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EFFECT OF CONTAMINATION WITH COPPER AND MINERAL OR ORGANIC AMENDMENTS ON THE CONTENT OF TRACE ELEMENTS IN SOIL

The effect of increasing contamination with copper on the content of trace elements in soil after application of compost, bentonite and zeolite has been examined. The contents of copper, cadmium, lead, chromium, zinc, nickel, manganese, iron and cobalt were determined in soil. Soil contamination with copper and the application of neutralizing substances (compost, bentonite and zeolite) had significant effects on the contents of trace elements in soil. Copper pollution mainly caused a very high increase in the content of copper and a smaller one in the amount of cadmium in soil. Copper contamination caused a decrease in the content of cobalt, nickel, zinc, manganese, iron and lead in soil. All of applied substances, especially zeolite, reduced the content of copper, as well as cadmium, chromium and, to a smaller extent, lead and manganese in soil. It is worth noticing that the effect of zeolite was much stronger than the effect of bentonite or compost. Compost acted similarly with respect to cobalt and nickel. Zeolite had a similar effect on the content of zinc and iron in soil. Bentonite had a comparable influence on the accumulation of zinc in the soil. In turn, bentonite and zeolite contributed to an increase in the content of nickel and cobalt in the soil.

1. INTRODUCTION

Industrial development has resulted in growing demand for raw materials and form of transport as well as the emission of pollutants to the environment when materials are obtained, processed and, finally, when products are transported to their destination [1]. Moreover, large amounts of pollutants are emitted to the environment when energy is generated in small stationary energy sources, such as detached houses and agrotechnical measures in agriculture, especially from fertilisers and plant protection products [2].

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The emission of pollutants is also related to the degree of industrialisation and socioeconomic policy as well as to the environmental awareness in society. However in Poland and in many European countries, the emission of pollutants to the environment has decreased considerably during the past 30 years. Their highest acceptable concentrations in the air and in other elements of the environment may be exceeded locally and during some seasons of the year [3]. There are also pollutants which can be accumulated in the environment, especially in soils and bottom deposits in water bodies [4].

Organic pollutants, mainly those permanent in nature and trace elements, especially heavy metals are a source of considerable issues [5, 6]. One of them is copper, which can accumulate in large amounts in the environment, usually near copper and zinc mines. An excessive content of copper in the environment, including soil, is not neutral to the growth of living organisms [7]. Copper is essential to their growth and development [4]. In excessive amounts, it can have a negative effect on living organisms. Copper has an effect on some physiological processes in plants such as photosynthesis and respiration [8]. It can inhibit their growth and, in extreme situations, it can result in their death [9]. Contamination with copper affects soil properties, especially microbiological and biochemical ones, and can disrupt circulation of elements and their uptake by plants [7]. This is closely related to the antagonistic and partly synergistic effect that copper has on other elements which (although not very strong) is not neutral with respect to their absorption by plants [4]. Reactions, the content of organic matter and clay fractions, sorption capacity, humidity, content of hydroxide of iron, manganese and aluminium play a very important role in reducing the influence of copper on plants. They cause complexing of copper and other heavy metals, which reduce their uptake by plants [10]. The bioavailability of copper increases on acid and very acid soils [11]. For this reason, the effect of soil contamination with copper on soil properties and plants which grow on it should be reduced. This can be done by *in-situ* and *ex-situ* methods, but – for economic reasons – *in-situ* methods are used more frequently [12]. They are cheap, easy to apply, fast and effective [13]. Bioremediation and phytoremediation are the most commonly used methods of remediation. Applications of various substances to the soil are much less frequent. Some of them are compost [14], bentonite [15] and zeolite [16]. In the above studies, they were used separately. The application of these substances is innovative and especially interesting. Therefore, the aim of the study was to determine the effect of increasing contamination with copper on the content of trace elements in soil after application of compost, bentonite and zeolite.

2. MATERIALS AND METHODS

A plant growth experiment was conducted in the vegetation hall of the University of Warmia and Mazury in Olsztyn. The experiment was set up on acidic soil formed from sand according to the United States Department of Agriculture (USDA) classification. It had the following properties: pH in 1 mol/dm^3 KCl 5.53, hydrolytic acidity (HAC) 27.5 mmol/kg, total exchangeable bases (TEB) 151.1 mmol/kg, cation exchange capacity (CEC) 178.6 mmol/kg, base saturation (BS) 84.6%, content of trace elements (mg/kg of soil): Cu 4.24, Cd 0.12, Pb 5.30, Cr 1.98, Zn 15.70, Ni 5.84, Mn 212.3, Fe 6954.2, Co 7.81. The soil was contaminated with copper (as $CuCl_2$) at 0, 50, 100, 150 and 200 mg Cu/kg of soil. The experiment was carried out in four series: with no amendments and with 3 wt. % of compost, 2 wt. % of bentonite and 2 wt. % of zeolite. Compost was prepared from leaves, manure and peat. The concentration of trace elements in these substances (in mg/kg) was as follows: in compost Cu 0.81, Cd 0.06, Pb 1.88, Cr 1.26, Zn 4.29, Ni 0.51, Mn 5.32, Fe 208; in bentonite Cu 21.3, Cd 0.27, Pb 9.90, Cr 2.67, Zn 11.8, Ni 2.32, Mn 145, Fe 4260; in zeolite Cu 12.38, Cd 1.36, Pb 18.0, Cr 1.81, Zn 14.68, Ni 409, Mn 2.04, Fe 4920. The soil was also mixed with fertilisers in the following amounts: 100 mg N, 35 mg P, 100 mg K, 50 mg Mg, 0.33 mg B, 5 mg Mn and 5 mg Mo per kg of soil. After being mixed with copper chloride, compost, bentonite, zeolite and fertilisers, the soil was put into 9 kg polyethylene pots and the plants were sown. Moisture content was maintained at 60% of the capillary water capacity during the experiment. The soil samples were taken for laboratory analyses after 63 days from the start of the experiment.

The soil samples were dried and passed through a sieve of 1 mm mesh. Wet mineralisation of samples of the soil, compost, bentonite and zeolite was carried out in concentrated nitric acid (HNO_3 analytically pure) at a concentration of 1.40 g/cm^3 in a MARS 5 microwave oven (CEM Corporation, USA), in HP 500 vessels, made of Teflon, by the US-EPA3051 method [17]. Concentrations of the following elements were determined by the flame atomic absorption spectrometry (FAAS): copper, cadmium, lead, chromium, zinc, nickel, manganese, iron and cobalt. The soil pH in 1 mol/dm^3 KCl solution was determined potentiometrically; the hydrolytic acidity (HAC) and the total exchangeable bases (TEB) by the Kappen method [18]. From the hydrolytic acidity (HAC) and total exchangeable bases (TEB), the cation exchange capacity (CEC) and base saturation (BS) were computed according to the following formulas: CEC = TEB + HAC; BS = TEB×CEC^{-1}×100 [18]. Statistical processing of the results was carried out by two-way analysis of variance ANOVA using the Statistica software package [19]. The effect of contamination with copper and of the neutralising substances on the content of trace elements in soil was assessed by the principal component analysis (PCA); the correlation coefficients have also been calculated.

3. RESULTS AND DISCUSSION

Contamination of soil with copper and the application of the neutralising substances had a significant effect on the content of copper and other trace elements (Tables 1–3).

Table 1

Content of copper, cadmium and lead in soil [mg/kg d.m.]

Cu dose [mg/kg of soil]	Without amendments	Compost	Bentonite	Zeolite	Average
Copper					
0	4.06	7.14	8.56	5.50	6.32
50	30.61	18.72	26.58	24.36	25.07
100	63.33	54.67	58.72	51.72	57.11
150	126.97	63.97	64.14	68.31	80.85
200	169.22	107.36	121.69	92.86	122.78
Average	78.84	50.37	55.94	48.55	58.42
r	0.988[b]	0.977[b]	0.963[b]	0.998[b]	0.992[b]
LSD for Cu dose 12.40[b], substance application 11.09[b], interaction – 24.79[b].					
Cadmium					
0	0.116	0.150	0.085	0.085	0.109
50	0.250	0.170	0.105	0.055	0.145
100	0.200	0.180	0.090	0.045	0.129
150	0.110	0.120	0.090	0.050	0.093
200	0.140	0.085	0.045	0.070	0.085
Average	0.163	0.141	0.083	0.061	0.112
r	–0.242	–0.734[a]	–0.667[a]	–0.338	–0.637[a]
LSD for Cu dose – 0.017[b], substance application – 0.015[b], interaction – 0.033[b].					
Lead					
0	5.250	5.083	5.000	4.083	4.854
50	5.583	3.917	4.333	4.083	4.479
100	4.500	5.167	3.917	3.917	4.375
150	4.250	4.333	4.667	3.833	4.271
200	4.583	4.250	4.750	1.583	3.792
Average	4.833	4.550	4.533	3.500	4.354
r	–0.754[b]	–0.360	–0.063	–0.881[b]	–0.961[b]
LSD for Cu dose – 0.591[b], substance application – 0.528[b], interaction – 1.181[b].					

Significant at $P = 0.05^a$, $P = 0.01^b$, LSD – least squares deviation, *r* – correlation coefficient.

In a series with no addition of the neutralising substances, contamination with copper caused a large increase in the content of copper in soil ($r = 0.988$) and a slight increase in the content of cadmium ($r = –0.242$). The largest doses of copper brought about a decrease in the content of cobalt ($r = –0.972$), nickel ($r = –0.789$), zinc ($r = –0.951$), manganese ($r = –0.806$), iron ($r = –0.970$) and lead ($r = –0.754$). The content of copper in soil increased with increasing doses and reached a maximum concentration of 42 times higher than that of the control object. Copper applied at the dose of 50 mg Cu/kg soil (unlike its larger doses) increased the content of cadmium and nickel in soil. The highest level of soil contamination with copper (200 mg Cu/kg) reduced the content of lead by 13%, iron by 15%, manganese by 20%, zinc by 27%, nickel by 48% and cobalt by 75%.

Table 2

Content of chromium, zinc and nickel in soil [mg/kg d.m.]

Cu dose [mg/kg of soil]	Without amendments	Compost	Bentonite	Zeolite	Average
Chromium					
0	1.930	1.870	1.335	0.885	1.505
50	1.565	1.470	1.445	0.675	1.289
100	1.555	1.390	1.350	0.595	1.223
150	1.970	1.785	1.020	0.385	1.290
200	1.840	1.310	0.840	0.135	1.031
Average	1.772	1.565	1.198	0.535	1.268
r	0.179	–0.513	–0.873[b]	–0.999[b]	–0.882[b]
LSD for Cu dose – 0.144[b], substance application – 0.129[b], interaction – 0.289[b].					
Zinc					
0	15.73	14.51	4.29	11.37	11.48
50	15.17	13.20	11.14	11.38	12.72
100	13.23	24.08	13.86	10.21	15.35
150	11.20	10.56	12.14	12.33	11.56
200	11.52	10.31	12.18	11.40	11.35
Average	13.37	14.53	10.72	11.34	12.49
r	–0.951[b]	–0.310	0.712[a]	0.212	–0.132
LSD for Cu dose 0.65[b], substance application – 0.58[b], interaction – 1.30[b].					
Nickel					
0	5.75	5.00	5.00	13.50	7.31
50	8.00	7.00	7.00	19.50	10.38
100	5.50	3.00	11.00	14.00	8.38
150	4.00	3.70	23.00	16.00	11.68
200	3.00	4.00	20.00	33.50	15.13
Average	5.25	4.54	13.20	19.30	10.57
r	–0.789[b]	–0.540	0.915[b]	0.697[a]	0.875[b]
LSD for Cu dose – 5.04[b], substance application – 4.51[b], interaction – 10.09[b].					

Significant at $P = 0.05^a$, $P = 0.01^b$, LSD – least squares deviation, *r* – correlation coefficient.

All substances used in the experiment were effective and reduced the content of copper, cadmium, and chromium in soil and, to a smaller extent, of lead and manganese (Tables 1–3). The effect of zeolite was much greater than those of bentonite and compost. Bentonite decreased the content of copper by 29% and zeolite by 38% in soil, compared to the control (with no amendments). Zeolite reduced the content of chromium by 70%, cadmium by 63%, lead and manganese by 28% in soil. The effect of compost was similar for cobalt and nickel, that of zeolite was similar for zinc and iron, and of bentonite was similar for zinc. Compost reduced the average content of cobalt in soil by 57% and that of nickel by 14%. Zeolite decreased the content of iron by 26% and that of zinc by 15% and bentonite reduced the content of zinc by 20% compared to the soil with no neutralising substances. Bentonite and zeolite increased the content of nickel in soil by 151% and 268% and the content of cobalt by 27% and 30%.

Table 3

Content of manganese, iron and cobalt in soil [mg/kg d.m.]

Cu dose [mg/kg of soil]	Without amendments	Compost	Bentonite	Zeolite	Average
Manganese					
0	209.5	218.9	159.5	155.4	185.8
50	205.9	171.0	177.9	158.4	178.3
100	208.2	169.9	175.1	157.0	177.6
150	200.2	157.7	168.3	166.4	173.2
200	166.7	156.7	161.8	72.9	139.5
Average	198.1	174.8	168.5	142.0	170.9
r	-0.806^{b}	-0.853^{b}	-0.098	-0.817^{b}	-0.854^{b}
LSD for Cu dose – 9.9^{b}, substance application – 8.9^{b}, interaction – 19.8^{b}.					
Iron					
0	6933.9	7648.7	6280.1	5974.5	6709.3
50	6804.1	6153.8	7153.6	5320.7	6358.1
100	6527.5	5969.0	7116.1	5430.6	6260.8
150	5978.8	6365.9	6493.7	5005.3	5960.9
200	5907.7	6001.6	6257.4	2041.9	5052.2
Average	6430.4	6427.8	6660.2	4754.6	6068.2
r	-0.970^{b}	-0.696^{a}	-0.252	-0.918^{b}	-0.935^{b}
LSD Cu dose – 107.7^{b}, substance application – 96.3^{b}, interaction – 215.4^{b}.					
Cobalt					
0	7.68	1.23	4.25	5.40	4.64
50	5.86	1.40	5.53	5.50	4.57
100	3.46	2.28	6.18	6.23	4.54
150	2.95	2.29	4.99	5.96	4.05
200	1.93	2.14	6.94	5.41	4.11
Average	4.38	1.87	5.58	5.70	4.38
r	-0.972^{b}	0.837^{b}	0.736^{b}	-0.981^{b}	-0.898^{b}
LSD for Cu dose – 1.21^{b}, substance application – 1.08^{b}, interaction – 2.41^{b}.					

Significant at $P = 0.05^{a}$, $P = 0.01^{b}$, LSD – least squares deviation, *r* – correlation coefficient.

Table 4

Correlation coefficients *r* between content of trace elements and some properties of soil

Factor	Cu	Cd	Pb	Cr	Zn	Ni	Mn	Fe	Co
pH_{KCl}	–0.316[a]	0.114	0.025	–0.171	0.126	0.162	0.046	–0.081	0.546[b]
HAC	0.652[b]	0.055	–0.224	0.262	–0.156	–0.233	–0.184	–0.232	–0.440[b]
TEB	–0.009	–0.179	–0.250	–0.226	–0.365[a]	0.227	–0.370[a]	–0.174	0.161
CEC	0.136	–0.161	–0.291	–0.160	–0.387[a]	0.168	–0.398[a]	–0.220	0.058
BS	–0.500[b]	–0.158	0.015	–0.372[a]	–0.086	0.353[a]	–0.098	0.059	0.493[b]
Cu		–0.147	–0.213	0.003	–0.070	0.067	–0.207	–0.312[a]	–0.197
Cd			0.399[a]	0.599[b]	0.497[b]	–0.475[b]	0.514[b]	0.383[a]	–0.386[a]
Pb				0.594[b]	0.244	–0.489[b]	0.716[b]	0.742[b]	–0.118
Cr					0.189	–0.750[b]	0.720[b]	0.707[b]	–0.435[b]
Zn						–0.142	0.284	0.153	–0.080
Ni							–0.598[b]	–0.622[b]	0.448[b]
Mn								0.831[b]	–0.141
Fe									–0.122

pH_{KCl} – pH in 1 mol/dm^3 KCl, HAC – hydrolytic acidity, TEB – total exchangeable bases, CEC – cation exchange capacity, BS – base saturation. Significant at $^*P = 0.05^a$, and $P = 0.01^b$.

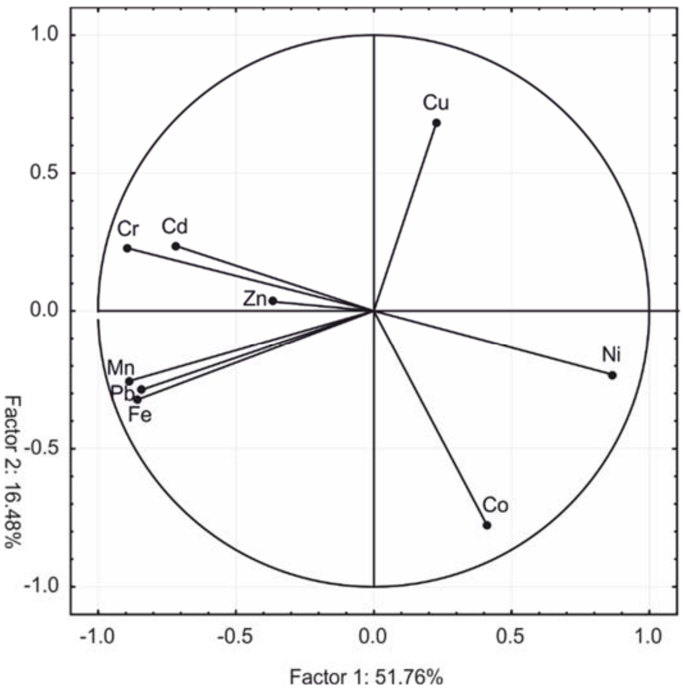

Fig. 1. Content of trace elements in the soils illustrated by the PCA method:
vectors represent the analyzed variables (content of Cu, Cd, Pb, Cr, Zn, Ni, Mn, Fe and Co)

The correlation coefficients and the PCA analysis (Table 4, Fig. 1) have shown significant relationships between the trace elements, especially between manganese, iron, and nickel and chromium and most of the other trace elements in soil. The PCA analysis has shown that the principal components represent 68.24%, with 51.76% for the first component and 16.48% for the second. The vectors illustrate the content of manganese, iron, nickel and chromium very well and the content of zinc rather poorly. The highest positive correlation coefficients were observed between iron and manganese on the one side and chromium and lead on the other; between cadmium and manganese, chromium and zinc; between chromium and lead; between cobalt and nickel. The negative correlation was observed between nickel and iron, manganese, cadmium, lead and chromium. Significant correlations were found between the content of copper and cobalt and hydrolytic acidity and cation exchange capacity (CEC) and between cobalt and soil pH; however, the correlation for copper was the opposite to those for cobalt. The PCA analysis confirmed a much greater effect of bentonite and especially zeolite than that of compost on the content of trace elements in soil (Fig. 2).

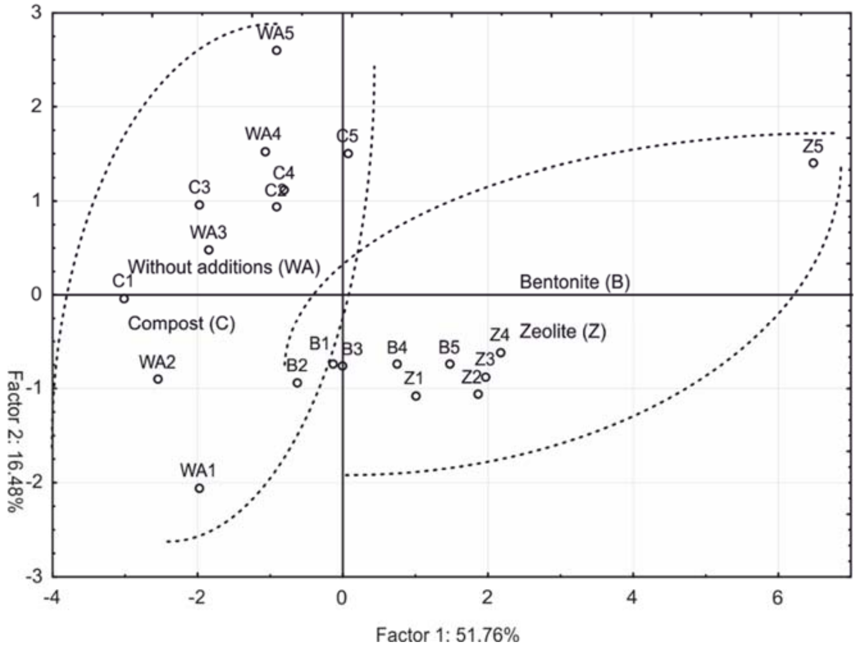

Fig. 2. Effect of neutralizing substances on the content of trace elements in the soils illustrated by the PCA method: points show soil samples with trace elements (WA – without additions, C – compost, B – bentonite, Z – zeolite; 1 – 0, 2 – 50 mg, 3 – 100 mg, 4 – 150 mg, 5 – 200 mg Cu/kg of soil)

Increasing the contamination of soil with copper caused an increase in its content, including soluble forms, which can be absorbed by plants. However, this can limit the content of soluble forms of other elements in soil. This is also associated with the quality and properties of soil, especially with pH, acidity and content of organic matter, especially humus, which is associated with more-or-less developed sorptive complex of the soil and with a greater or smaller extent of adsorption of copper and other elements [1, 20]. A special role is played by humus, silty minerals and hydrated iron, manganese and aluminium oxides, i.e., the main components which determine sorptive properties of soil [1, 21]. The soil pH determines the availability of trace elements to plants [21, 22]. A decrease in its value results in an increase in the content of available species of many trace elements. An increase in pH rapidly reduces their content [23]. When pH is high, metal ions can be removed from the soil solution nearly completely and they can become unavailable to plants [22]. Changing the soil pH by liming is an easy method of limiting the effect of copper and other trace elements on plants. A similar effect can be achieved by the application of various substances to soil [20]. Studies carried out by many authors [2, 24] have indicated that such effective substances may be zeolites and bentonites [24] as well as organic matter [2, 20]. Compost seems to be particularly effective. However, its effect on soil properties is not uniform and frequently depends on the crop species. In a study by Park et al. [2], compost, manure, sludge and household waste were used as a source of nutrients to improve the physical properties and fertility of soil, as well as to reduce the bioavailability of metals. According to Wyszkowski and Sivitskaya [23, 25], compost and bentonite reduced the content of copper and iron in soil, and zeolite reduced the content of cadmium and lead [23] but they did not have a favorable effect on the content of manganese, chromium or lead [25]. Janoš et al. [24] found that mobility of copper in soil was significantly reduced by applying zeolite. A stabilizing effect of zeolite on heavy metals in soil was also confirmed by Zorpas et al. [26].

In our research, the positive effect of compost and especially zeolite and bentonite on sorptive properties and sorption of copper in soil caused reduction of the content of many trace elements in soil. High content of nickel and cobalt in bentonite and zeolite caused an increase the content of these elements in soil.

4. CONCLUSIONS

The soil contamination with copper and the application of neutralizing substances (compost, bentonite and zeolite) has significant effects on the content of copper and other trace elements in soil. In the series with no neutralizing substances, copper pollution mainly caused a very high increase of copper content in soil and a smaller one in the amount of cadmium. In the same series, the highest doses of copper led to a decrease in the content of cobalt, nickel, zinc, manganese, iron and lead in soil. All amendments used in the experiment were effective and reduced the content of copper, cadmium, and chromium and, to a smaller extent, lead and manganese in soil. It is worth noticing that the effect of zeolite was much stronger than the effect of bentonite or compost. Compost acted similarly with respect to cobalt and nickel. Zeolite had a similar effect on the content of zinc and iron in soil. Bentonite had a comparable influence on the accumulation of zinc in soil. In turn, bentonite and zeolite contributed to an increase in the content of nickel and cobalt in soil.

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