Contents of various forms of cadmium, copper, lead and chromium in soil after application of untreated and composted tannery sewage sludge

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ABSTRACT

Fertilization with tannery materials positively influenced the soil pH and increased the content of alkaline cations in soil. After four years of investigations organic carbon content decreased most in the soil fertilized with untreated sludge, mineral salts and in the control soil. Irrespective of fertilization used and year of studies cadmium occurred mainly in most mobile fractions (mobile, exchangeable and bound to manganese oxides). Copper was mainly bound in fractions less available to plants. After four years of studies an increase in mobile copper forms was registered in all treatment soils. Lead in the soil was present mainly in the form bound to organic matter and amorphous iron oxides. Distribution of lead points to the small share of this metal in the mobile and exchangeable forms, both immediately after fertilization applied and after four years of studies. Chromium became fixed in fractions less available to plants, mainly bound to iron oxides and in residual fraction. On the other hand, an apparent effect of fertilization with materials of tannery origin on this element total forms content was registered.

Keywords: tannery sludge; compost; vermicompost; cadmium; copper; lead; chromium

Contents of heavy metals in soil are very important because soil is the first link in the food chain, therefore it has a determining effect on these elements translocation to plants and animal organisms.

While using sewage sludge for soil fertilization one should remember to prevent soil contamination with toxic substances. It is necessary to monitor the effect of sewage sludge containing some heavy metals on this mobility. Heavy metals supplied to the soil undergo various processes. As a result metal forms of different solubility are created (Chang et al. 1984, Borůvka et al. 1997).

Bioassimilability and solubility of heavy metals depend on a metal chemical form and soil properties. Oxy-reductive conditions, soil pH and also a number and a kind of humus compounds and silt particles are very important for immobilization of these substances (Steinbrich and Turski 1986, Swift and McLaren 1991, Alva et al. 2000, Heredia et al. 2001, Boruvka and Drabek 2004). In literature, besides investigations on the mentioned factors causing immobilization of heavy metals, works concerning introduction of synthetic substances capable of absorbing mobile forms of e.g. cadmium or lead become frequent contributions (Hlušek and Richter 1992, Tlustoš et al. 2001).

Apart form chromium, which is not very mobile in soils, concentrations of the other heavy metals in tannery sewage sludge do not pose a hazard to natural environment. However, to prove this thesis it is necessary to find out the effect of fertilization with untreated, composted or vermicomposted tannery sludge on bioavailability of selected heavy metals (cadmium, copper, lead and chromium), which conditions the rate of their penetration into the soil solution.

MATERIAL AND METHODS

A pot experiment was conducted in a vegetation hall of Agricultural Chemistry Department, Agricultural University of Krakow in 1996–1999 in Mitscherlich pots containing 5 kg of air-dried soil. In the experiment sewage sludge from the chemical treatment plant of tannery sludge was used as well as compost and vermicompost prepared from this sludge with straw addition. Straw addition to compost made up 10% of the sludge dry matter.

Composting lasted for 9 months. After this time a portion of compost was vermicomposted using *Eisenia fetida* redworm for 6 months. Farmyard manure and mineral salts (NPK) were used as a comparative treatment. Tannery materials used for fertilization were more abundant in nitrogen, calcium, and sodium than FYM, contained comparable with FYM amounts of magnesium and much less phosphorus and potassium. Heavy metal contents in materials originating from the tannery were higher than in FYM (Table 1).

The pot experiment was set up in the spring 1996 by the method of independent series and comprised 6 treatments in 4 replications (Table 4).

The experiment was conducted on brown medium compact soil of sand-silt loam texture, containing 23% of particles < 0.02 mm. The soil pH measured in 1 mol/dm^3 KCl solution was 6.45 and in water 6.61. Soil base exchange capacity was 86.5 mmol(+)/kg and hydrolytic acidity 9.50 mmol(+)/kg. The soil contained 0.87 g/kg of total nitrogen and 9.10 g of organic carbon in dry matter. The content of assimilated phosphorus was 84.23 mg P/kg and potassium 184.26 mg K/kg of soil dry matter. Heavy metal concentrations in forms approaching total and extracted with a mixture of HNO_3:$HClO_4$ (2:1) amounted to: Cr – 8.05; Zn – 103; Mn – 240; Cd – 1.57; Cu – 5.19; Pb – 21.97; Ni – 5.60 and Fe – 6875 (mg/kg of dry soil mass).

Doses of organic fertilizers (applied in the first year of the experiment) were computed on the basis of their nitrogen concentrations (1.0 g N/pot). Phosphorus fertilization was supplemented to 0.35 g P and potassium to 1.25 g K per pot (Table 2). Phosphorus and potassium were supplemented with chemically pure salts (P – $Ca(H_2PO_4)_2.H_2O$ and K – KCl). On the object with mineral treatment, components were used as solutions of chemically pure salts (N – NH_4NO_3, P – $Ca(H_2PO_4)_2.H_2O$ and K – KCl).

In the first year of the experiment, millet, Gierczyckie cv. was cultivated as the first crop. After seed emergence the plants were thinned and 15 plants per pot were left. After millet harvesting and application of supplementary nitrogen fertilization, white mustard Nakielska (Table 2) was sown. After emergence mustard plants were thinned and 12 pieces were left per pot. Both crops cultivated in the first year were harvested at the flowering phase. In the second year of the experiment maize plants KLG 2210 cv. were used as test plants, planted 5 items per pot and sunflower

Table 1. Chemical composition of materials used in experiment

Determination	Farmyard manure	Sewage sludge (not converted)	Compost (sewage sludge + straw)	Vermicompost (sewage sludge + straw)
Dry mass (g/kg)	190	295	328	340
g/kg dry matter				
Organic C	237	163	160	166
Total N	16.7	24.0	19.2	10.5
C:N ratio	14.2	6.8	8.3	15.8
P	4.1	0.8	1.1	1.0
K	11.4	0.6	1.1	1.0
Ca	9.3	27.5	22.7	22.4
Mg	3.9	2.4	3.4	2.9
Na	1.8	4.6	7.6	5.3
mg/kg dry matter				
Cu	3.6	11.2	10.1	9.5
Zn	170	195	297	300
Cr	15.1	875	458	386
Ni	4.1	24.0	15.0	14.2
Pb	9.2	20.3	40.7	29.8
Cd	0.55	0.39	0.27	0.27

Table 2. Plant cultivars and doses of mineral fertilizers

Year	Cultivated plant	Cultivar	Amount of plant in pot	Fertilization g/pot		
				N	P	K
1996	millet	Gierczyckie	15	1.00*	0.35**	1.25**
	white mustard	Nakielska	12	0.50	–	–
1997	maize	KLG 2210	5	1.00	0.35	1.08
	sunflover	Armawijskij	5	0.50	–	–
1998	spring triticale	Gabo	15	0.80	0.26	1.00
1999	maize	KLG 2210	6	0.20	–	–

*in form of organic fertilizers, **supplemented mineral

Armawijskij cv. During maize vegetation nitrogen deficiency in plants was observed showing as leaf yellowing and growth inhibition, therefore top N dressing was applied in the dose of 0.5 g N/pot applied as NH_4NO_3 on all treatments except the control. Maize was harvested at the stage of leaf sheaf thickening. Following the maize harvesting and additional nitrogen fertilization sunflower seeds were sown (Table 3). It was left at a density of 5 plants per pot. Sunflower plants were harvested at the flowering phase. In the third year of research spring triticale, Gabo cv. was sown and 15 plants per pot were left after emergence and harvested at full ripeness stage. In the fourth year after organic fertilizer application an after – effect of sludge, compost and vermicompost was researched with only 0.2 g N/pot applied on all treatments except the control. The last plants cultivated in this experiment was maize KLG 2210 cv. There were 6 plants per pot and they were harvested at the stage of leaf sheaf thickening.

After the harvest of plant tops in three successive years of the experiment, the roots of each plant were also collected. After each year of the investigations soil was sampled for chemical analyses.

In the organic materials (sludge, compost, vermicompost and farmyard manure) dry matter was assessed after drying in a dryer with the hot air flow (at 70°C). Further chemical analyses were conducted on dried and ground material. The total nitrogen was assayed after sample mineralization in concentrated sulphurous acid in an open system in automatic Kjeltec II Plus set (Tecator) using the Kjeldahl method. The organic carbon content was determined using the Tiurin method – after sample mineralization in potassium dichromate. The contents of ash components in organic materials were assessed after sample mineralization in a muffle furnace (at 450°C for 5 hrs) and dissolving the ash in nitric acid (1:2). Phosphorus content was assayed by the colorimetric method on Beckman DU 640 spectrophotometer at wave length 436 nm. Potassium, sodium and calcium were determined by flame photometry (FES), magnesium, chromium and other heavy metals by atomic absorption spectrometry (AAS) on Philips PU 9100X apparatus (Ostrowska et al. 1991).

In soil samples, dried and sifted through a 1 mm mesh, pH was determined after the first and fourth year of the experiment by potentiometer in 1 mol/dm^3 KCl and water suspension at soil to water ratio 1:2.5 (Ostrowska et al. 1991). Organic carbon was assessed by the Tiurin method after sample mineralization in potassium dichromate

Table 3. Heavy metals fractions in sequential extraction according to Zeien and Brümmer (1989)

Fraction	Description	Extracting agent	pH
F(I)	mobile	1 mol/dm^3 NH_4NO_3	natural
F(II)	exchangeable	1 mol/dm^3 ammonium acetate (NH_4-OAc)	6.0
F(III)	bound to MnOx	1 mol/dm^3 NH_2OH-HCl + 1 mol/dm^3 NH_4-OAc	6.0
F(IV)	organically bound	0.025 mol/dm^3 NH_4EDTA	4.6
F(V)	bound to amorphous FeOx	0.2 mol/dm^3 ammonium oxalate (NH_4-Oxal.)	3.25
F(VI)	bound to crystalline FeOx	0.2 mol/dm^3 NH_4-Oxal. + 1 mol/dm^3 ascorbic acid	3.25
F(VII)	residuum	65% $HClO_4$	–

(Ostrowska et al. 1991), cation exchange capacity was determined after extraction with 0.1 mol/dm^3 HCl (for 1 hr) at the ratio of soil to solution 1:10 using the Kappen method (Ostrowska et al. 1991). In the analyzed soil samples contents of individual fractions of cadmium, copper, lead and chromium were determined according to sequential chemical extraction of Zeien and Brümmer (1989), in which fractions presented in Table 3 were isolated. The contents of heavy metals in the obtained extracts were assayed by the ICP-AES method in JY 238 Ultrace apparatus. The total content of studied heavy metals was computed as a sum of F(I) to F(VII) fractions.

Chemical analyses of fertilizers and soil samples were conducted on materials prepared as weighted means from four replications (Polish standard-83/R-04012.00). On the basis of obtained results standard deviation (*SD*) and variability coefficient (*VC*%) were computed. For selected physico-chemical soil parameters (pH, organic C, sum of alkaline cation) and for individual fractions of researched heavy metals Spearman's coefficient of rank correlation (*r*) was computed ($P < 0.05$). Statistical computations were conducted using Statistica PL packet (Stanisz 1998). All chemical analyses were carried out in two simultaneous replications. The results of chemical analysis were accepted as reliable if random sampling error (*RSD*) of two replications did not exceed 5%.

RESULTS AND DISCUSSION

Among the applied organic materials untreated tannery sludge had the greatest effect on cadmium uptake and only plants receiving mineral fertilization absorbed slightly larger amounts of this element. The total uptake of copper by plants over the four years was the highest on the objects fertilized with farmyard manure and minerals. The plants fertilized with tannery materials absorbed lesser quantities of this element. The total amount of lead taken up by plants since the first until the fourth year was the smallest (besides the control) on objects fertilized with farmyard manure and tannery sludge. Plants fertilized with compost absorbed this element in the amounts comparable to these registered in plants receiving minerals, whereas the plants fertilized with vermicompost took up the largest quantities. Plants treated with materials of tannery origin, as might have been expected, absorbed the largest quantities of chromium (Table 4). However, it should be emphasized that the element became accumulated mainly in the root system, so in the organs, which are not destined for animal fodder.

After the first year of the experiment pH (measured in water suspension) of soil fertilized with untreated sludge, compost and vermicompost revealed lower values than in soil fertilized with farmyard manure. The lowest pH value was registered in soil fertilized with mineral salts. After four years of investigations soil pH declined most in the control soil (by 0.25 of pH unit) and in soil fertilized with farmyard manure (by 0.30 of pH unit), whereas treatment with tannery materials maintained soil pH at the same (Table 5). Changes in soil pH measured in 1 mol/dm^3 KCl solution (after the first year of the experiment) revealed similar tendencies as measured in water solution. Chemical analysis of soil after the fourth year of studies confirmed a positive effect of tannery materials on soil pH as compared to farmyard manure and mineral salts. Also Andrzejewski and Doręgowska (1987) registered a decline in soil acidification as a result of application of tannery waste materials.

Table 4. Heavy metals uptake (sum too four years) with plant biomass (in mg/pot)

Treatment	Cr	Cd	Cu	Pb
Soil no fertilization	0.147	0.096	0.440	0.364
Soil + farmyard manure	0.531	0.470	1.775	1.782
Soil + mineral fertilization	0.612	0.649	1.931	1.618
Soil + sewage sludge	0.820	0.638	1.670	1.633
Soil + compost	0.817	0.533	1.692	1.741
Soil + vermicompost	0.836	0.537	1.768	1.971
SD	0.267	0.203	0.550	0.580
VC%	43	42	36	38

Table 5. Some physico-chemical properties of soil

Treatment	pH		Organic C (g/kg)	CEC (mmol(+)/kg)
	H_2O	KCl		
After 1st year of experiment				
Soil no fertilization	6.80	6.18	8.6	48.7
Soil + farmyard manure	6.84	6.13	9.5	45.0
Soil + mineral fertilization	6.46	5.60	8.4	43.7
Soil + sewage sludge	6.57	6.14	8.3	43.9
Soil + compost	6.32	5.96	9.0	46.1
Soil + vermicompost	6.56	6.17	7.7	47.4
SD	0.20	0.23	0.62	1.99
VC%	3	4	7	4
After 4th year of experiment				
Soil no fertilization	6.55	6.13	6.6	36.3
Soil + farmyard manure	6.54	6.05	9.0	31.4
Soil + mineral fertilization	6.46	5.52	6.6	35.8
Soil + sewage sludge	6.65	6.42	6.3	38.0
Soil + compost	6.42	6.15	9.2	45.0
Soil + vermicompost	6.34	6.09	7.6	30.9
SD	0.11	0.30	1.28	5.14
VC%	2	5	17	14

Treatment with organic materials did not visibly affect diversification in soil organic carbon content after the first year of the experiment (Table 5). Determined quantities of organic carbon were smaller than found in soil sampled prior to the experiment outset (9.1 g/kg), except the soil fertilized with farmyard manure. After four years of studies, the largest decrease in organic C content was registered in the soil treated with untreated sludge, mineral salts as well as in the control soil, whereas only a slight decline was observed after fertilization with farmyard manure, compost and vermicompost.

Treatment with organic materials led to an increase in the cation exchange capacity of soil (in comparison with soil fertilized with farmyard manure and mineral salts) after the first year of the experiment. After the fourth year, the value decreased most (in comparison with the soil sampled after the first year) as a result of treatment with farmyard manure and mineral salts. Fertilization with compost maintained the value on a similar level as the value registered after the first year (Table 5). According to Filipek-Mazur and Gondek (2000) significant changes, which occurred in soil as a result of fertilization with organic tannery materials, concern the cation exchange capasity and the value of base saturation. Obtained results are in agreement with the quoted ones (Filipek-Mazur and Gondek 2000).

Total cadmium concentrations in soil after the first year of the experiment did not reveal great diversification among treatments and ranged between 0.59 mg/kg to 0.70 mg/kg (Figure 1). The contents were smaller than registered in soil prior to the experiment outset (1.57 mg/kg). Total cadmium content decreased after four years and ranged between 0.37 mg/kg to 0.50 mg/kg (Figure 2). In comparison with untreated soil, cadmium supplied with organic materials did not cause any visible increase in the share of the most mobile Cd forms in its total content, although its share in mobile fractions was diversified. After the first year between 0.04 and 0.25 mg/kg of mobile cadmium forms F(I) were registered, which made up between 6.2 and 38.3% of total cadmium content (Table 6). The share of manganese oxides and organic matter in cadmium binding varied and the sum of both

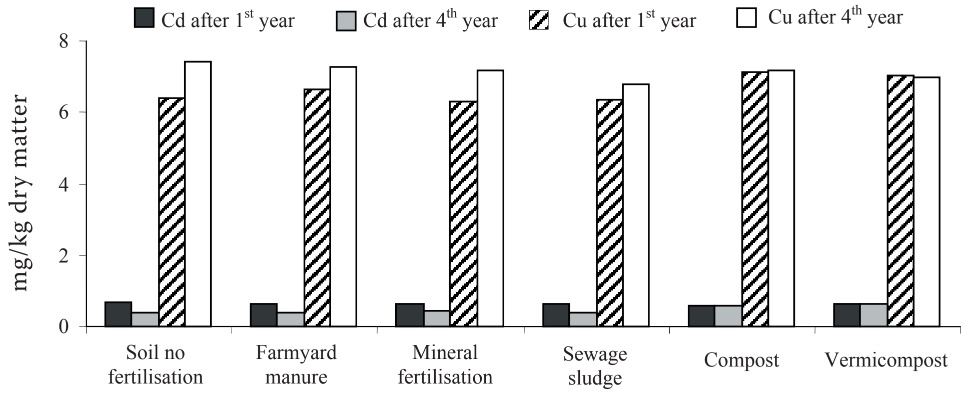

Figure 1. Total content cadmium and copper in soil of experiment

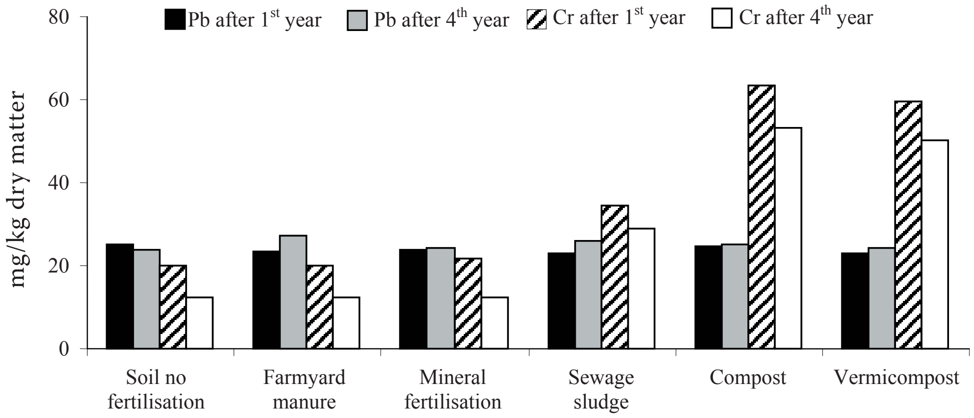

Figure 2. Total content lead and chromium in soil of experiment

fractions; F(III) and F(IV) fell within the 8.8 and 18.6% range of total contents. Total proportion of fractions bound with iron oxides F(V) and F(VI) after the first year constituted between 30.9 and 42.3% of total cadmium content. In the analysed soil cadmium did not occur in residual fraction F(VII). After four years of studies, the proportion of the most mobile fractions of Cd (fractions F(I); F(II) and F(III) differentiated reaching 78.7% in soil fertilized with vermicompost. After 4 years the share of cadmium bound by soil organic matter was similar to the quantity determined after the first year. Fraction bound to iron oxides accumulated similar amounts. Like in soil after the first year of the experiment cadmium did not occur in residual fraction. On the basis of conducted statistical analysis a significant positive relationship was registered between the CEC and cadmium content (after the first year) in fraction bound to manganese oxides F(III) ($r = 0.941$; $P < 0.05$) and cadmium bound to crystalline iron oxides F(VI) ($r = 0.927$; $P < 0.05$). Such relationship was not found after four years of the studies. Fertilization with organic materials did not cause any excessive activation of cadmium, whose mobility depends considerably on soil pH (Li et al. 2001), although Holm et al. (2003) found that at higher soil pH this element mobilization is affected by base exchange capacity, whereas at lower pH values iron oxides play an important role in cadmium binding. Increased cadmium retention in soils after application of sewage sludge was reported also by Hettiarachchi et al. (2003). According to Kabata-Pendias and Pendias (1999) municipal wastes and cadmium compounds supplied to the soil cause its considerable activation. It happens because wastes, particularly municipal ones, are characterized by high concentrations of this metal, largely exceeding its levels in tannery materials. Lack of the cadmium residual form in soil after the first and fourth year of investigations was not confirmed by results of experiments conducted

Table 6. Cadmium fraction in soil (mg/kg dry matter of soil)

Treatment	Fraction						
	F(I)	F(II)	F(III)	F(IV)	F(V)	F(VI)	F(VII)
After 1st year of experiment							
Soil no fertilization	**0.13**	**0.19**	**0.06**	**0.06**	**0.13**	**0.13**	**0.00**
	18.14	27.29	9.14	9.14	18.14	18.14	0.00
Soil + farmyard manure	**0.19**	**0.13**	**0.00**	**0.06**	**0.16**	**0.10**	**0.00**
	30.00	20.00	0.00	10.00	25.00	15.00	0.00
Soil + mineral fertilization	**0.25**	**0.14**	**0.00**	**0.06**	**0.12**	**0.09**	**0.00**
	38.31	22.00	0.00	8.77	17.69	13.00	0.00
Soil + sewage sludge	**0.04**	**0.23**	**0.00**	**0.09**	**0.17**	**0.09**	**0.00**
	6.23	37.54	0.00	14.10	28.20	14.10	0.00
Soil + compost	**0.06**	**0.20**	**0.04**	**0.07**	**0.13**	**0.09**	**0.00**
	10.00	33.73	7.46	11.19	22.54	15.08	0.00
Soil + vermicompost	**0.05**	**0.21**	**0.05**	**0.05**	**0.16**	**0.10**	**0.00**
	8.39	33.39	8.39	8.39	25.00	16.61	0.00
SD	0.086	0.039	0.030	0.012	0.022	0.016	–
VC%	72	21	112	18	15	16	–
After 4th year of experiment							
Soil no fertilization	**0.19**	**0.04**	**0.09**	**0.03**	**0.02**	**0.03**	**0.00**
	46.34	10.73	21.46	8.05	5.37	8.05	0.00
Soil + farmyard manure	**0.18**	**0.02**	**0.09**	**0.02**	**0.02**	**0.05**	**0.00**
	47.11	5.79	23.42	5.79	5.79	11.84	0.00
Soil + mineral fertilization	**0.23**	**0.03**	**0.06**	**0.04**	**0.03**	**0.05**	**0.00**
	53.95	5.81	14.42	8.60	5.81	11.63	0.00
Soil + sewage sludge	**0.21**	**0.03**	**0.07**	**0.03**	**0.03**	**0.04**	**0.00**
	53.50	6.25	18.50	6.25	6.25	9.25	0.00
Soil + compost	**0.28**	**0.06**	**0.13**	**0.04**	**0.04**	**0.06**	**0.00**
	46.61	9.49	22.20	6.44	6.44	9.49	0.00
Soil + vermicompost	**0.30**	**0.04**	**0.15**	**0.04**	**0.04**	**0.06**	**0.00**
	48.39	6.13	24.19	6.13	6.13	9.03	0.00
SD	0.048	0.013	0.034	0.007	0.008	0.010	–
VC%	21	38	35	22	27	21	–

numerator – mg/kg, denominator – % of total content

by Chłopecka (1994) who detected the highest amounts of cadmium (50%) in the residual form, less (15%) in exchangeable and carbonate forms, while manganese and iron oxides accumulated relatively small quantities of this element.

Total copper concentrations in soil after the first year of studies were similar in all treatments and ranged between 6.29 and 7.13 mg/kg dry mass of soil (Figure 1). The total content of copper after four years did not change much (Figure 2). Amounts of copper accumulated in the most mobile fractions F(I)–F(III) were small, whereas considerable Cu quantities were bound by soil organic matter (Steinbrich and Turski

Table 7. Copper fraction in soil (mg/kg dry matter of soil)

Treatment	Fraction						
	F(I)	F(II)	F(III)	F(IV)	F(V)	F(VI)	F(VII)
After 1st year of experiment							
Soil no fertilization	**0.28**	**0.17**	**0.09**	**1.72**	**1.41**	**1.13**	**1.60**
	4.30	2.64	1.47	26.98	21.99	17.61	25.02
Soil + farmyard manure	**0.28**	**0.39**	**0.11**	**1.69**	**1.43**	**1.14**	**1.60**
	4.14	5.93	1.69	25.42	21.48	17.23	24.11
Soil + mineral fertilization	**0.23**	**0.15**	**0.09**	**1.58**	**1.41**	**1.16**	**1.68**
	3.58	2.38	1.49	25.05	22.37	18.49	26.64
Soil + sewage sludge	**0.24**	**0.24**	**0.08**	**1.63**	**1.39**	**1.01**	**1.77**
	3.73	3.84	1.18	25.64	21.81	15.91	27.89
Soil + compost	**0.21**	**0.28**	**0.11**	**1.75**	**1.61**	**1.16**	**2.00**
	2.97	3.96	1.58	24.47	22.64	16.33	28.06
Soil + vermicompost	**0.25**	**0.23**	**0.19**	**1.86**	**1.46**	**1.20**	**1.85**
	3.56	3.20	2.67	26.40	20.80	17.07	26.32
SD	0.026	0.088	0.039	0.097	0.084	0.065	0.158
VC%	11	36	35	6	6	6	9
After 4th year of experiment							
Soil no fertilization	**0.68**	**0.60**	**0.73**	**1.88**	**0.79**	**1.01**	**1.75**
	9.08	8.08	9.84	25.24	10.61	13.62	23.55
Soil + farmyard manure	**0.60**	**0.49**	**0.75**	**1.73**	**0.77**	**1.22**	**1.68**
	8.25	6.71	10.32	23.76	10.58	16.78	23.05
Soil + mineral fertilization	**0.63**	**0.56**	**0.79**	**1.69**	**0.73**	**1.16**	**1.63**
	8.70	7.83	10.97	23.50	10.18	16.18	22.63
Soil + sewage sludge	**0.43**	**0.51**	**0.71**	**1.65**	**0.81**	**0.94**	**1.75**
	6.26	7.47	10.50	24.32	11.89	13.81	25.77
Soil + compost	**0.30**	**0.56**	**0.83**	**1.69**	**0.98**	**0.98**	**1.88**
	4.17	7.81	11.46	23.44	13.54	13.54	26.04
Soil + vermicompost	**0.33**	**0.49**	**0.86**	**1.65**	**0.88**	**0.98**	**1.80**
	4.66	6.98	12.36	23.62	12.62	13.97	25.77
SD	0.163	0.047	0.058	0.084	0.089	0.115	0.088
VC%	33	9	7	5	11	11	5

numerator – mg/kg, denominator – % of total content

1986, Merritt and Erich 2003). After the first year of the experiment between 1.58 mg/kg (i.e. 25.1% of total content) in soil receiving mineral salts and 1.86 mg/kg (i.e. 26.4% of total content) in soil fertilized with vermicompost fell for fractions bound to organic matter (Table 7). After the first year, copper in soil was also accumulated in fractions bound to iron oxides: F(V) and F(VI) and in residual fraction F(VII). After four years in soils of all treatments an increase in copper mobile forms was registered. The sum of the mobile fraction F(I), exchangeable F(II) and bound to manganese oxides F(III) was between 1.65 and 2.00 mg/kg, which made up between 24.2 and 26.9% in rela-

Table 8. Lead fraction in soil (mg/kg dry matter of soil)

Treatment	Fraction						
	F(I)	F(II)	F(III)	F(IV)	F(V)	F(VI)	F(VII)
After 1st year of experiment							
Soil no fertilization	**0.03**	**1.20**	**3.23**	**8.44**	**6.81**	**2.55**	**2.70**
	0.10	4.81	12.93	33.83	27.29	10.22	10.82
Soil + farmyard manure	**0.11**	**1.33**	**3.36**	**8.53**	**5.31**	**2.40**	**2.55**
	0.48	5.64	14.23	36.17	22.50	10.17	10.81
Soil + mineral fertilization	**0.07**	**1.07**	**3.34**	**8.42**	**5.29**	**2.49**	**3.20**
	0.31	4.48	13.98	35.25	22.14	10.44	13.40
Soil + sewage sludge	**0.08**	**0.90**	**2.64**	**8.48**	**5.76**	**2.33**	**2.82**
	0.33	3.91	11.49	36.85	25.03	10.11	12.28
Soil + compost	**0.09**	**0.73**	**2.51**	**9.19**	**6.43**	**2.57**	**3.22**
	0.35	2.96	10.15	37.13	25.99	10.38	13.03
Soil + vermicompost	**0.19**	**0.68**	**2.42**	**8.68**	**5.59**	**2.44**	**2.80**
	0.82	2.96	10.61	38.10	24.52	10.70	12.29
SD	0.054	0.261	0.437	0.292	0.622	0.093	0.273
VC%	58	26	15	3	11	4	9
After 4th year of experiment							
Soil no fertilization	**0.75**	**1.39**	**5.51**	**7.31**	**4.42**	**1.89**	**2.70**
	3.13	5.79	22.99	30.49	18.45	7.90	11.26
Soil + farmyard manure	**0.65**	**1.58**	**4.82**	**6.94**	**4.33**	**2.72**	**6.23**
	2.38	5.78	17.68	25.45	15.89	9.97	22.84
Soil + mineral fertilization	**1.25**	**1.78**	**4.54**	**7.24**	**4.84**	**2.04**	**2.77**
	5.11	7.28	18.55	29.59	19.78	8.35	11.34
Soil + sewage sludge	**0.80**	**1.74**	**5.08**	**8.32**	**4.91**	**2.08**	**2.88**
	3.10	6.75	19.68	32.24	19.03	8.06	11.14
Soil + compost	**0.58**	**1.24**	**4.01**	**7.99**	**5.98**	**2.08**	**3.03**
	2.31	4.97	16.11	32.08	24.02	8.36	12.15
Soil + vermicompost	**0.85**	**1.18**	**4.39**	**7.63**	**5.23**	**2.08**	**2.88**
	3.51	4.87	18.10	31.49	21.58	8.59	11.86
SD	0.237	0.255	0.532	0.514	0.602	0.288	1.383
VC%	29	17	11	7	12	13	41

numerator – mg/kg, denominator – % of total content

tion to total content. The greatest proportion of mobile forms was detected in soil of untreated object. Organic matter had a significant share in copper binding in soil after four years of studies; it bound between 23.4 and 25.2% of this element. The greatest proportion of this fraction was registered in the untreated soil. After the first year copper content in fraction bound to organic matter was positively correlated with the CEC ($r = 0.828$; $P < 0.05$). After four year of studies a significant relationship was found between the content of copper bound in organic fraction F(IV) and soil pH ($r = 0.840$; $P < 0.05$). In experiments conducted by Filipek-Mazur et

Table 9. Chromium fraction in soil (mg/kg dry matter of soil)

Treatment	Fraction						
	F(I)	F(II)	F(III)	F(IV)	F(V)	F(VI)	F(VII)
After 1st year of experiment							
Soil no fertilization	**0.20**	**0.21**	**0.11**	**0.32**	**2.55**	**3.49**	**13.10**
	1.00	1.03	0.56	1.60	12.77	17.49	65.58
Soil + farmyard manure	**0.13**	**0.21**	**0.11**	**0.32**	**2.61**	**3.53**	**12.99**
	0.63	1.04	0.57	1.60	13.10	17.72	65.35
Soil + mineral fertilization	**0.43**	**0.19**	**0.13**	**0.34**	**2.63**	**3.47**	**15.03**
	0.57	0.86	0.60	1.54	11.99	15.84	68.61
Soil + sewage sludge	**0.09**	**0.19**	**0.15**	**0.39**	**7.22**	**8.76**	**17.73**
	0.25	0.54	0.43	1.14	20.91	25.37	51.35
Soil + compost	**0.08**	**0.26**	**0.19**	**0.56**	**10.51**	**24.05**	**21.30**
	0.12	0.41	0.30	0.89	16.61	38.01	33.66
Soil + vermicompost	**0.08**	**0.26**	**0.21**	**0.54**	**14.93**	**22.50**	**20.98**
	0.13	0.44	0.35	0.91	25.09	37.82	35.26
SD	0.046	0.032	0.042	0.110	5.158	9.762	3.739
VC%	39	15	28	27	77	89	22
After 4th year of experiment							
Soil no fertilization	**0.13**	**0.28**	**0.53**	**0.41**	**2.46**	**2.98**	**5.73**
	1.00	2.25	4.20	3.30	19.64	23.84	45.78
Soil + farmyard manure	**0.18**	**0.21**	**0.56**	**0.39**	**2.40**	**3.38**	**5.23**
	1.41	1.66	4.54	3.18	19.37	27.25	42.58
Soil + mineral fertilization	**0.20**	**0.23**	**0.51**	**0.43**	**2.44**	**3.11**	**5.60**
	1.60	1.80	4.05	3.45	19.48	24.88	44.76
Soil + sewage sludge	**0.15**	**0.21**	**0.56**	**0.51**	**6.96**	**6.51**	**13.95**
	0.52	0.72	1.95	1.76	24.12	22.56	48.37
Soil + compost	**0.35**	**0.26**	**0.64**	**0.62**	**17.53**	**13.89**	**20.10**
	0.66	0.49	1.19	1.16	32.83	26.02	37.64
Soil + vermicompost	**0.28**	**0.30**	**0.65**	**0.64**	**15.84**	**13.55**	**19.03**
	0.55	0.60	1.30	1.27	31.50	26.95	37.83
SD	0.084	0.038	0.058	0.109	7.019	5.190	6.986
VC%	39	15	10	22	88	72	60

numerator – mg/kg, denominator – % of total content

al. (2001) organic fertilization did not have any marked effect on copper mobility. Also Gambuś (1989) studied this element behavior depending on soil pH and organic matter content. The experiment mentioned above is important because of large quantities of calcium and organic matter supplied to the soil together with tannery sewage sludge. On the basis of research carried out on two soils with clay silt and strong loamy sand texture Gambuś (1989) found that copper supplied to the soil became unchangeably bound to organic matter, while an increase in organic matter level and soil reaction caused a decline in copper quantities in fractions considered best available to plants. In their studies on many-years mineral and organic fertilization effect on fractions of *inter alia* copper in soil, Jakubus et al. (1996) demonstrated that the fertilization did not cause any excessive copper accumulation in soil whereas farmyard manure decreased the share of Cu easily soluble fraction in its total content and mineral treatment increased the share.

Total content of lead in soil after the first and fourth year of the experiment remained at the similar level (Figures 1 and 2). Fertilization with tannery materials did not have a significant effect on the contents of Pb total forms. Lead accumulated mainly in a form bound to soil organic matter and to amorphous iron oxides. Distribution of lead reveals small proportion of its mobile and exchangeable forms, both immediately after applied fertilization and after four years of investigations (Table 8). Treatment with organic materials did not cause changes in shares of individual lead forms in comparison with farmyard manure treatment and mineral salts or to the control soil. A small content of lead in mobile forms detected in the presented work corroborates some earlier research (Filipek-Mazur et al. 2001). The quoted work also confirms considerable share of this metal in fraction bound to organic matter and in compounds with amorphous and crystalline iron oxides (Kabata-Pendias and Pendias 1999).

No greater diversification was found in the proportion of the most mobile chromium forms (mobile, exchangeable and bound to manganese oxides) when organic materials of tannery origin were used for treatment (Table 9). Chromium became fixed in fractions less available to plants, mainly bound to iron oxides and in residual fraction (Table 9). On the other hand, an apparent effect of fertilization with materials of tannery origin on this element content of total forms was registered (Figures 1 and 2).

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