

## EFFECT OF VARIOUS ORGANIC FERTILISERS ON THE HEAVY METAL FRACTIONS IN THE SOIL

### Part 1. LEAD, COPPER AND NICKEL

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**A b s t r a c t.** The present investigations aimed at determining the effect of various organic materials, i.e. farmyard manure (FYM), organic tannery sludge and compost of such sludge and peat on lead, copper and nickel fractions content in soil. Doses of peat compost and organic sludge were calculated according to the nitrogen amount per a FYM dose.

After four years of experiment, fractions of Pb, Cu and Ni compounds were assessed in the soil from individual plots using the Zeien and Brummer's sequence chemical extraction method. Heavy metal contents were determined using a ICP-AES in JY 238 Ultrace apparatus.

Lead accumulated mainly in the form bound with organic matter and with amorphous iron oxides. This metal distribution reveals its slight share in the mobile and exchangeable forms. Composts and sludge introduced into the soil did not affect any significant changes of the individual lead forms share as compared to FYM and NPK treated plots and the control.

Some amount of copper occurred as mobile forms in all the soils. In the soil of all the treated plots, copper occurred mainly bound with organic matter and amorphous iron oxides.

The basic share of nickel was found in the residual fraction bound with internal crystalline nets of initial elements. Beside the residual form, nickel was connected mainly with organic matter.

**K e y w o r d s:** soil, organic materials, chemical extraction, lead, copper, nickel.

## INTRODUCTION

Crop yields and their quality depend on both properly selected fertilisers [21] and site conditions, particularly on the soil properties modified by anthropopressure. Heavy metal contamination resulting from dust and gas emissions, and also industrial and municipal wastes and fertilisers considerably affect the level of soil degradation [17]. The factor modifying degradation is organic matter which enriches soil in humus substances and nutrients indispensable for plants and stimulating soil biological activity [1,3,13,16]. Sewage sludge and industrial and

municipal wastes provide an important source of organic matter. At the same time they may cause biological and chemical contamination of soils, especially with heavy metals [20,22]. Unfavourable influence of those metals on plants depends on the form in which they occur in the soil, which decides about their bio-availability.

The present investigations aimed at determining the forms in which lead, copper and nickel occur in soil after application of various organic fertilisers.

#### MATERIAL AND METHODS

The paper is based on a four-year field experiment conducted in 1993-1996. It was set up on brown soil, silty-clay with  $\text{pH}_{\text{KCl}}=5.40$ , 1.92% of organic carbon and 0.26% total nitrogen. The contents of available forms of potassium and phosphorus fell within medium value range and were as follows, respectively per 100 g of soil: 18.75  $\text{K}_2\text{O}$  and 13.75 mg  $\text{P}_2\text{O}_5$ . The contents of heavy metals (Pb, Cu, Ni, Zn, Mn, Fe, Cr and Cd) approximated to natural contents had been assessed in  $\text{HNO}_3$  and  $\text{HClO}_4$  mixture before the outset of experiment using the AAS method in a 9100 X Philips apparatus. Detailed soil characteristics are presented in Table 2.

The experiment, including 9 plots in 4 replications, was set up using randomised blocks method. Mixed farmyard manure (FYM) was the control fertiliser; it was applied in two doses: 30 and 60  $\text{t ha}^{-1}$ . The doses of peat compost and raw organic sludge were calculated according to the amount of nitrogen in the applied FYM dose (120 and 240  $\text{kg N ha}^{-1}$ ). Phosphorus on the plots with manure and raw organic sludge was supplemented with superphosphate to the amount applied in the peat compost (283 and 566  $\text{kg P}_2\text{O}_5 \text{ ha}^{-1}$ ), while potassium was supplemented up to its amount in manure doses (157 and 314  $\text{kg K}_2\text{O ha}^{-1}$ ) as 60% potassium salt. Peat compost used in the experiment had been prepared from organic sludge supplied by a sewage treatment plant of Cracow Tannery with an addition of 10% of dry mass of "garden peat" in relation to dry sludge mass. The composting period was 12 months. Chemical composition of the materials used in the experiments is presented in Table 3. In the first year of the experiment, a mixture of mustard and sunflower was cultivated, and potatoes, fodder beets and potatoes in the following three years.

After four years of the experiment, the contents of heavy metals (Pb, Cu, and Ni) were assayed in average soil samples from individual experimental plots using the Zeien and Brummer's sequential chemical extraction

**Table 1.** Heavy metal fractions in sequential extraction according to Zeien and Brummer

Fraction No.	Description	Extracting agent	pH
F <sub>1</sub>	Mobile	1 mol dm <sup>-3</sup> NH <sub>4</sub> NO <sub>3</sub>	natural
F <sub>2</sub>	Exchangeable	1 mol dm <sup>-3</sup> ammonium acetate (NH <sub>4</sub> -OAc)	6.0
F <sub>3</sub>	Bound to MnOx	1 mol dm <sup>-3</sup> NH <sub>2</sub> OH-HCl + 1 mol dm <sup>-3</sup> NH <sub>4</sub> -OaAc	6.0
F <sub>4</sub>	Organically bound	0.25 mol dm <sup>-3</sup> NH <sub>4</sub> EDTA	4.6
F <sub>5</sub>	Bound to crystalline FeOx	0.2 mol dm <sup>-3</sup> ammonium oxalate (NH <sub>4</sub> -Oxal.)	3.25
F <sub>6</sub>	Bound to crystalline FeOx	0.2 mol dm <sup>-3</sup> NH <sub>4</sub> -Oxal. + 1 mol dm <sup>-3</sup> ascorbic acid	3.25
F <sub>7</sub>	Residium	65% HClO <sub>4</sub>	-

**Table 2.** Physical and chemical properties of soil before the experiment

Property		Soil
Fraction <0.02 mm	(%)	48
Organic C	(%)	1.92
Total N	(%)	0.26
BEC	(cmol kg <sup>-1</sup> )	9.81
Hydrolytic H	(cmol kg <sup>-1</sup> )	3.90
CEC	(cmol kg <sup>-1</sup> )	13.71
pH(H <sub>2</sub> O)		6.50
pH(KCl)		5.40
P <sub>2</sub> O <sub>5</sub>	(mg 100 g <sup>-1</sup> )	13.75
K <sub>2</sub> O	(mg 100 g <sup>-1</sup> )	18.75
	Extraction HNO <sub>3</sub> + HClO <sub>4</sub> (mg kg <sup>-1</sup> soil)	
Pb		25.72
Cu		13.75
Ni		21.80
Zn		61.50
Mn		1205.75
Fe		28425.00
Cr		21.80
Cd		0.98

method [24]. A list of assayed fractions is presented in Table 1. The assessment of heavy metal contents in individual fractions was done according to ICP-AES method in JY 238 Ultrace apparatus.

**Table 3.** Properties of materials used in experiment

Property	FYM	Peat compost	Raw sludge
Dry mass (%)	27.96	37.80	19.73
Content in dry mass (%)			
Ash	25.20	45.42	35.24
Total N	1.42	1.00	5.07
P <sub>2</sub> O <sub>5</sub>	1.28	2.34	2.02
K <sub>2</sub> O	1.84	0.12	0.08
Ca	0.70	4.80	5.70
Mg	0.82	0.46	0.28
Na	0.07	0.62	1.16
Content in dry mass (mg kg <sup>-1</sup> )			
Cr	166.0	3019.0	2854.0
Zn	35.6	156.1	180.0
Mn	120.0	443.0	444.0
Cd	0.25	1.86	2.02
Cu	5.44	25.50	27.83
Pb	9.91	24.84	27.15
Ni	3.32	20.46	22.05
Fe	995.0	8670.0	8035.0

## RESULTS AND DISCUSSION

No clear differentiation in total lead contents in the studied soil has been observed between plots after the experiment was completed. Soil from the plots fertilised with a single and double dose of raw sludge revealed the highest contents (Table 4).

**Table 4.** Percentage distribution of lead fractions in Pb total content in air-dry mass of soil

Fertilizer object	Total concentration (mg kg <sup>-1</sup> )**	Contribution of particular fractions (%)***						
		F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>	F <sub>7</sub>
No fertilization	13.00	0.13	1.45	5.22	43.16	32.66	5.00	12.39
FYM I*	13.29	0.46	2.82	2.98	38.60	37.32	5.40	12.42
FYM II*	12.74	0.25	3.13	4.21	42.42	35.59	4.25	9.77
Peat compost I*	12.88	1.20	1.82	3.64	42.23	36.02	4.91	11.14
Peat compost II*	12.75	1.02	2.67	4.44	45.70	30.13	4.72	11.14
Sludge I*	14.82	0.92	3.55	5.93	39.88	35.43	4.67	9.52
Sludge II*	19.26	0.75	3.69	8.70	30.33	40.68	3.64	12.00
H. Mineral fertilization I*	12.48	2.12	2.01	3.77	43.73	35.00	4.96	9.77
Mineral fertilization II*	11.81	2.12	2.45	3.83	43.59	32.63	3.40	11.98

\*I-single dose, II - double dose; \*\* sum of fraction F<sub>1</sub> - F<sub>7</sub>; \*\*\*For fraction description see Table 1.

Distribution of lead in the isolated fractions points to a small proportion of this metal in the mobile  $F_1$  and exchangeable  $F_2$  forms, which are the most active and available to plants. Peat compost based on tannery sludge applied as fertiliser and raw sludge caused a slight increase in the mobile form share, which in soil from plots treated with compost constituted between 1.20 and 1.02% of total contents, while in soil fertilised with sludge the values were lower, respectively 0.92 and 0.75% of total contents. A small share of lead soluble forms in total contents of this metal was caused by the soil reaction which, in all treatments, was higher than pH 5. It has been commonly accepted that lead is easily activated and reveals higher dynamics of translocation when soil reaction is acid, particularly when pH takes the value below 5 [5].

The highest share of mobile form has been detected in the soil of NPK mineral treatments. It constituted 2.12% of the total contents irrespective of the fertiliser dose. Similar results were obtained in some earlier studies [2]. Slightly higher percentage of lead in its total contents was observed in  $F_2$  and  $F_3$  fractions, especially following the sludge treatment. The most of lead (Table 4) occurred in the combinations with soil organic matter  $F_4$  (30.330-45.70% of lead total) and in combinations with amorphous iron oxides  $F_5$  and  $F_6$  (30.13-40.86% of lead total).

Some other authors [4,6,11,18,23] pointed to a significant role of iron oxides and soil organic matter in accumulation of lead. In the residual fraction  $F_7$ , a small amount of this metal was found (9.52-12.42%). Introduction into the soil of both compost of tannery sludge with added peat and the sludge itself did not significantly affect a change in the proportions of individual fractions of lead in soil in comparison to soil from plots fertilised with manure and NPK organic fertilisers, as well as to the soil from the control (untreated).

Total content of copper was similar, i.e. between 15.13 and 18.56 mg kg<sup>-1</sup> depending on the treatment (Table 5). In all the soil samples very little copper occurred as a mobile form (1.20-2.00% of total contents) caused by a strong fixation of this metal by organic matter and clayey minerals and its precipitation as sulphates, sulphides and carbonates, which limited its mobility [8]. Soil reaction is also important. It is decisive for copper solubility, similarly as for lead. The above has been confirmed in literature [5,23]. About 9.1% of the total contents in the soil fertilised with a single dose of peat compost and 11.8% in the soil treated with a double dose of NPK mineral fertilisers was an exchangeable fraction and the fraction connected with manganese oxides ( $F_2$  and  $F_3$ ). In the soil of all the treatments, copper occurred mainly linked to organic matter ( $F_4$ ) and to amorphous iron oxides

**Table 5.** Percentage distribution of copper fractions in Cu total content in air-dry mass of soil

Fertilizer objects*	Total concentration (mg kg <sup>-1</sup> )	Contribution of particular fractions (%)						
		F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>	F <sub>7</sub>
No fertilization	18.56	2.0	4.8	5.5	32.4	29.7	9.2	16.5
FYM I	18.01	1.8	5.2	5.4	33.2	27.7	10.8	15.8
FYM II	17.27	1.8	3.7	5.6	33.4	31.5	10.2	14.1
Peat compost I	16.58	1.4	3.5	5.6	33.9	30.2	9.4	15.6
Peat compost II	16.82	1.9	3.9	5.9	32.2	31.1	9.4	16.1
Sludge I	17.10	1.5	4.1	6.1	32.2	29.3	9.6	16.9
Sludge II	17.16	1.2	4.9	6.0	31.3	29.5	8.3	18.5
Mineral fertilization I	16.68	1.6	4.6	5.7	33.7	29.4	9.6	15.8
Mineral fertilization II	15.13	1.6	5.1	6.7	36.1	24.6	7.7	18.2

\*For explanations see Tables 1 and 4.

(F<sub>5</sub>), the fact stated by other authors [8,23]. Jointly, both fractions constituted over 60% of the total copper contents, while the form attached to organic matter slightly prevailed. The results have been confirmed by Mocek and Owczarzak [15] and Jasiewicz [7]. The phenomenon of copper binding by organic matter should be considered beneficial as it limits this metal penetration into the soil solution and at the same time temporarily limits its availability to plants preventing its excessive share in the farther links of food chain.

Following diversified treatment, total nickel contents in soil (Table 6) reached an average level of 11.59 mg kg<sup>-1</sup>, except for the soil from plots fertilised with double doses of FYM (17.81 mg Ni kg<sup>-1</sup>) and with peat compost (17.99 mg Ni kg<sup>-1</sup>). Irrespective of the total nickel contents in the investigated soil, percentage of this element in individual fractions was similar. The highest amount of nickel was detected in the residual fraction attached to the inner crystal lattices of primeval minerals. Particularly high proportion of this fraction was detected in the soil fertilised with double doses of manure (55.8%), with peat compost (52.4%) and in the soil from the control (48.9%). Such a high share of the residual form in the control soil could have been caused by high natural contents of this element in soil before the experiment. Beside the residual form, nickel was linked mainly with organic matter, which has been confirmed by Kabata-Pendias [8]. The combinations constituted between 15.9 and 22.1% of the total nickel contents in the soil. In the mobile F<sub>1</sub> fraction, between 4.5 and 9.3% of nickel was detected, and iron oxides (F<sub>5</sub> and F<sub>6</sub>) jointly absorbed between 16.3-27.3% Ni total. The proportions of this fraction decreased along with a decrease in the soil acidity. Other authors [8,12,14] obtained similar results.

**Table 6.** Percentage distribution of nickel fractions in Ni total content in air-dry mass of soil

Fertilizer objects*	Total concentration (mg kg <sup>-1</sup> )	Contribution of particular fractions (%)						
		F <sub>1</sub>	F <sub>2</sub>	F <sub>3</sub>	F <sub>4</sub>	F <sub>5</sub>	F <sub>6</sub>	F <sub>7</sub>
No fertilization	14.46	5.8	3.3	4.9	16.4	10.9	9.7	48.9
FYM I	12.27	8.2	4.7	5.0	17.8	13.2	11.1	40.1
FYM II	17.81	8.8	3.8	3.9	12.8	8.7	7.6	55.8
Peat compost I	11.53	4.5	4.8	6.5	20.8	13.8	11.9	33.3
Peat compost II	17.99	8.1	3.7	4.7	15.9	10.7	8.1	52.4
Sludge I	11.80	8.9	4.7	5.5	21.2	15.4	11.0	34.1
Sludge II	11.75	7.1	5.5	6.0	20.5	12.3	12.2	34.5
Mineral fertilization I	10.57	9.3	4.9	5.7	22.1	14.5	12.8	32.8
Mineral fertilization II	11.22	9.3	5.4	8.3	19.8	13.4	7.4	36.5

\*For explanations see Tables 1 and 4.

### CONCLUSIONS

1. The applied organic fertilisers did not cause an increase in the total Pb, Cu and Ni contents in comparison to the soil from the control (untreated).
2. The highest amounts of lead and copper were detected in the fractions attached to the soil organic matter and amorphous iron oxides.
3. Nickel was found mainly in the residual fraction linked with the inner crystal lattice of primeval minerals.
4. The least amounts of Pb, Cu and Ni were found in the mobile and exchangeable fractions.

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