content increase in 2003 and 2004 as compared to 2002) of above-mentioned metals was observed.

The content of lead in the soil samples from the first year was higher from 0.4 (object with calcium sulfate tetraurea) to 1.9 mg·kg⁻¹ (object with Polifoska 8), as compared to the control. In the second year, in all objects the increase (3.3 mg·kg⁻¹ on average) of pseudo-total Pb content occurred in comparison with the first year. Significant differences between the objects with fertilizers was not observed. In the last year the pool of lead slightly decreased (in fertilized objects slightly higher, as compared to the control object and the highest decrease was in the soil of objects from 5 to 8).

Table 1. Chemical composition of mineral fertilizers used in experiment.

Fertilizer	N	P	K	Mg	Zn	Cu	Pb	Ni	Cd	Cr
	g·kg ⁻¹			mg·kg ⁻¹						
Urea	460	-	-	-	-	-	-	-	-	-
Ammonium nitrate	340	-	-	-	0.2	10.0	0.17	7.5	0.03	2.3
Agrecol	-	96	266	-	-	-	-	-	-	-
Polifoska 6	60	87	250	-	31.2	1.7	1.19	38.0	3.12	24.0
Polifoska 8	80	105	200	-	159.3	3.9	2.45	35.1	16.17	19.6
Polifoska B	80	48	200	-	87.2	2.8	2.11	33.0	11.40	32.9
Polimag 305	50	70	200	48	28.5	2.8	1.50	97.0	1.61	31.2
Polimag 405	50	44	166	36	36.4	1.3	1.59	295.1	1.22	25.1
Calcium sulfate tetraurea	280	2	-	-	3.3	1.9	3.81	1.5	2.19	0.9
Granulate	61	21	108	6	560.0	217.0	89.97	26.0	1.13	9.8
Chloride potassium salt	-	-	498	-	436.0	9.3	1.17	0.4	0.01	-
Phosphogypsum	-	6	-	-	9.2	5.5	11.03	4.3	6.10	3.7
Salmag	-	275	-	24	153.4	2.5	0.07	0.6	0.09	18.1
Triple superphosphate	-	201	-	-	16.1	21.6	0.04	6.5	4.82	12.3
* Lubofos 10	50	100	150	25	80.0	12.0	<1.60	<1.0	<0.70	<1.0
* Ekolist Standard	100	-	50	16	3.0	5.0	<1.00	<1.0	<1.00	<1.0

*contents according to the manufacturer

Table 2. Pseudo-total Pb, Cd, and Cr content (mg·kg⁻¹ DM) in soil.

Object	pseudo-total Pb				pseudo-total Cd				pseudo-total Cr			
	2002	2003	2004	\bar{x} B	2002	2003	2004	\bar{x} B	2002	2003	2004	\bar{x} B
1	5.1	9.3	8.0	7.5	0.65	0.91	0.85	0.80	19.3	27.2	29.8	25.4
2	6.8	9.4	8.7	8.3	0.68	1.24	0.88	0.93	18.6	20.1	20.3	19.7
3	6.5	9.3	8.6	8.1	0.66	1.15	0.90	0.90	22.3	29.4	25.9	25.9
4	7.0	9.2	8.5	8.2	0.66	0.99	0.88	0.84	18.1	29.9	21.5	23.2
5	6.2	9.6	9.2	8.3	0.66	1.03	0.79	0.83	24.7	29.7	31.6	28.7
6	6.3	9.6	9.7	8.5	0.65	1.12	0.90	0.89	23.5	27.1	29.7	26.8
7	5.4	9.1	9.0	7.8	0.67	1.00	0.79	0.82	19.4	26.5	22.0	22.6
8	5.5	9.8	9.2	8.2	0.65	1.26	0.87	0.93	22.1	31.1	23.4	25.5
9	6.2	9.6	8.6	8.1	0.67	1.15	0.91	0.91	23.4	30.0	28.3	27.2
10	5.7	9.4	8.8	8.0	0.65	1.09	0.86	0.87	20.2	27.6	27.7	25.2
\bar{x} A	6.1	9.4	8.8		0.66	1.09	0.86		21.2	27.9	26.0	

1 – control, 2 – urea (65 kg·ha⁻¹)+64 kg·ha⁻¹ P₂O₅ (Agrecol)+94 kg·ha⁻¹ K₂O (Agrecol), 3 – Polifoska 6 (500 kg·ha⁻¹), 4 – Polifoska 8 (375 kg·ha⁻¹) 5 – Polifoska B (375 kg·ha⁻¹), 6 – Polimag 305 (600 kg·ha⁻¹), 7 – Polimag 405 (600 kg·ha⁻¹), 8 – calcium sulfate tetraurea (112 kg·ha⁻¹)+64 kg·ha⁻¹ P₂O₅ (Agrecol)+ 94 kg·ha⁻¹ K₂O (Agrecol), 9 – granulate (430 kg·ha⁻¹)+84 kg·ha⁻¹ K₂O (potassium salt), 10 – phosphogypsum (3,500 kg·ha⁻¹)+ 30 kg·ha⁻¹ N (Salmag) + 96 kg·ha⁻¹ K₂O (potassium salt) + 40 kg·ha⁻¹ P₂O₅ (triple superphosphate)

LSD – $\alpha = 0.05$ $\alpha^*=0.01$

A – years 0.51

B – fertilization not significant

LSD – $\alpha = 0.05$ $\alpha^*=0.01$

A – years 0.07

B – fertilization not significant

LSD – $\alpha = 0.05$ $\alpha^*=0.01$

A – years 1.92

B – fertilization 4.92

Table 3. The amount of Pb, Cd, and Cr (g·ha⁻¹) introduced into soil with applied fertilizers in particular years.

Object	Pb					Cd					Cr				
	2001	2002	2003	2004	total	2001	2002	2003	2004	total	2001	2002	2003	2004	total
1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	-	0.02	0.26	0.36	0.64	-	0.004	0.280	0.160	0.444	-	0.29	5.01	0.22	5.52
3	0.60	0.02	0.26	0.36	1.24	1.560	0.004	0.280	0.160	2.004	12.00	0.29	5.01	0.22	17.52
4	0.92	0.02	0.26	0.36	1.56	6.060	0.004	0.280	0.160	6.504	7.35	0.29	5.01	0.22	12.87
5	0.79	0.02	0.26	0.36	1.43	4.280	0.004	0.280	0.160	4.724	12.34	0.29	5.01	0.22	17.86
6	0.90	0.02	0.26	0.36	1.54	0.970	0.004	0.280	0.160	1.414	18.72	0.29	5.01	0.22	24.24
7	0.95	0.02	0.26	0.36	1.59	0.730	0.004	0.280	0.160	1.174	15.06	0.29	5.01	0.22	20.58
8	0.43	0.02	0.26	0.36	1.07	0.250	0.004	0.280	0.160	0.694	0.10	0.29	5.01	0.22	5.62
9	38.85	0.02	0.26	0.36	39.49	0.490	0.004	0.280	0.160	0.934	4.21	0.29	5.01	0.22	9.73
10	38.81	0.02	0.26	0.36	39.45	21.780	0.004	0.280	0.160	22.224	15.99	0.29	5.01	0.22	21.51

An increase of average pseudo-total lead content in 2003 and 2004 in comparison with 2002 was observed. It was the effect of ploughing the rapeseed straw and roots. Plants take up and accumulate 93-96% of lead cations in roots (they can take from 3 to about 50 times more lead than leaves) [13].

In the soil samples from 2002, from fertilized objects, Cd levels were comparable and near to the control. In the second year, in all objects the increase of pseudo-total Cd content was higher than in control object as compared to 2002 (0.43 mg·kg⁻¹ on average). Significant differences between fertilized objects were not observed. In 2004 the pool of cadmium decreased. In the most fertilized objects it was slightly higher than in control object.

A significant increase of average Cd content in the 2003 soil, as compared to the previous year, was observed. Similar to the case of lead, it could be the effect of ploughing the rapeseed straw and roots (most Cd in plants is accumulated in roots).

In 2002 accumulation of chromium in the soil of most objects in comparison with control object was noted. The content increase was significantly higher only in soil from objects with Polifoska B, which can be explained by the high Cr content in this fertilizer (the highest among applied fertilizers). In the second year in the soil of all objects the increase of chromium content was found as compared to the previous year. Generally, the contents were higher than in the control object. Between fertilized objects significant differences were not observed. Only the soil from objects fertilized with urea contained significantly less chromium as compared to the other fertilized objects and to the control. In the soil from the year 2004 the chromium content was significantly differentiated by the applied fertilization. In the soil from objects with urea, Polifoska 8, and Polimag 405 the content was significantly lower as compared to the other fertilized objects and to the control object.

In soil from 2003, average Cr content increased as compared to 2002, and was statistically proven to be significant. The cause, similar to the above-mentioned elements, was chromium applied to the soil with ploughed rape straw and especially its roots, in which this plant accumulates most chromium [14].

A significant decrease of average Pb, Cd, and Cr pseudo-total content, as compared to 2003, was probably caused by removal by plants uptake or shifting deeper into the soil.

With applied fertilization during the experiment, minimal amounts of lead, cadmium, and chromium (Table 3) were introduced into the soil.

pH value during the experiment remained at a constant level with a slight decreasing tendency (Table 4). The influence of NPK fertilization on pH decrease (within four years) was confirmed by study of Kalembasa and Kuziemska [15].

Organic matter content increased in all objects after the third year (as compared to that after the first year), and the highest increase occurred in objects with granulate (8.3%). It's a result of high organic matter content in the sewage sludge, which is the main component of granulate. Mazur [16], studying crop rotation with increasing NPK mineral fertilization, also stated organic matter content increase in the soil, which ranged from 0.18 to 0.61%.

Content decrease in four objects (with Polifoska 6, Polifoska B, Polimag 305, and Polimag 405) in 2003 (above 10% in comparison to 2002), can be explained by errors on the sample preparation stage, before organic carbon determination. The mean sample must be very well homogenized. This is critical, since sample weight during determination did not exceed a few milligrams.

In general, sorption capacity of the soil slightly increased in 2004, in comparison to 2002. The highest increase (0.9%) was noted in objects with granulate, where organic matter content increased the most.

Table 4. pH (in 1 mol·dm⁻³ KCl), organic matter content (%) and CEC (mmol(+)·kg⁻¹) in soil.

Object	pH			Organic matter			CEC		
	2002	2003	2004	2002	2003	2004	2002	2003	2004
1	7.49	7.44	7.47	2.48	2.51	2.53	46.6	45.8	46.8
2	7.48	7.42	7.43	2.96	2.94	3.11	48.8	47.6	49.1
3	7.48	7.43	7.47	3.06	2.85	3.32	46.8	46.5	46.3
4	7.49	7.44	7.44	3.04	2.94	3.13	46.1	47.6	46.5
5	7.53	7.39	7.45	3.10	2.98	3.24	48.8	47.7	49.0
6	7.49	7.47	7.42	2.92	2.67	2.93	47.9	47.5	47.9
7	7.60	7.46	7.44	3.02	2.93	3.16	48.4	47.1	47.9
8	7.49	7.46	7.37	2.39	2.70	2.58	48.7	48.2	48.9
9	7.48	7.38	7.47	2.19	2.25	2.37	48.9	49.8	49.8
10	7.52	7.34	7.37	2.05	2.01	2.16	48.7	46.9	48.8

CEC – cation exchange capacity

Lead

The average content of mobile lead forms was significantly differentiated by applied fertilization (Table 5). The highest amount was found in the 9th object (16.7%), as a result of high Pb content in granulate (which was many times greater compared to the other applied fertilizers). The lowest Pb amount was observed in objects with Polifoska B (12.2%). The average percentage of lead in three fractions increased as compared to the control (which means mobility increase) in objects with Polifoska 6, Polifoska 8, granulate, and with phosphogypsum. In the soil of the rest of objects percentage was lower than in control soil.

Mineral fertilization caused significant differentiation of lead content in the fractions. The highest Pb content was observed in Fe/Mn oxide-bound fractions (25.8%), while the lowest (2.3%) was in the exchangeable fraction, which is the most available. Such distribution of lead between fractions in the soil is confirmed by studies of Banat et al. [17]. The average lead content (in 39 samples of agricultural soil from different locations in Jordan) in the oxide fractions constituted 26% of total content, while in the exchangeable fraction authors have determined 13.6% Pb on average. Residual fraction, similar to studies discussed in this paper (Table 6), contained the highest amount of lead (28.7% of total content).

The significant differences of lead content in soil samples in the particular years were stated. The highest amount of discussed elements were found in fraction F2, where its gradual content increase was observed. In 2004 it occurred due to the partial redistribution of Pb from residual fraction. The content of lead in exchangeable fraction during the experiment remained at the same level. Other results present Tu et al. [18] on the basis of a three-year study on red soil. Mineral fertilization with nitrogen and phosphorus caused significant decreases of Pb content in exchangeable fraction. The increase of lead content in this fraction

occurred as a result of potassium fertilization. Significant influence of mineral fertilization on Pb content in fractions bound with organic matter, similar to our investigations, was not stated. On the basis of the above-mentioned study and our investigations, it can be stated that fertilizers do not only provide plants with nutrients, but may also act to change the chemical forms of heavy metals in the soil and thus their bioavailability.

Average lead content in three fractions, during the first two years of experiment, remained on the same level. Its increase occurred in 2004 as a result of Pb content decrease in the residual fraction. Soil microorganism activity was probably the cause of that part of the metal being released from residual fraction, since a radical change of environmental conditions (especially pH decrease) in this year was not observed.

The soil in particular years was significantly differentiated by the average percentage of mobile lead fractions. The soil samples from 2002 and 2003 contained similar amounts of lead. In 2004 a significant Pb content increase in the soil occurred due to the redistribution of this element from the residual fraction (Table 6). The cause was described above.

Cadmium

The average content of mobile cadmium forms in the soil was not significantly differentiated by applied fertilization (Table 7). The highest amount was found in control object (16.9%) and the lowest in objects with calcium sulfate tetraurea (15.1%). The increase of cadmium mobility (increase of the average percentage in three fractions as compared to the control) was not stated.

The content of cadmium in fractions was significantly differentiated. The highest amount of this element (26.6%), a three-year average, was bound with Fe/Mn oxides. These oxides have sites on their surface that pro-

Table 5. Lead fractions (% of pseudo-total Pb) in studied soil by BCR method.

Object	2002			2003			2004			\bar{x} B·C			\bar{x} C
	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3	
1	2.4	26.1	17.2	2.0	24.0	16.3	2.5	25.2	17.8	2.3	25.1	17.1	14.8
2	2.5	19.3	12.7	2.6	25.1	14.1	1.7	33.9	17.0	2.3	26.1	14.6	14.3
3	3.1	19.3	15.8	1.7	26.3	16.8	2.7	36.7	14.2	2.5	27.4	15.6	15.2
4	3.2	21.8	15.6	2.0	21.9	15.8	2.8	37.8	15.3	2.7	27.2	15.6	15.1
5	2.4	16.6	14.2	1.6	18.5	12.5	2.1	28.0	13.9	2.0	21.0	13.5	12.2
6	2.5	20.1	16.4	1.3	18.0	15.4	1.8	33.0	15.4	1.9	23.7	15.7	13.8
7	1.7	25.4	17.0	1.4	21.7	18.0	2.3	32.8	12.4	1.8	26.6	15.8	14.7
8	2.4	20.0	15.4	1.3	18.9	13.3	2.4	31.4	14.3	2.0	23.4	14.3	13.3
9	4.1	22.8	13.3	2.6	26.2	17.3	3.2	42.4	18.1	3.3	30.5	16.2	16.7
10	1.7	18.0	17.3	1.6	21.7	16.8	2.6	40.3	16.6	2.0	26.7	16.9	15.2
A·B	2.6	20.9	15.5	1.8	22.2	15.6	2.4	34.2	15.5				
	\bar{x} A1 13.0			\bar{x} A2 13.2			\bar{x} A3 17.4						
	\bar{x} B1 2.3			\bar{x} B2 25.8			\bar{x} B3 15.5						

1 – control, 2 – urea (65 kg·ha⁻¹)+64 kg·ha⁻¹ P₂O₅ (Agrecol)+94 kg·ha⁻¹ K₂O (Agrecol), 3 – polifoska 6 (500 kg·ha⁻¹), 4 – polifoska 8 (375 kg·ha⁻¹) 5 – polifoska B (375 kg·ha⁻¹), 6 – polimag 305 (600 kg·ha⁻¹), 7 – polimag 405 (600 kg·ha⁻¹), 8 – calcium sulfate tetraurea (112 kg·ha⁻¹)+64 kg·ha⁻¹ P₂O₅ (Agrecol)+ 94 kg·ha⁻¹ K₂O (Agrecol), 9 – granulate (430 kg·ha⁻¹)+84 kg·ha⁻¹ K₂O (potassium salt), 10 – phosphogypsum (3,500 kg·ha⁻¹)+ 30 kg·ha⁻¹ N (salmag) + 96 kg·ha⁻¹ K₂O (potassium salt) + 40 kg·ha⁻¹ P₂O₅ (triple superphosphate)

LSD – $\alpha = 0.05$ $\alpha^* = 0.01$

A – years 1.44

B – fractions 1.44

C – fertilization 3.63*

A·B 3.37

A·C not significant

B·C not significant

mote specific adsorption of divalent cations, which is one of the reasons behinds its extraordinary cadmium adsorption ability [19].

The significant differences of cadmium content in soil samples in the particular years were stated. Most cadmium (49.7% on an average) was found in fraction F2 in 2002. This fraction during the experiment has accumulated the highest amounts of cadmium. The average Cd content in this fraction, in 2004, decreased by 68% as compared to 2002. During the experiment an average amount of Cd in fraction F3 dropped by 47.6%. In the following years a gradual increase of cadmium content in fraction F1, most mobile, was stated. In 2002 it was caused by redistribution from fraction F2 and to a lesser degree from fraction F3, while in 2004 the increase was connected with redistribution from residual soil fraction. Significant changes of Cd content in an easily soluble and exchangeable fraction, bound with Fe/Mn oxides and organic matter in the four-year experiment, were not observed by Gondek [14]. His pot experiment was conducted on brown soil. In objects with mineral fertilization he used salt solutions such as NH₄NO₃, Ca(H₂PO₄)₂·H₂O, and KCl. Like the author says, the highest amounts of cadmium were found in easily soluble fractions (according to Zeien and Brümmer) extracted with NH₄NO₃ solution.

The soil in particular years was significantly differentiated by the average percentage of mobile Cd fractions due to its content changes in residual fraction (Table 8) and pseudo-total content. The most amount of mobile cadmium (19.7% on an average) in soil samples from 2002 was determined, while the less amount (10.7%) in soil from 2003.

Chromium

Applied fertilization significantly differentiated average percentage of mobile chromium in the soil samples (Table 9). The most Cr was found in objects fertilized with Polimag 405 (3.08% on an average), while the least in objects with Polimag 305 (2.10% on an average). The increase of chromium mobility in all objects (except objects with Polifoska B and Polimag 305) was observed.

The content of chromium in fractions was also significantly differentiated. The highest amounts of this element were found, during the experiment, in fraction F3 (4.56% on an average). The least chromium was noted in fraction F1 (0.15% on an average). Filipek-Mazur and Gondek [7] obtained similar results in the two-year experiment. They were using three doses of Cr (5, 15, 45 mg·kg⁻¹ of soil DM) in the form of K₂Cr₂O₇ and KCr(SO₄)₂·12H₂O against a

Table 6. Percentage of mobile lead fractions and residual fractions in pseudo-total content by BCR method.

Objects	2002		2003		2004		\bar{x} F1+F2+F3	\bar{x} residual
	F1+F2+F3	residual	F1+F2+F3	residual	F1+F2+F3	residual		
1	45.7	54.3	42.3	57.7	45.5	54.5	44.5	55.5
2	34.5	65.5	41.8	58.2	52.6	47.4	43.0	57.0
3	38.2	61.8	44.8	55.2	53.6	46.4	45.5	54.5
4	40.6	59.4	39.7	60.3	55.9	44.1	45.4	54.6
5	33.2	66.8	32.6	67.4	44.0	56.0	36.6	63.4
6	39.0	61.0	34.7	65.3	50.2	49.8	41.3	58.7
7	44.1	55.9	41.1	58.9	47.5	52.5	44.2	55.8
8	37.8	62.2	33.5	66.5	48.1	51.9	39.8	60.2
9	40.2	59.8	46.1	53.9	63.7	36.3	50.0	50.0
10	37.0	63.0	40.1	59.9	59.5	40.5	45.5	54.5
\bar{x}	39.0	61.0	39.7	60.3	52.1	47.9		

Table 7. Cadmium fractions (% of pseudo-total Cd) in studied soil by BCR method.

Object	2002			2003			2004			\bar{x} B·C			\bar{x} C
	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3	
1	3.5	47.7	5.9	16.2	18.5	4.1	32.9	19.0	3.9	17.5	28.4	4.6	16.9
2	2.9	50.2	6.5	11.5	11.4	3.8	32.2	16.6	4.1	15.5	26.1	4.8	15.5
3	3.2	53.5	6.2	13.1	13.6	3.9	34.7	13.4	2.9	17.0	26.8	4.3	16.1
4	2.8	45.3	6.8	14.0	15.5	4.7	32.6	18.6	2.6	16.5	26.5	4.7	15.9
5	2.8	50.3	5.2	13.9	15.2	5.3	36.8	13.0	3.1	17.8	26.2	4.5	16.2
6	3.1	52.5	7.2	13.3	13.4	4.6	32.0	16.9	3.1	16.1	27.6	5.0	16.2
7	3.1	51.1	5.8	13.9	14.7	5.3	35.7	13.1	4.8	17.6	26.3	5.3	16.4
8	2.8	44.8	6.5	12.1	12.0	3.5	32.2	19.4	2.9	15.7	25.4	4.3	15.1
9	2.9	52.2	7.2	13.4	13.9	4.4	28.4	13.3	2.6	14.9	26.5	4.7	15.4
10	3.7	49.7	5.9	13.6	13.2	5.0	30.2	15.9	3.1	15.8	26.3	4.7	15.6
\bar{x} A·B	3.1	49.7	6.3	13.5	14.1	4.5	32.8	15.9	3.3				
	\bar{x} A1 19.7			\bar{x} A2 10.7			\bar{x} A3 17.3						
	\bar{x} B1 16.5			\bar{x} B2 26.6			\bar{x} B3 4.7						

1 – control, 2 – urea (65 kg·ha⁻¹)+64 kg·ha⁻¹ P₂O₅ (Agrecol)+94 kg·ha⁻¹ K₂O (Agrecol), 3 – Polifoska 6 (500 kg·ha⁻¹), 4 – Polifoska 8 (375 kg·ha⁻¹) 5 – Polifoska B (375 kg·ha⁻¹), 6 – Polimag 305 (600 kg·ha⁻¹), 7 – Polimag 405 (600 kg·ha⁻¹), 8 – calcium sulfate tetraurea (112 kg·ha⁻¹)+64 kg·ha⁻¹ P₂O₅ (Agrecol)+ 94 kg·ha⁻¹ K₂O (Agrecol), 9 – granulate (430 kg·ha⁻¹)+84 kg·ha⁻¹ K₂O (potassium salt), 10 – phosphogypsum (3,500 kg·ha⁻¹)+ 30 kg·ha⁻¹ N (salmag) + 96 kg·ha⁻¹ K₂O (potassium salt) + 40 kg·ha⁻¹ P₂O₅ (triple superphosphate)

LSD – $\alpha = 0.05$ $\alpha^* = 0.01$

A – years 1.21

B – fractions 1.21

C – fertilization not significant

A·B 2.82

A·C not significant

B·C not significant

Table 8. Percentage of mobile cadmium fractions and residual fractions in pseudo-total content by BCR method.

Objects	2002		2003		2004		\bar{x} F1+F2+F3	\bar{x} residual
	F1+F2+F3	residual	F1+F2+F3	residual	F1+F2+F3	residual		
1	57.1	42.9	38.8	61.2	55.8	44.2	50.6	49.4
2	59.6	40.4	26.7	73.3	52.9	47.1	46.4	53.6
3	62.9	37.1	30.6	69.4	51.0	49.0	48.2	51.8
4	54.9	45.1	34.2	65.8	53.8	46.2	47.6	52.4
5	58.3	41.7	34.4	65.6	52.9	47.1	48.5	51.5
6	62.8	37.2	31.3	68.7	52.0	48.0	48.7	51.3
7	60.0	40.0	33.9	66.1	53.6	46.4	49.2	50.8
8	54.1	45.9	27.6	72.4	54.5	45.5	45.4	54.6
9	62.3	37.7	31.7	68.3	44.3	55.7	46.1	53.9
10	59.3	40.7	31.8	68.2	49.2	50.8	46.8	53.2
\bar{x}	59.1	40.9	32.1	67.9	52.0	48.0		

Table 9. Chromium fractions (% of pseudo-total Cr) in studied soil by BCR method.

Object	2002			2003			2004			\bar{x} B·C			\bar{x} C
	F1	F2	F3	F1	F2	F3	F1	F2	F3	F1	F2	F3	
1	0.14	1.80	1.73	0.14	1.88	1.44	0.17	4.18	9.83	0.15	2.62	4.33	2.37
2	0.13	1.68	1.82	0.17	2.49	1.94	0.21	5.69	12.79	0.17	3.29	5.52	2.99
3	0.10	2.33	1.55	0.10	1.78	1.28	0.17	5.71	9.11	0.12	3.27	3.98	2.46
4	0.11	2.71	2.03	0.11	1.81	1.42	0.23	6.31	11.88	0.15	3.61	5.11	2.96
5	0.08	1.39	1.22	0.09	1.64	1.43	0.18	5.62	8.63	0.12	2.88	3.76	2.25
6	0.08	1.48	1.30	0.11	1.69	1.28	0.19	3.66	9.07	0.13	2.28	3.88	2.10
7	0.11	2.45	2.49	0.10	1.75	2.03	0.22	5.86	12.67	0.14	3.35	5.73	3.08
8	0.12	1.59	1.64	0.12	1.94	1.53	0.25	4.69	11.06	0.16	2.74	4.74	2.55
9	0.12	2.00	2.07	0.10	1.52	1.26	0.24	5.64	9.00	0.15	3.05	4.11	2.44
10	0.14	2.68	2.41	0.12	1.83	1.23	0.21	4.15	9.67	0.16	2.89	4.44	2.49
\bar{x} A·B	0.11	2.01	1.83	0.12	1.83	1.48	0.21	5.15	10.37				
	\bar{x} A1 1.32			\bar{x} A2 1.14			\bar{x} A3 5.24						
	\bar{x} B1 0.15			\bar{x} B2 3.00			\bar{x} B3 4.56						

1 – control, 2 – urea (65 kg·ha⁻¹)+64 kg·ha⁻¹ P₂O₅ (Agrecol)+94 kg·ha⁻¹ K₂O (Agrecol), 3 – Polifoska 6 (500 kg·ha⁻¹), 4 – Polifoska 8 (375 kg·ha⁻¹) 5 – Polifoska B (375 kg·ha⁻¹), 6 – Polimag 305 (600 kg·ha⁻¹), 7 – Polimag 405 (600 kg·ha⁻¹), 8 – calcium sulfate tetraurea (112 kg·ha⁻¹)+64 kg·ha⁻¹ P₂O₅ (Agrecol)+ 94 kg·ha⁻¹ K₂O (Agrecol), 9 – granulate (430 kg·ha⁻¹)+84 kg·ha⁻¹ K₂O (potassium salt), 10 – phosphogypsum (3,500 kg·ha⁻¹)+ 30 kg·ha⁻¹ N (salmag) + 96 kg·ha⁻¹ K₂O (potassium salt) + 40 kg·ha⁻¹ P₂O₅ (triple superphosphate)

LSD – $\alpha = 0.05$ $\alpha^* = 0.01$

A – years 0.33

B – fractions 0.33

C – fertilization 0.84

A·B 0.78

A·C not significant

B·C not significant

Table 10. Percentage of mobile chromium fractions and residual fractions in pseudo-total content by BCR method.

Objects	2002		2003		2004		\bar{x} F1+F2+F3	\bar{x} residual
	F1+F2+F3	residual	F1+F2+F3	residual	F1+F2+F3	residual		
1	3.7	96.3	3.5	96.5	14.2	85.8	7.1	92.9
2	3.6	96.4	4.6	95.4	18.7	81.3	9.0	91.0
3	4.0	96.0	3.2	96.8	15.0	85.0	7.4	92.6
4	4.9	95.2	3.3	96.7	18.4	81.6	8.9	91.1
5	2.7	97.3	3.2	96.8	14.4	85.6	6.8	93.2
6	2.9	97.1	3.1	96.9	12.9	87.1	6.3	93.7
7	5.1	95.0	3.9	96.1	18.8	81.3	9.2	90.8
8	3.4	96.7	3.6	96.4	16.0	84.0	7.6	92.4
9	4.2	95.8	2.9	97.1	14.9	85.1	7.3	92.7
10	5.2	94.8	3.2	96.8	14.0	86.0	7.5	92.5
\bar{x}	4.0	96.1	3.4	96.6	15.7	84.3		

background of constant NPK fertilization. Chromium was accumulated mainly in residual fractions of studied soil and fractions bounded with Fe oxides. In the two most mobile fractions (according to Tessier) the amount of Cr was very low.

The content of discussed elements in fractions from particular years was significantly differentiated. Fractions bound with Fe/Mn oxides contained the most chromium (from about 2 to above 5% on average). Only in 2004 did more Cr contain fractions bounded with soil organic matter (due to redistribution from residual fraction). The content of chromium in this fraction, in 2004, was higher as compared to 2002 and 2003. In the case of exchangeable fractions, slight Cr content increase was also observed. This was the result of redistribution from F3 fraction in 2004. The average chromium content in fractions F2 and F3 in 2003 decreased, as compared to the year 2002. It was caused by pseudo-total Cr content increase in this year, as well as by redistribution from fractions F1, F2, and F3 to residual fractions of soil (Table 10). Such redistribution in a one-year study on sandy agricultural soil was observed by Han et al. [20]. Chromium in the form of nitrate applied into the soil was shifting as the time went by from soluble and exchangeable fractions into more stable fractions (bound with carbonates, Fe/Mn oxides, organic matter, and residual fraction). Chromium redistribution between particular fractions in the mineral fertilized soil was not stated by Zhao et al. [21].

Significant differences of chromium content in soil samples from particular years were observed. Its highest amount (5.24%) was found in soil samples from 2004. It was caused by redistribution of chromium from residual fraction (Table 10) into all three mobile fractions (especially into F3 fraction). The reason for such shifting is described above.

Conclusions

1. The accumulation of lead, cadmium, and chromium in soil was observed.
2. Mineral fertilization significantly influenced the content of lead and chromium mobile forms in the soil.
3. The lead content (mean values) in particular fractions can be arranged quantitatively in a sequence: F2 (26%)>F3 (16%)>F1 (2%), in the case of cadmium: F2 (27%)>F1 (17%)>F3 (5%), and in the case of chromium: F3 (4.6%)>F2 (3.0%)>F1 (0.2%).
4. The amount of most mobile cadmium and chromium forms (soluble + exchangeable fraction) increased during the experiment.

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References

1. HAYGARTH P.M., JONES K.C. Atmospheric deposition of metals to agricultural surfaces. In: Biogeochemistry of trace elements. Adriano D.C. (Eds.), Lewis Publishers, pp. 249-276, 1992.
2. SZYCZEWSKI P., SIEPAK J., NIEDZIELSKI P., SOBCZYŃSKI T. Research on heavy metals in Poland. Pol. J. Environ. Stud. **18**, (5), 755, 2009.
3. GRUPE M., KUNTZE H. Investigations about the availability of heavy metals in soils with lithogenic and anthropogenic enrichment. 1. Cd and Cu. Z. Pflanzenernähr. Bodenkd. **151**, 319, 1988.
4. BRESLIN V.T. Retention of metals in agricultural soils after

- amending with MSW and MSW-biosolids compost. *Water, Air, Soil Pollut.* **109**, 163, **1999**.
5. KLUGE R. Risk of heavy metal pollution of soils during application of composts. In: *Applying composts: Benefits and Needs.. European Commission Seminar Proceedings, Brussels 22-23 November*, pp. 207-208, **2001**.
 6. SANGHAMITRA S., GYANA R.R., PREMANANDA D. Role of chromium on plant growth and metabolism. *Acta Physiol. Plant.* **20**, 201, **1998**.
 7. FILIPEK-MAZUR B., GONDEK K. Impact of Cr(III) and (VI) on plant yielding and fractions of this metal in soil. *Zesz. Probl. Post. Nauk Roln.* **472**, 203, **2000** [In Polish].
 8. SHARMA P., DUBEY R.S. Lead toxicity in plants. *Braz. J. Plant Physiol.*, **17**, 35, **2005**.
 9. PAVLÍKOVÁ D., PAVLÍK M., VOKÁČ K., STASZKOVÁ L., BALÍK J., SZÁKOVÁ J., TLUSTOŠ, P. The effect of cadmium on plant metabolism. In: *Proceedings of the International Symposium on Trace Elements in the Food Chain. Szilágyi M., Szentmihályi K. (Eds.), Institute of Materials and Environmental Chemistry of the HAS, Budapest*, pp. 256-260, **2006**.
 10. SHANKER A.K., CERVANTES C., LOZA-TAVERA H., AVUDAINAYAGAM S. Chromium toxicity in plants. *Environ. Int.* **31**, 739, **2005**.
 11. RAURET G., LÓPEZ-SÁNCHEZ J.F., SAHUQUILLO A., RUBIO R., DAVIDSON C., URE A., QUEVAUVILLER Ph. Improvement of the BCR three-step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monit.* **1**, 57, **1999**.
 12. KABATA-PENDIAS A., PENDIAS H. Trace elements in soils and plants. 2nd Ed. CRS Press Inc., Boca Raton, Fl., USA, pp. 365, **1992**.
 13. GRUCA-KRÓLIKOWSKA S., WACŁAWEK W. Metals in the environment. Part II. Effect of heavy metals on plants. *Chemia-Dydaktyka-Ekologia-Metrologia* **11**, 41, **2006** [In Polish].
 14. GONDEK K. Contents of various forms of cadmium, copper, lead and chromium in soil after application of untreated and composted tannery sewage sludge. *Plant Soil Environ.* **52**, 199, **2006**.
 15. KALEMBASA S., KUZIEMSKA B. The influence of origin and application dates of sewage sludge on reaction and available zinc forms content in soil. In: *The circulation of heavy metals in nature. Gworek B., Misiak J., (Eds.), Institute of Environmental Protection, Warsaw*, pp. 326-328, **2003** [In Polish].
 16. MAZUR T. Quantity and perspective of organic matter balance in the agricultural soils. *Zesz. Probl. Post. Nauk Roln.* **421**, 267, **1995** [In Polish].
 17. BANAT K.M., HOWARI F. M., TO'MAH M. M. Chemical fractionation and heavy metal distribution in agricultural soils, north of Jordan Valley. *Soil Sediment Contam.* **16**, 89, **2007**.
 18. TU C., ZHENG C.R., CHEN H.M. Effect of applying chemical fertilizers on forms of lead and cadmium in red soil. *Chemosphere* **41**, 133, **2000**.
 19. CHRISTENSEN T.H., HUANG P.M. Solid phase cadmium and the reactions of aqueous cadmium with soil surfaces. In: *Cadmium in soils and plants. McLaughlin M.J., Singh B.R., (Eds.), Kluwer Academic Publishers*, pp. 65-96, **1999**.
 20. HAN F.X., BANIN A., LI Z.P. Redistribution index and relative binding intensity of heavy metals in salt-amended soils. *J. Environ. Sci. Health A Tox. Hazard Subst. Environ. Eng.* **36**, 1787, **2001**.
 21. ZHAO B., MAEDA M., ZHANG J., ZHU A., OZAKI Y. Accumulation and chemical fractionation of heavy metals in andisols after a different, 6-year fertilization management. *Environ. Sci. Pollut. Res. Int.* **13**, 90, **2006**.