

THE INFLUENCE OF THIURAM ON THE MOBILITY OF HEAVY METALS IN SOILS

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Abstract: The work is a continuation of previous studies on the effect of thiuram on the mobility of heavy metals in soils. The introductory part of the work involved the analysis of properties of the soils used for the examination i.e.: the content of organic matter, acidity and mechanical properties. The content of lead, copper, manganese and zinc was determined in soils (1M HCl extracts) free from additives and soils sprayed with thiuram after 3, 6, 9 and 12 weeks. The content of total metals was determined in mineralizates (soils without thiuram) obtained by a conventional method according to the ISO standards. The analysis showed that the soils used for the examination were not contaminated with any of the determined elements. The contents of Pb, Cu, Mn and Zn in soils with thiuram were different depending on metals and the time of contact of the soils with thiuram.

Keywords: lead, copper, manganese, zinc, thiuram, soils.

INTRODUCTION

Determination of heavy metals in soils is the result of a general interest in the condition of the environment and the degree of its degradation. Widespread use of pesticides in agriculture may be one of the factors affecting heavy metal migration in soil. According to literature data, heavy metals may form a large number of complexes with fungicides (Turek et al., 2004). The solubility of these complexes in the soil medium and half-life of the active compounds present in pesticides also play an important role in metal migration in soil. The present work is a continuation of previous studies on the effects of fungicides, particularly thiuram, on the mobility of heavy metals in soils (Adamczyk, 2006; Jankiewicz et al. 2004).

Thiuram (tetramethyl thiuram disulfide) belongs to the group of dithiocarbamate fungicides. It is commonly used as an anti-fungal agent to protect arable crops, vegetables, decorative plants and herbs (Róžański, 1998). Thiuram is sparingly soluble in water (30 mg/l at 20°C) and tends to be adsorbed on soil particles so it does not pollute underground waters. Its half-life in soil is 15 days (Wauchope et al. 1992).

The decomposition of thiuram is strongly affected by the reaction of the soil and its composition and type. It proceeds much faster in acidic soils and soils rich in organic matter (Howard, 1989). Thiuram can form complexes with copper (Yong-Gang, 2003; Victoriano et al., 2000; Victoriano and Cortes, 1996) and zinc (Nieuwenhuizen et al. 1999).

MATERIALS AND METHODS

Experimental Procedures

The soil samples for analysis were taken from a recreational plot in the town/village of Jedlicze situated about 20 km from Łódź (soil samples I-VII) and allotments in the center of Łódź (VIII-X). The soil samples were collected in 2006 from the surface layer (0-20 cm) according to the standards (Polish Standards, 1999).

The following properties of all soil samples used in the study were determined: pH, the content of organic matter and mechanical properties. Air – dried samples were analyzed. Soil pH was determined according to standards (Polish Standards, 1997) in H₂O and 1M KCl solutions. Soil pH was measured using a pH-meter Delta 350 (Mettler-Toledo, Giessen, Germany). For organic matter determination dry soil was placed in a muffle furnace to follow the decrease in mass at a temperature of 550°C (Ostrowska et al. 1991). The difference in the mass of the sample before and after roasting is the basis for calculation of proportion of the content of organic matter in the examined soil. The mechanical analysis was carried out using a set of three steel screens with 0.02; 0.1; 1.0 mm mesh diameter according to the Polish Standards (Polish Standards, 1998). The screen method using air dry soil was applied. The results of the analyses are given in Table 1.

Preparation of soil extracts and mineralizates

Soil extracts in which Pb, Zn, Cu and Mn were determined were prepared in the following way: the weighed portions of soil (ground before in a porcelain mortar and sifted through a screen with 2 mm mesh diameter) and mass about 10 g (\pm 0.001 g) were placed in plastic beakers and 50.0 ml of 1 mol/l HCl solution was added. Then the content of the beaker was stirred with a magnetic agitator for 1 hour at a rate of about 40 rev/min. The solution was then passed through a medium filter and the first part of the filtrate was rejected (Polish Standards, 1992 a, 1992 b, 1992 c).

In order to determine the pseudo-total content of lead, copper, manganese, and zinc soils, mineralizates were prepared by conventional mineralization in aqua regia (Polish Standards, 2002). The method involves wet decomposition of the samples of the analyzed soil in boiling aqua regia. The weighed sample (about 3 g) of air-dry soil (previously ground in a porcelain mortar and sifted through a screen with 0.1 mm mesh diameter) was placed in a round bottomed flask, and 28 ml of aqua regia were added. Then it was left at room temperature for 16 hours. Mineralization was carried out (2 hours) using a water cooling system. When the process ended, the cooled liquid gathered over the precipitate was decanted on an analytical funnel using a medium filter. The solid residue was transferred to a filter and washed several times with 0.5 M HNO₃. The filtrate was collected in a measuring flask.

Table 1. The results of analysis of soils

No	Organic matter determination [%]	Mechanical analysis [%]			Soil pH	
		Fractions:			in H ₂ O	in 1M KCl
		Φ 1 \div 0.1	Φ 0.1 \div 0.02	Φ < 0.02		
I	5.43	89.45	9.91	0.64	6.8	5.8
II	15.80	84.02	15.14	0.84	7.3	6.7
III	8.66	91.45	8.33	0.22	7.4	6.7
IV	3.43	92.00	7.70	0.30	5.2	4.0
V	4.91	93.75	6.00	0.25	6.3	5.7
VI	7.23	83.06	16.23	0.74	6.1	5.0
VII	6.97	91.50	8.21	0.29	7.2	6.8
VIII	5.46	84.25	15.36	0.39	7.9	7.3
IX	8.30	84.94	14.18	0.88	7.6	6.9
X	5.75	91.58	8.16	0.26	7.8	7.3

Table 2. Statistical analysis for the total content of metals and content of metals in 1 M HCl extracts

No	Pb		Zn		Mn		Cu	
	Total content	Extracts 1M HCl	Total content	Extracts 1M HCl	Total content	Extracts 1M HCl	Total content	Extracts 1 M HCl
	Confidence intervals [ppm]	Confidence intervals [ppm]	Confidence intervals [ppm]	Confidence intervals [ppm]	Confidence intervals [ppm]	Confidence intervals [ppm]	Confidence intervals [ppm]	Confidence intervals [ppm]
I	40.0 ± 2.1	5.33 ± 0.26	84.4 ± 6	7.48 ± 0.58	88.7 ± 5	10.8 ± 0.6	19.6 ± 0.8	1.99 ± 0.08
II	22.3 ± 1.1	8.25 ± 0.42	170 ± 8	10.6 ± 0.5	518 ± 26	148 ± 7	53.4 ± 2.6	21.6 ± 1.0
III	26.5 ± 1.4	8.37 ± 0.50	62.3 ± 3.1	3.17 ± 0.21	151 ± 8	42.4 ± 3.1	16.2 ± 1.8	3.53 ± 0.25
IV	26.2 ± 1.0	4.79 ± 0.15	20.8 ± 0.8	7.71 ± 0.49	19.1 ± 0.5	2.07 ± 0.17	4.89 ± 0.33	0.70 ± 0.05
V	28.3 ± 1.9	7.96 ± 0.60	49.0 ± 3.1	12.5 ± 0.7	57.3 ± 4.0	23.1 ± 1.9	4.86 ± 0.24	1.05 ± 0.06
VI	23.5 ± 1.2	7.37 ± 0.44	93.8 ± 5.1	19.9 ± 0.8	109 ± 4	20.7 ± 0.9	12.4 ± 0.9	2.32 ± 0.17
VII	30.4 ± 1.7	8.89 ± 0.56	191 ± 7	18.1 ± 0.6	124 ± 6	17.2 ± 1.1	14.0 ± 2.2	2.33 ± 0.17
VIII	42.6 ± 2.8	40.8 ± 2.6	100 ± 4	35.3 ± 1.2	290 ± 13	154 ± 7	25.6 ± 2.6	17.3 ± 0.9
IX	64.4 ± 3.9	53.7 ± 3.1	251 ± 12	94.5 ± 3.1	266 ± 12	161 ± 8	42.9 ± 3.1	23.6 ± 1.1
X	20.9 ± 0.9	11.7 ± 0.7	83.2 ± 2.9	20.69	272 ± 12	128 ± 4	46.6 ± 2.7	23.7 ± 1.3

Principles and procedure of determination of the selected elements by FAAS method

The concentration of each of the metals was determined in soil extracts or mineralizates by means of an atomic absorption spectrophotometer (AAS) in the reducing oxy-acetylene flame. Prior to each series of measurements a calibration line was created for each of the elements. The concentration range was different for each element and was from 0.00 to 10 µg/ml for Pb and from 0.00 to 5.00 µg/ml for Zn, Mn and Cu. All the solutions were diluted with 1 M HCl solution. The results of analysis are given in Table 2 (n = 3; n – number of sample; p = 95 %; p-confidence level; RSD – relative standard deviations).

The accuracy of the method was confirmed by the analysis of certified reference material Light sand Soil with normal analyte levels 7001, certificate No. 0217-CM-7001-04. The results of the determination of lead, manganese and zinc in the certified reference material are presented in Table 3.

Table 3. Comparison of the determined and certified values of lead, zinc, copper and manganese

Metals	Certified value [mg/kg]	Found [mg/kg]	Recovery [%]
Lead	24.1 ± 1.7	27.5 ± 1.9	114
Zinc	108 ± 3.5	106.9 ± 2.2	99
Copper	28.9 ± 0.8	26.9 ± 0.7	96
Manganese	479 ± 18	427 ± 10	89

*n = 5; p = 95 %, n- number of sample, p – confidence level

The influence of thiuram on the mobility of metals

Four 500 g samples of each soil were placed in plastic containers and 3 mg of thiuram dissolved in 5 ml ethyl alcohol were added to each sample. The dose of thiuram was calculated on the basis of the manufacturer's recommendation (2.4-3.6 kg/ha). The soil sample was mixed thoroughly. The content of lead, copper, zinc and manganese in 1M HCl extracts was determined after 3, 6, 9 and 12 weeks. All results presented in the tables 4 and 5 are the means of measurements of three samples taken from the same container. The error in the determination did not exceed 10 %.

RESULTS AND DISCUSSION

The examined soil contains medium amounts of organic matter apart from sample II, where the content of organic matter is high and amounts to about 16 %.

Mechanical analysis carried out by the sieve method showed that all the examined soils belong to the same granulometric subgroup of loose sand (pl). In agricultural chemistry and agricultural science the examined soils are classified as very light and most liable to erosion. The measurements of the soil pH showed that they are neutral, slightly to strongly acidic, which facilitates heavy metal migration.

Total contents of Pb, Cu, Mn and Zn in all the examined soil samples are within the permissible limits established for arable land (according to the data established in the Directive of the Minister of Environment Protection of 9 September 2002).

Table 4. The contents of copper and lead in soil extracts.

No	Cu					Pb				
	Without thiuram [ppm]	With thiuram [ppm]				Without thiuram [ppm]	With thiuram [ppm]			
		After 3 weeks	After 6 weeks	After 9 weeks	After 12 weeks		After 3 weeks	After 6 weeks	After 9 weeks	After 12 weeks
I	1.99	2.79	3.3	3.34	3.71	5.33	8.88	7.82	8.72	8.94
II	21.6	14.1	13.2	11.8	14.3	8.25	7.82	4.80	5.81	6.99
III	3.53	2.99	2.94	2.80	2.46	8.37	7.79	6.28	6.24	5.90
IV	0.70	0.44	0.64	0.55	0.47	4.79	5.14	4.65	4.35	5.26
V	1.05	0.81	0.89	0.52	0.71	7.96	8.98	7.14	7.49	6.54
VI	2.32	2.94	2.99	3.07	2.82	7.37	11.6	10.0	10.7	9.37
VII	2.33	2.60	2.54	2.22	2.22	8.89	9.48	10.4	11.5	10.3
VIII	17.3	16.8	15.2	17.7	21.0	40.8	60.9	30.0	43.1	29.4
IX	23.6	22.8	23.7	20.6	28.9	53.7	45.2	54.5	52.9	62.3
X	23.7	30.4	23.8	31.1	37.1	11.7	12.3	11.1	11.4	11.8

Table 5. The contents of manganese and zinc in soil extracts.

No	Mn					Zn				
	Without thiuram [ppm]	With thiuram [ppm]				Without thiuram [ppm]	With thiuram [ppm]			
		After 3 weeks	After 6 weeks	After 9 weeks	After 12 weeks		After 3 weeks	After 6 weeks	After 9 weeks	After 12 weeks
I	10.8	19.6	18.4	19.3	18.4	7.48	12.0	10.5	11.0	11.5
II	148	133	109	134	120	10.6	37.0	26.6	35.5	18.6
III	42.4	36.0	35.0	34.0	30.2	3.17	9.60	8.15	8.07	7.13
IV	2.07	2.41	1.96	1.84	2.10	7.71	3.15	2.72	2.63	3.40
V	23.1	17.5	13.9	9.98	12	12.5	8.23	6.26	3.93	5.44
VI	20.7	37.4	29.5	36.2	31.6	19.9	18.1	17.0	18.0	16.8
VII	17.2	48.5	40.3	38.7	98.9	18.1	43.0	43.2	43.8	99.7
VIII	154	195	190	224	196	35.3	66.0	70.3	64.3	61.6
IX	162	173	175	193	184	94.5	148	171	159	146
X	128	174	171	202	180	20.7	30.8	47.2	48.2	37.2

According to Polish Standards on the content of available zinc in soil, the examined samples contain high amount of this element. Only 10 % of them are in class II of zinc content (0.7-3.3 ppm) and contain medium levels of zinc. 60 % of the samples showed high levels of zinc (class I > 3.3 ppm). In the other 30 % of the samples the permissible level was exceeded (> 20 ppm).

Based on Polish Standards, most of the examined soils (80 %) belong to class II of manganese content (17-150 ppm) and contain medium amounts of this element. Low levels of manganese were found in 20 % of the examined samples and there were no samples with high Mn content.

The examined soil contains high amounts of copper. Following Polish Standards, 50 % of the samples are in class I for very light soils (over 2.5 ppm), and low Cu content was observed only in one of them (class III of Cu content < 0.9 ppm).

The amounts of the determined elements (extracts 1 M HCl) at the same time depend on factors such as the value of the soil pH and the content of organic matter.

Moreover, the behaviour of the metals in the soil is affected by interactions with other (major, minor and trace) elements. Every change in the soil environment may mobilize the elements which were present in the soil in bound forms (Kabata-Pendias et al. 1999).

Therefore the results of determination of Pb, Mn, Cu and Zn content in the soils with the addition of thiuram do not allow explicit conclusions on the effect of the fungicide on their mobility in soil. When both the content of organic matter and soil pH are high (II soil) a decrease in the content of Pb, Mn and Cu in the soil with the addition of thiuram is observed (after 12 weeks) (fig. 1).

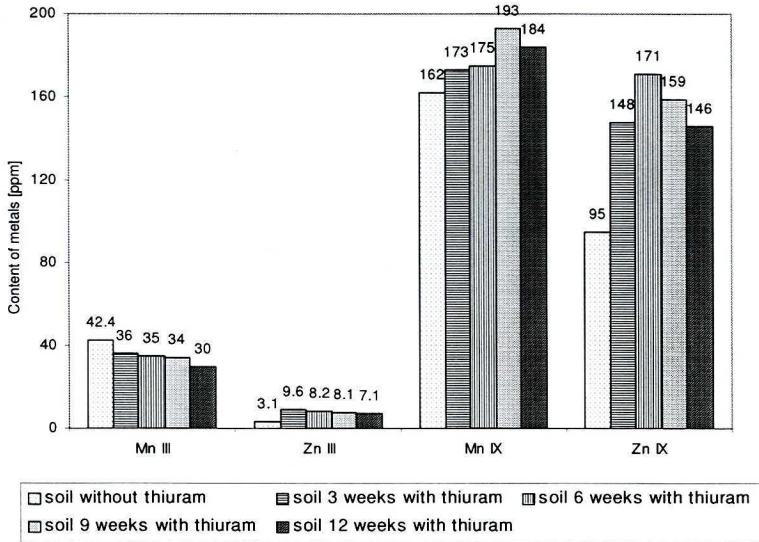


Fig.1. The effect of organic matter (OM) and soil pH on the content of metals in soil samples (II and VIII.)

Zn is an exception as its concentration increased by 75 %. Whereas low content of organic matter and high soil pH (VIII soil) causes an increase of the content of Zn, Cu and Mn. Lead behaves differently and its amount 12 weeks from TMTD addition decreased by 30 %.

The analysis of the impact of the time of contact of thiuram with soil on the content of metals is difficult in the case of soil samples with different physicochemical parameters. Soil pH and content of organic matter reach the closest levels in samples III and IX though they come from different (previously defined: III and IX) areas so their examples were used in figures 2 and 3.

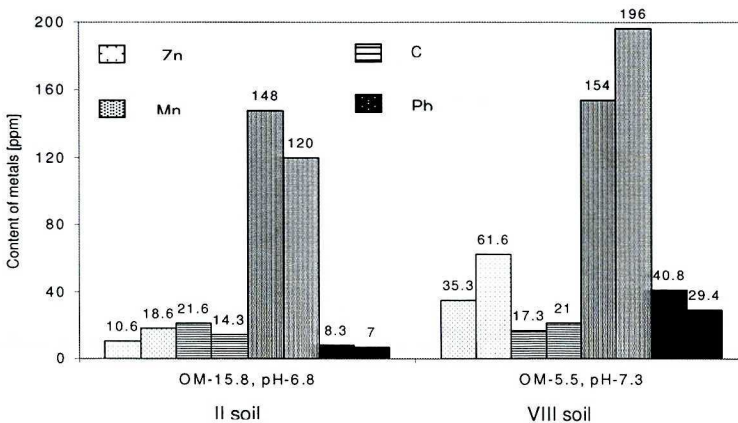


Fig. 2. The effect of the time of soil contact with thiuram on the content of Mn and Zn in soil samples (III and IX).

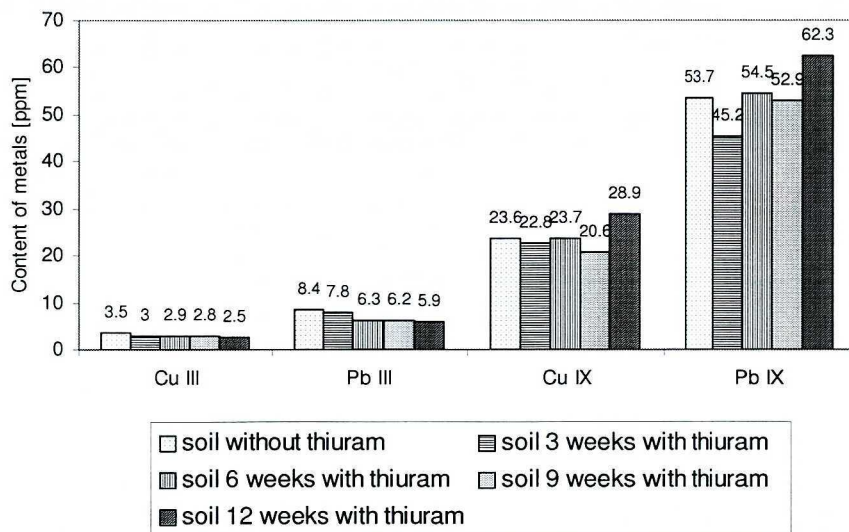


Fig. 3.. The effect of the time of contact soil with thiuram on the content of Cu and Pb in soil samples and IX).

The results show that the behavior of the metals determined is affected not only by the physicochemical properties of the soil. The behaviour of metals in samples III and IX under the influence of TMTD (in spite of their similar properties) is different. In soil sample IX exposed to anthropogenic contamination after 12 weeks with thiuram a clear increase of all the metals determined is observed as compared to the primary sample, irrespective of their content in the soil after 3, 6 or 9 weeks with thiuram.

In sample III (collected in the area free from contamination) a gradual decrease of the content of bioavailable forms of these elements occurs in successive weeks of contact of the soil with TMTD (by about 30% in all). Zinc, whose amount in most of the samples increases even as early as the 3rd week and after 12 weeks reaches a value higher than its initial content, is an exception.

CONCLUSIONS

Total contents of Pb, Cu, Mn and Zn in all the examined soil samples are within the permissible limits established for arable land. The amounts of the determined elements at the same time depend on factors such as the value of the soil pH and the content of organic matter. Every change in the soil environment may mobilize the elements which were present in the soil in bound forms. When both the content of organic matter and soil pH are high (II soil) a decrease in the content of Pb, Mn and Cu in the soil with the addition of thiuram is observed. Zn is an exception as its concentration increased by 75 %. Whereas low content of organic matter and high soil pH (VIII soil) causes an increase of the content of Zn, Cu and Mn. Lead behaves differently and its amount 12 weeks from TMTD addition decreased by 30 %.

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