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INFLUENCE OF SOIL CONTAMINATION WITH NICKEL AND LIMING ON LEAD AND MANGANESE CONTENTS IN RED CLOVER BIOMASS

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Abstract: In general, industrial pollution contributes to deeper degradation of agricultural production space, which leads to accumulation of heavy metals in soils. Nickel is a heavy metal. At small amounts, it is necessary for the growth and development of living organisms, while it is toxic in excess. The influence of soil contamination with nickel (50, 100, and 150 mg Ni/kg of soil – $NiSO_4 \cdot 7H_2O$) on Pb and Mn at red clover was studied in four-year pot experiments on a background of varied liming levels (according to 0.5, 1, and 1.5 H_h of soil – $CaCO_3$). Metal contents were determined by means of ICP-AES technique after sample dry digestion in muffle furnace at 450°C and dissolution of ash in 10% HCl. The results were statistically processed using variance analysis and F-Fisher-Snedecor's distribution according to F.R. Anal. ver. 4.1. software, while $LSD_{0.05}$ values were calculated according to Tukey's test. To find interactions between studied traits, a linear correlation analysis was performed. Both metals concentrations at plants grown on polluted soils were higher as compared to those cultivated on non-contaminated ones, which may indicate the synergism between nickel and both discussed heavy metals. Applied liming (regardless the amount of $CaCO_3$) caused significant decrease of both metals contents at a test plant. The studies revealed synergistic dependencies between nickel and lead and manganese.

INTRODUCTION

Contamination of agricultural production area due to heavy metals has been the subject of many studies for over twenty years. The elements contents at vegetables, namely in their parts for direct consumption, are of special interests. However, there are few works upon the heavy metals content in general crop species cultivated under production conditions [2, 8, 12, 14, 15].

Soil is a principle source of heavy metals for plants. Due to the soil, majority of metals are incorporated into the trophic chain [7, 11]. The process of their uptake by plants depends on a variety of factors: their total contents in the soil, sorption capacity, acidity, organic matter content, humidity [6, 9, 12], and other heavy metals the up taken element can enter the antagonistic or synergistic reactions with [1, 3].

The aim of the present study was to evaluate the influence of soil contamination with nickel on lead and manganese contents at red clover (*Trifolium pratense* L.) on a background of varied liming.

MATERIAL AND METHODS

The 4-year pot experiments were carried out at a greenhouse of University of Podlasie in Siedlce in completely randomized pattern in three replications. The following factors were examined:

I. soil contamination with nickel (50, 100, 150 mg Ni/kg soil);

II. liming (without liming or with liming in doses calculated for 0.5, 1.0, and 1.5 H_h of soil).

Liming was applied at the beginning of May in a form of $CaCO_3$, while nickel was introduced into the soil at the beginning of June in a form of $NiSO_4 \cdot 7H_2O$ solution. The 15 dm^3 pots were filled with 10 kg of soil material collected from the humus layer of dusty sandy loam podsolic soil with the following physicochemical features: pH in 1 M KCl – 5.49, $C_{org.}$ – 6.5 g/kg soil, $N_{tot.}$ – 0.61 g/kg soil, available P and K [mg/kg soil] – 71 and 110, respectively; total contents of Ni, Pb, and Mn [mg/kg] – 10.1, 5.9, and 76.0, respectively. Pots were left with no tillage and cultivation for one vegetation period, maintaining the moisture contents at 60% of the field water capacity, and then red clover (*Trifolium pretense* L. of Jubilatka cv.) was cultivated for four seasons. Every year, before sowing, the following mineral fertilization was applied: N – 0, P – 0.053 g/kg of soil in a form of granulated triple superphosphate (19% P), K – 0.17 g/kg of soil in a form potassium salt (41% K).

For four years and for every red clover cut, concentrations of Pb and Mn in each cut of test plant were determined by means of ICP-AES technique after dry digestion in muffle furnace at 450°C and subsequent ash grinding and dissolution in 10% HCl [13]. Results were statistically processed using variance analysis and F-Fisher-Snedecor's distribution according to F.R. Anal. ver. 4.1. software, while $LSD_{0.05}$ values were calculated according to Tukey's test. To find interactions between studied traits, a linear correlation analysis was also performed.

RESULTS AND DISCUSSION

Lead contents at particular cuts of plants (Figs 1–4) were significantly differentiated by both examined factors: soil contamination with nickel and liming. Less lead was found at plants of the 2nd and 3rd cuts of plants cultivated with uncontaminated soil for all study years than those grown on contaminated soils regardless the nickel amount introduced into the soil. In majority, there were statistically significant differences. At the same time, for all years, in 1st cut plants as well as in the first and fourth years in 3rd cut plants cultivated on soils limed with the highest calcium rate calculated according to 1.5 H_h, lower lead contents in relation to red clover grown on non limed and limed using lower calcium doses were recorded, and the differences were in most cases significant. Both studied factors differentiated mean values (for four years) of lead level in particular red clover cuts (Tab. 1). Considerably lower mean concentration of lead was found at plants of the first three cuts and grown on soils that were not nickel-contaminated as compared to those cultivated on contaminated soils, regardless the pollution extent. Different dependencies were observed in 4th cut plants. Considerably the lowest mean lead concentration was determined at plants cultivated on soils polluted with nickel to the highest level (150 mg Ni/kg of soil). In the case of all red clover cuts in plants grown on limed soils according to 1.5 H_h, lower mean value of discussed element was recorded as compared to plants grown on other fertilization objects, and in majority there were significant differences. For all experimental years, the lowest mean lead content was found in plants grown on soils that were not polluted with nickel (Fig. 5) and those limed with the highest calcium dose calculated according to 1.5 H_h of soil (Fig. 6), which was consistent with studies by Lipiński and Lipińska [7]. Those authors examined the influence of organic matter and acidity on heavy metals contents in soils and plants of green lands finding that the soil acidity exerted the strongest effects on heavy metals concentrations. The increase of pH contributed to the decrease of lead content at these plants. For all experimental years, lead contents at particular cuts of red clover did not exceed 10 mg/kg D.M., which allows for using it for fodder purposes [2, 5].

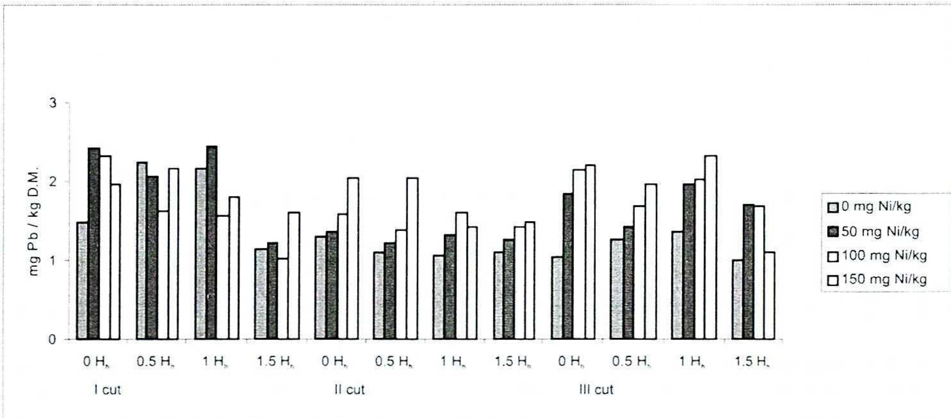

Fig. 1. Lead content in red clover [mg/kg D.M.] (first experimental year)

	I cut	II cut	III cut
$LSD_{0.05}$ for:			
doses of nickel	n.i.	0.534	0.454
liming	0.653	n.i.	0.454
interaction: doses of nickel x liming	n.i.	n.i.	n.i.

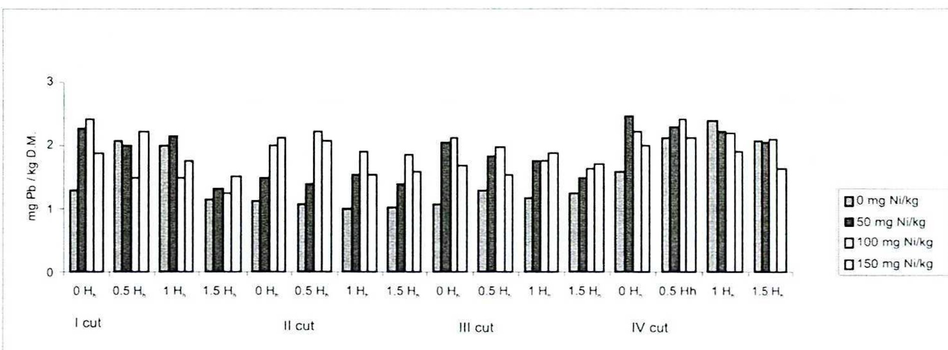

Fig. 2. Lead content in red clover [mg/kg D.M.] (second experimental year)

	I cut	II cut	III cut	IV cut
$LSD_{0.05}$ for:				
doses of nickel	n.i.	0.648	0.438	n.i.
liming	0.582	n.i.	n.i.	n.i.
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.

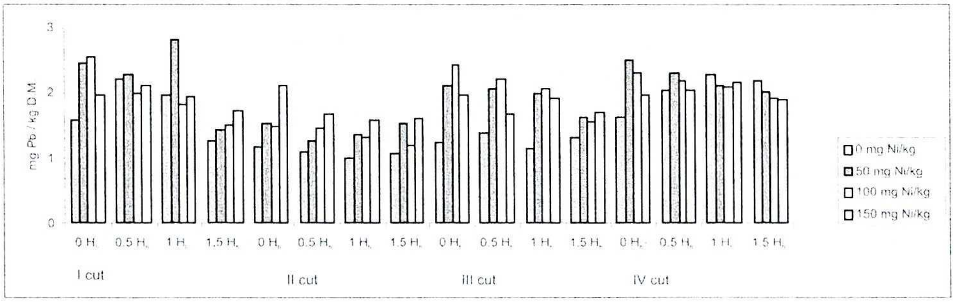

Fig. 3. Lead content in red clover [mg/kg D.M.] (third experimental year)

	I cut	II cut	III cut	IV cut
$LSD_{0.05}$ for:				
doses of nickel	n.i.	0.287	0.584	n.i.
liming	0.621	n.i.	n.i.	n.i.
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.

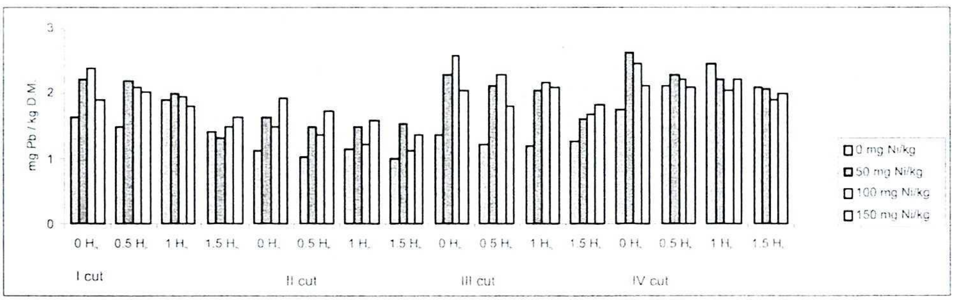

Fig. 4. Lead content [mg/kg D.M.] in red clover (fourth experimental year)

	I cut	II cut	III cut	IV cut
$LSD_{0.05}$ for:				
doses of nickel	n.i.	0.310	0.365	n.i.
liming	0.472	n.i.	0.365	n.i.
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.

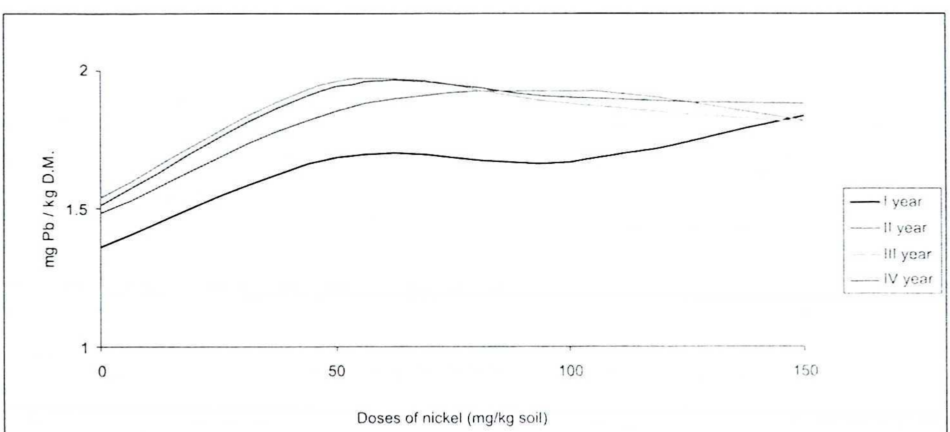

Fig. 5. Lead content (mean for cuts) in red clover depending on soil contamination with nickel [mg/kg D.M.]

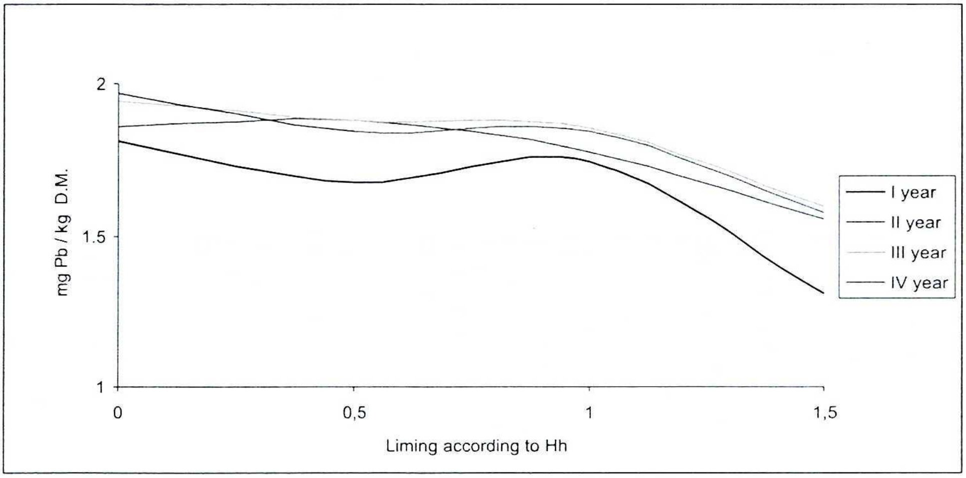

Fig. 6. Lead content (mean for cuts) in red clover depending on different liming [mg/kg D.M.]

Table 1. Four-year mean lead content in red clover [mg/kg D.M.]

Cut	Doses of nickel [mg/kg soil]	Liming according to H_h				Mean
		0 H_h	0.5 H_h	1 H_h	1.5 H_h	
I	0	1.50	2.00	2.01	1.24	1.69
	50	2.33	2.13	2.35	1.32	2.03
	100	2.42	1.80	1.71	1.32	1.81
	150	1.93	1.88	1.84	1.62	1.81
Mean		2.05	1.95	1.98	1.37	1.84
II	0	1.18	1.07	1.05	1.05	1.09
	50	1.51	1.35	1.42	1.42	1.42
	100	1.64	1.61	1.51	1.40	1.54
	150	2.05	1.89	1.52	1.56	1.74
Mean		1.59	1.48	1.38	1.34	1.45
III	0	1.19	1.29	1.23	1.21	1.23
	50	2.07	1.86	1.94	1.61	1.87
	100	2.32	2.04	2.00	1.63	2.00
	150	1.98	1.75	2.05	1.60	1.84
Mean		1.89	1.73	1.80	1.51	1.73
IV	0	1.65	2.09	2.37	2.12	2.06
	50	2.53	2.30	2.18	2.05	2.26
	100	2.32	2.26	2.11	1.97	2.17
	150	2.03	2.09	2.09	1.84	2.01
Mean		2.13	2.18	2.19	1.99	2.12

	I cut	II cut	III cut	IV cut
$LSD_{0.05}$ for:				
doses of nickel	0.210	0.178	0.183	0.107
liming	0.210	0.178	0.183	0.107
interaction: doses of nickel x liming	0.419	n.i.	0.365	0.214

The statistical analysis revealed significant dependencies between soil contamination with nickel and mean value (for four years) of lead content at particular cuts of red clover. The correlation coefficients were: for the 2nd cut r = 0.83** (** – significant at 0,01), for the 3rd cut r = 0.70**, for the 4th cut r = 0.89**. Positive values of these coefficients may prove the synergism of nickel and lead. The analysis also revealed significant interactions between soil liming and content (mean for experimental years) of lead at particular cuts of red clover. The correlation coefficients amounted to: for the 1st cut r = -0.78**, for the 2nd cut r = -0.72**, for the 3rd cut r = -0.67**, and for the 4th cut r = -0.51* (* – significant at 0,05). Negative values of these coefficients confirm well-known fact that the solubility of heavy metals as well as mobility decreases with the increase of pH value [4, 7, 9, 10].

Contents of the second studied heavy metal – manganese – at red clover of particular cuts are presented in Figures 7–10. In the first experimental year (Fig. 7), in 2nd cut plants grown on soils not contaminated with nickel, lower level of the metal was found than at those cultivated on polluted soils; the differences were statistically significant in relation to those grown on soils where 150 mg Ni/kg of soil was introduced. Similar dependence was observed for the 3rd cut, for which in plants cultivated on soil contaminated with nickel to the highest extent, significantly higher content of examined metal was recorded as compared to red clover grown on less polluted soils (50 and 100 mg Ni/kg of soil). At the same time, considerably lower manganese concentration was recorded in the 2nd cut plants cultivated on non-limed vs. limed soils, regardless the amount of the calcium fertilizer introduced into the soil, which was not consistent with other authors' findings [2, 3, 5], and which can be attributed to slow transformations of calcium fertilizers in soil. In plants of 3rd and 4th cuts in the second year (Fig. 8), 1st, 2nd, and 3rd cuts in the third year (Fig. 9), as well as 2nd, 3rd, and 4th cuts in the last experimental year (Fig. 10) cultivated on non-nickel-contaminated soils, lower levels of manganese in relation to those grown on polluted soils were found, and in most cases, the contents of the metal in plants increased along with the increase of nickel amounts introduced into the soil. At the same time, at plants of the 1st and 4th cuts in the second year (Fig. 8), 1st, 2nd, and 4th cuts in the third year (Fig. 9), and 3rd and 4th cuts in the fourth year (Fig. 10) cultivated on non-limed soils, higher contents of manganese were recorded, and in majority, its concentration at plants decreased along with the increase of calcium rate introduced as a fertilizer.

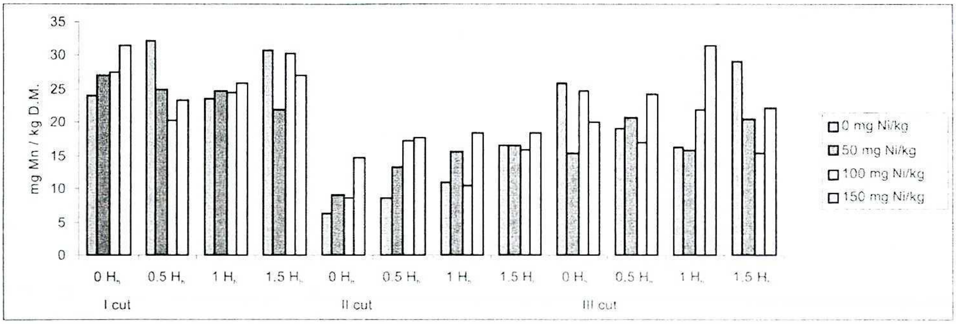

Fig. 7. Manganese content in red clover [mg/kg D.M.] (first experimental year)

	I cut	II cut	III cut
$LSD_{0.05}$ for:			
doses of nickel	n.i.	3.759	4.635
liming	n.i.	3.759	n.i.
interaction: doses of nickel x liming	n.i.	n.i.	n.i.

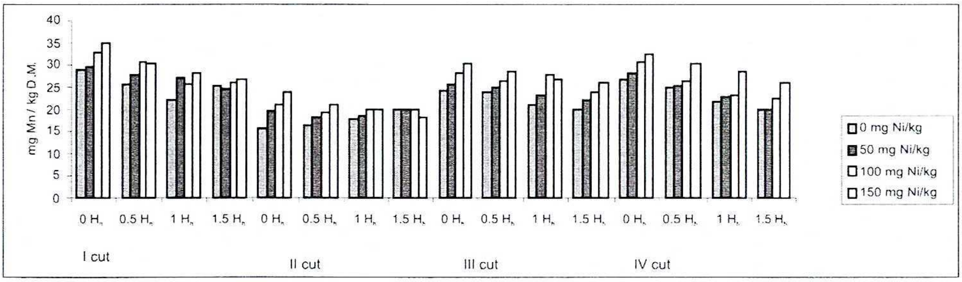

Fig. 8. Manganese content in red clover [mg/kg D.M.] (second experimental year)

	I cut	II cut	III cut	IV cut
$LSD_{0.05}$ for:				
doses of nickel	n.i.	n.i.	4.396	5.018
liming	5.333	n.i.	n.i.	5.018
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.

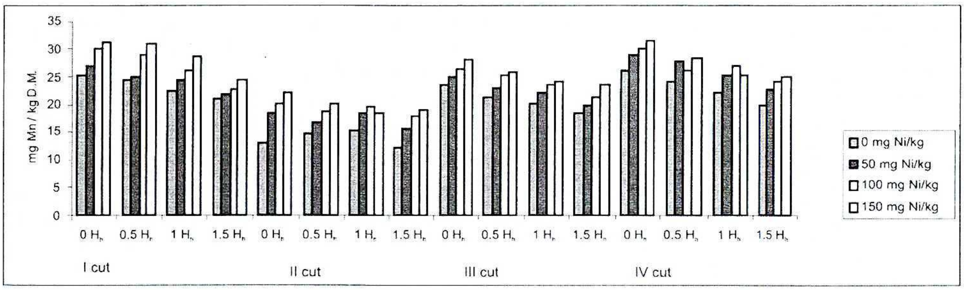

Fig. 9. Manganese content in red clover [mg/kg D.M.] (third experimental year)

	I cut	II cut	III cut	IV cut
$LSD_{0.05}$ for:				
doses of nickel	3.783	5.055	4.415	n.i.
liming	3.783	n.i.	4.415	3.793
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.

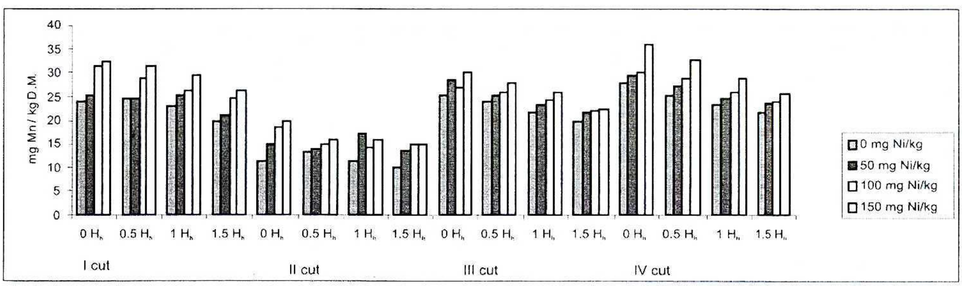

Fig. 10. Manganese content in red clover [mg/kg D.M.] (fourth experimental year)

	I cut	II cut	III cut	IV cut
$LSD_{0.05}$ for:				
doses of nickel	n.i.	3.781	3.033	5.860
liming	n.i.	n.i.	3.033	5.860
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.

Mean value of manganese content for all experimental years at particular cuts of red clover significantly differentiated (Tab. 2), both due to soil nickel contamination, and liming. In all cuts plants grown on soils that were not polluted with nickel, significantly lower manganese contents were recorded as compared to its concentration in plants cultivated on contaminated soils. Plants of all cuts cultivated on soils polluted with nickel to the highest extent (150 mg Ni/kg of soil) were characterized by considerably the highest manganese content, which seems to confirm a thesis on the synergism of nickel and manganese. In plants of the 1st, 2nd, and 4th cuts grown on non-limed soils, significantly higher manganese contents were found in relation to red clover cultivated on limed soils; in most cases, its content in plants considerably decreased along with the increase of calcium fertilizer rate introduced into the soil. In the first experimental year, the lowest mean value (for cuts) of discussed element was found in plants cultivated on soils, to which 50 mg Ni/kg of soil was introduced (Fig. 11) as well as those grown on non-limed soils (Fig. 12). In subsequent years, the lowest mean manganese levels for cuts were recorded in plants cultivated on soils that were not polluted with nickel (Fig. 11), and those grown on soil limed with the highest calcium fertilizer rate calculated according to 1.5 H_h of soil (Fig. 12), which was confirmed by experiments of Rogoż [9]. Values of correlation

Table 2. Four-year mean manganese content in red clover [mg/kg D.M.]

Cut	Doses of nickel [mg/kg soil]	Liming according to H_h				Mean
		0 H_h	0.5 H_h	1 H_h	1.5 H_h	
I	0	25.5	26.8	22.8	24.2	24.8
	50	27.2	25.7	25.4	22.4	25.2
	100	30.5	27.2	25.6	26.0	27.3
	150	32.5	29.1	28.1	26.2	29.0
Mean		28.9	27.2	25.5	24.7	26.6
II	0	24.7	22.0	19.7	21.9	22.1
	50	23.6	23.5	21.1	21.0	22.3
	100	26.5	23.7	24.4	20.6	23.8
	150	27.1	26.7	27.2	23.6	26.1
Mean		25.5	24.0	23.1	21.8	23.6
III	0	11.7	13.2	13.8	14.7	13.4
	50	15.6	15.6	17.5	16.5	16.4
	100	17.1	17.6	16.1	17.1	17.0
	150	20.1	18.7	18.1	17.7	18.7
Mean		16.1	16.3	16.4	16.5	16.3
IV	0	27.0	24.8	22.3	20.7	23.7
	50	28.9	26.7	24.3	22.1	25.5
	100	30.2	27.2	25.3	23.5	26.6
	150	33.4	30.5	27.6	25.5	29.3
Mean		29.9	27.3	24.9	23.0	26.3

	I cut	II cut	III cut	IV cut
$LSD_{0.05}$ for:				
doses of nickel	2.488	3.058	3.209	1.570
liming	2.488	3.058	n.i.	1.570
interaction: doses of nickel x liming	n.i.	n.i.	n.i.	n.i.

coefficients achieved from the statistical computations revealed significant dependence between nickel content in the soil and mean manganese concentration (for experimental years) in plants of the 1st cut (r = 0.74**), 2nd cut (r = 0.61*), and 3rd cut (r = 0.50*), as well as between soil liming and mean value of manganese content for years in red clover of the 1st cut (r = -0.71**).

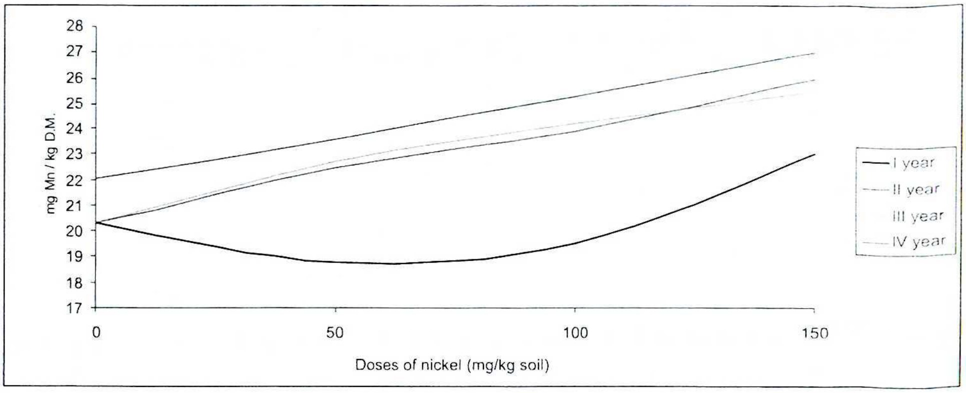

Fig. 11. Manganese content (mean for cuts) in red clover depending on soil contamination with nickel [mg/kg D.M.]

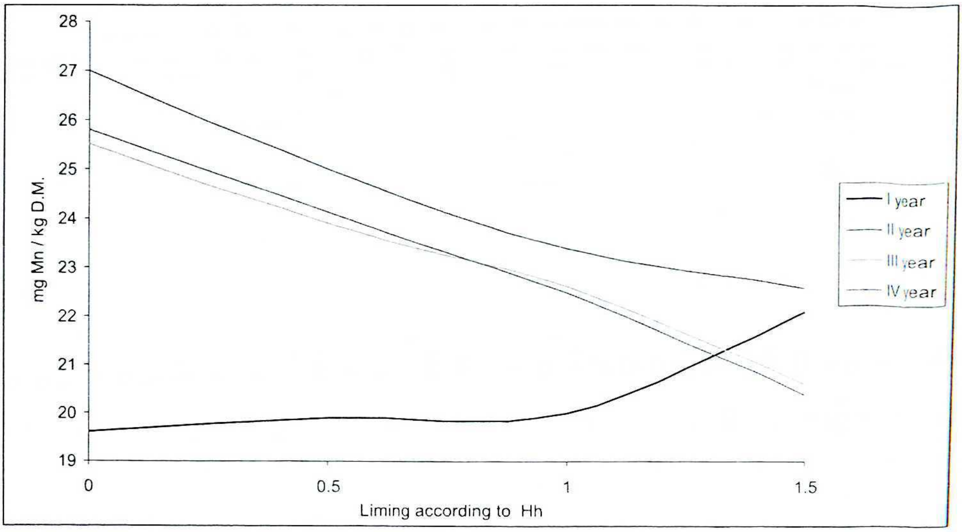

Fig. 12. Manganese content (mean for cuts) in red clover depending on different liming [mg/kg D.M.]

It may be suggested that both studied experimental factors (soil contamination with nickel and liming) significantly differentiated lead and manganese contents at red clover. Both metals concentrations in plants grown on polluted soils were higher as compared to those cultivated on non-contaminated ones, which may indicate the synergism between nickel and both discussed heavy metals. Applied liming (regardless the amount of $CaCO_3$) caused a significant decrease of both metals contents in test plant, whereas the lowest mean values of them were found in plants grown on soils limed according to 1.5 H_h of soil, which was consistent with other authors studies [7, 9, 10].

CONCLUSIONS

1. Soil contamination with nickel caused the increase of lead and manganese contents in red clover.
2. Liming caused significant decrease of lead and manganese concentrations in test plant.
3. Studies revealed synergistic interactions between nickel and lead and manganese.

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WPŁYW ZANIECZYSZCZENIA GLEBY NIKLEM I WAPNOWANIA NA ZAWARTOŚĆ OŁOWIU I MANGANU W BIOMASIE KONICZYNY CZERWONEJ

Zanieczyszczenia przemysłowe przyczyniają się z reguły do pogłębienia degradacji rolniczej przestrzeni produkcyjnej, prowadząc między innymi do nagromadzenia metali ciężkich w glebie. Do grupy metali ciężkich

zaliczany jest nikiel, który w małych ilościach jest niezbędny dla wzrostu i rozwoju organizmów żywych, natomiast występujący w nadmiarze jest toksyczny. W czteroletnim doświadczeniu wazonowym badano wpływ zanieczyszczenia gleby niklem (50, 100 i 150 mg Ni/kg gleby zastosowanego w formie $NiSO_4 \cdot 7H_2O$) na tle zróżnicowanego wapnowania (wg 0,5; 1 i 1.5 H_h gleby zastosowanego w formie $CaCO_3$) na zawartość Pb i Mn w koniczynie czerwonej. Zawartość metali oznaczono metodą ICP-AES po wcześniejszej mineralizacji materiału roślinnego „na sucho" w piecu muflowym w temperaturze 450°C i rozpuszczeniu popiołu w 10% roztworze HCL. Wyniki badań opracowano statystycznie analizą wariancji z wykorzystaniem rozkładu F-Fishera-Snedecora wg programu F.R. Anal.var 4.1., a wartość $NIR_{0,05}$ wyliczono wg testu Tukey-a. W celu znalezienia związków między badanymi cechami w pracy przeprowadzono również analizę korelacji liniowej. Zawartość obu metali w roślinach uprawianych na glebach zanieczyszczonych niklem była większa w odniesieniu do roślin uprawianych na glebach niezanieczyszczonych, co może świadczyć o synergizmie niklu i omawianych metali. Zastosowane wapniowanie (niezależnie od ilości $CaCO_3$ wprowadzonego do gleby) powodowało istotne zmniejszenie zawartości obu metali w roślinie testowej. Przeprowadzone badania wykazały synergistyczne zależności pomiędzy niklem a ołowiem i manganem.