EFFECT OF ORGANO-MINERAL TREATMENT ON PRODUCTIVITY OF ALFALFA GROWN ON COPPER AND ZINC POLLUTED SOILS

Antoaneta Arsova*, Toshko Raychev

N. Poushkarov Institute of Soil Science and Agroecology, 7 Shosse Bankja Str., 1080 Sofia, Bulgaria

Summary. A two-year-long pot experiment was carried out with alfalfa grown on a light gray forest soil (Albic Luvisol) polluted with Cu, Zn and Cu/Zn (pH 5.1; Cu = 300 mg.kg^{-1}; Zn = 300 mg.kg^{-1}). The soil was treated with combined waste products of carbonate deposit and anthracite coal powder applied in the following ratios 1:4, 1:8, 1:12, 1:16. The content of carbonate deposit was constant, corresponding to the optimal liming rate for acid soils, while coal powder varied in the range 10–40 g.kg^{-1}. The effect of the organo-mineral treatments on alfalfa productivity and Cu and Zn uptake was studied. The maximal biomass production from seven cuts was obtained at the optimal dose of 2.3 g.kg^{-1} carbonate deposit and 20 g.kg^{-1} coal powder (1:8) applied in copper, zinc and copper/zinc polluted soils. The relevant sorption capacity (300 mequ per 100 g) of humic acids in the coal powder was determined. The organo-mineral treatment of the heavy metal polluted soils maintained pH in the optimal range (pH 5.8–6.2) during the whole experiment which immobilized Cu^{2+} and Zn^{2+} ions in the soil and decreased their content in alfalfa biomass.

Key words: acid soil, alfalfa production, carbonate deposit, coal powder, copper and zinc pollution, copper and zinc uptake, organo-mineral soil treatment

Introduction

Heavy metal polluted acid soils have to be ameliorated for recovery of their fertility. The main problem of liming such soils is the short-term effect of lime materials be-

* Corresponding author, e-mail: *unioncon@sps.bg*

cause of bicarbonates' leaching in vertical and lateral water flow. Many reports concern the use of different waste products as soil amendments for improving soil chemical properties and plant growth (Munoz et al., 1994; Marschner et al., 1995; Sajwan et al., 1995; Che et al., 1998; Shamshuddin, 1998; Gonzalez et al., 1999). It is commonly known that heavy metals form complexes with the soil organic matter thus decreasing their activity in the soil solution. Thus, an addition of organic compounds should have a positive chemical melioration effect on polluted soils. The use of brown coals as a meliorant of humus conditions and detoxicant for soils polluted with heavy metals because of their binding with the humic acids has been reported (Shestopalov and Gorbov, 1998).

According to a theoretically elaborated scheme combined treatment of polluted acid soils with lime materials and organic products (anthracite coals), containing compounds with a high degree of humification (humic acids), should increase soil pH and decrease heavy metals' mobility, due to an association of their ions (Cu^{2+}, Zn^{2+}) in stable organo-mineral complexes (Raychev, 1996). The priority of anthracite coals over brown coals is the higher content of humic acids due to the advanced stage of humification of the humus compounds.

In this aspect waste carbonate deposit and anthracite coal powder were tested in laboratory and pot experiments and their applicability for soil acidity neutralization and heavy metals' immobilization was confirmed (Dimitrova et al., 1992; Raychev, 1996; Arsova, 1998). A positive effect of ameliorating naturally polluted soils with a mixture of carbonate deposit and anthracite coal powder on plant growth was established (Arsova and Raychev, 1999). A compost of carbonate deposit and anthracite coal powder was patented as a meliorant for copper polluted acid soils (Raychev et al., 1999).

The effect of organo-mineral treatment on plant growth under conditions of copper–zinc pollution of the soils has not been studied. Besides, more detailed investigations are necessary to determine the optimal quantitative ratio between the waste products providing a maximal effectiveness. The amount of carbonate deposit and coal powder applied in the polluted soils has to be considered in parallel with the toxic soil acidity and the sorption capacity of the humus components as well. The sorption capacity of the humic acids (T_{HA}) varies in the range 150–570 mequ per 100 g (Orlov, 1985). The determination of the optimal coal powder content in the combined waste products should define more precisely the value of the sorption capacity of humic acids.

The aim of the study is to establish the optimal dose of the combined waste products for improving the productivity of alfalfa grown on acid soils polluted with copper and zinc.

Materials and Methods

Two-year-long pot experiments were carried out with alfalfa grown on a light gray forest soil (Albic Luvisol) with the following physico-chemical characteristics:

pH(H$_2$O) 5.1; exch. Al = 2.4 mequ/100 g; exch. H$_{8.2}$ = 8.5 mequ/100 g; exch. (Ca^{2+} + Mg^{2+}) = 16.8 mequ/100 g; CEC = 24.6 mequ/100 g. Soil pH was measured in water suspension 1:2.5. The exchangeable acidity (exch. Al) was determined titrimetrically after displacement of Al^{3+} ions by 1 N CaCl$_2$. The total acidity (exch. H$_{8.2}$) and exchangeable bases were determined, titrimetrically and complexometrically, respectively, after saturation of the soil sample with buffer solution (Na-acetate and K-maleinate, pH 8.2). The cation exchange capacity (CEC) was calculated by the sum of exch. H$_{8.2}$ and exch. bases (Ganev and Arsova, 1980).

The soil was polluted with copper and zinc applied in the following concentrations:

-   Cu = 300 mg.kg^{-1} added as CuO = 0.375 g.kg^{-1};
-   Zn = 300 mg.kg^{-1} added as ZnO = 0.460 g.kg^{-1};
-   Combined pollution Cu + Zn = 600 mg.kg^{-1} added as CuO and ZnO in the above-mentioned concentrations.

The soil pollution exceeded several times the permissible contaminant levels, which were 40 mg.kg^{-1} and 60 mg.kg^{-1} for Cu and Zn, respectively, at pH 5.0.

The following waste products were used:

-   Carbonate deposit (Ca$_{opt.}$) – a product of lime decarbonization and water coagulation in a power station near Burgas, containing 74.3% CaCO$_3$. The neutralizing capacity was 2200 mequ per 100 g material, or n = 0.045 g per 1 mequ;
-   Anthracite coal powder (B) – a waste product from the "Svoge" coalmine, containing 85% humic acids (HA).

In all treatments the amount of carbonate deposit was constant (Ca$_{opt.}$ = 0.23 g per 100 g), calculated according to the formula for the optimal liming rate of acid soils (Ganev, 1987): Ca$_{opt.}$ g/100 g = [2 exch. Al + 0.8×% humus × exch. Al / exch. Al + exch. (Ca+Mg)] × n.

The coal powder (B) was added in increasing amounts taking into account the range of the sorption capacity of humic acids (T$_{HA}$). The highest capacity value (T$_{HA}$ = 570 mequ/100 g) calculated for 85% humic acids in the coal powder was approximately T(B) = 500 mequ/100 g, or 50 mequ (1 g Ca) per 10 g coal powder. On the basis of this capacity an initial ratio 1:4 between the carbonate deposit and coal powder was accepted. This ratio corresponded to 2.3 g carbonate deposit (Ca$_{opt.}$) and 10 g coal powder per kg soil. The increase of the coal powder amount in the presence of a constant carbonate deposit content, which was about 50 mequ Ca per kg soil (Ca$_{opt.}$/n = 2.3/0.045 = 50 mequ per kg), should lead to a decrease in the sorption capacity T(B) in the range mentioned above.

Organo-mineral treatment of the soil was applied according to the following scheme:

-   Control – polluted soils with Cu, Zn and Cu/Zn;

- $Ca_{opt.}$ – carbonate deposit added in an amount corresponding to the optimal liming rate ($Ca_{opt.} = 2.3$ g.kg^{-1});
- K_1 – carbonate deposit ($Ca_{opt.}$) and coal powder (B_1) in a ratio 1:4 ($Ca_{opt.} + B_1 = 2.3$ g + 10 g per kg soil, $T(B_1) = 500$ mequ/100 g, corresponding to 50 mequ Ca/10 g coal powder);
- K_2 – carbonate deposit ($Ca_{opt.}$) and coal powder (B_2) in a ratio 1:8 ($Ca_{opt.} + B_2 = 2.3$ g + 20 g per kg soil, $T(B_2) = 250$ mequ/100 g, corresponding to 50 mequ Ca/20 g coal powder);
- K_3 – carbonate deposit ($Ca_{opt.}$) and coal powder (B_3) in a ratio 1:12 ($Ca_{opt.} + B_3 = 2.3$ g + 30 g per kg soil, $T(B_3) = 166$ mequ/100 g, corresponding to 50 mequ Ca/30 g coal powder);
- K_4 – carbonate deposit ($Ca_{opt.}$) and coal powder (B_4) in a ratio 1:16 ($Ca_{opt.} + B_4 = 2.3$ g + 40 g per kg soil, $T(B_4) = 25$ mequ/100 g, corresponding to 50 mequ Ca/40 g coal powder).

The experiments were conducted in three replications with 1.2 kg soil per pot and moisture 60% of the field capacity. Manure of 10 g.kg^{-1} was applied. A preliminary interaction between the soil additives was carried out in the course of two months.

The alfalfa cuts were harvested in the beginning of the blowing stage. The dry biomass from seven cuts was weighted. Copper and zinc content in the biomass (I and II cuts) was determined by atomic absorption spectrometry (AAS) methods. Soil pH was measured in soil–water suspension 1:2.5 at the end of the experiment. A dispersion analysis was performed to evaluate the alfalfa production.

Results and Discussion

Criteria for evaluating the effectiveness of the organo-mineral treatment of polluted soils are soil pH, alfalfa production from seven cuts (Table 1) and copper and zinc content in the biomass (Table 2).

Soil pH was maintained in the optimal range (pH 5.8–6.3) during the treatment with the carbonate deposit, applied either separately ($Ca_{opt.}$) or in combination with the coal powder (K_{1-4}). Additional acidification (pH 4.2–4.4) was observed in the control variants in comparison to the initial soil pH value (pH 5.1) caused by the soil pollutants. Treatment with the highest coal powder content (K_4) soil pH showed a tendency of a decrease (pH 5.8) in relation to the other combined treatments (K_{1-3}), most probably due to an insufficiency of carbonate deposit for neutralizing the acidic groups (-COOH) of the humic acids.

In the variant of copper pollution the biomass amount from the I cut was highest after treatment with carbonate deposit and coal powder in a ratio 1:4 (K_1). The differences, however, between this amount and the amount obtained upon treatment with

Table 1. Alfalfa production and soil pH depending on the organo-mineral treatment of acid soils polluted with Cu, Zn and Cu/Zn. Values are given as mean average from three replications.

Treatment	Soil pH H_2O	I cut	II cut	III cut	IVcut	V cut	VI cut	VII cut
					g DW/10 plants			
Contamination with Cu								
Control	4.4	1.46	1.24	0.87	0.63	0.39	0.74	0.72
$Ca_{opt.}$	6.0	2.28	2.23	1.70	1.76	2.26	3.00	2.90
K_1	6.1	2.38	1.98	1.50	2.00	2.53	4.55	4.00
K_2	6.1	2.19	2.60	1.75	2.17	2.87	4.83	4.97
K_3	6.2	1.87	1.64	1.22	1.38	2.12	3.17	3.01
K_4	5.8	1.97	1.55	1.22	1.33	1.73	2.90	2.82
LSD 1%		0.27	0.23	0.15	0.07	0.08	0.10	0.35
0.1%		0.38	0.30	0.20	0.09	0.12	0.19	0.41
Contamination with Zn								
Control	4.2	0.93	0.37	0.20	0.00	0.00	0.00	0.00
$Ca_{opt.}$	6.2	1.07	1.12	1.16	1.00	1.87	2.24	2.15
K_1	6.3	1.02	1.09	1.02	1.67	1.77	1.95	1.65
K_2	6.3	1.39	1.50	1.20	1.89	2.17	2.64	2.91
K_3	5.9	1.15	1.11	0.65	1.63	2.37	3.84	3.24
K_4	5.9	1.10	1.06	0.84	0.99	1.18	1.40	1.29
LSD 1%		0.21	0.10	0.06	0.19	0.09	0.42	0.35
0.1%		0.29	0.14	0.09	0.29	0.13	0.59	0.50
Contamination with Cu/Zn								
Control	4.2	0.34	0.31	0.30	1.28	0.00	0.00	0.00
$Ca_{opt.}$	6.0	1.44	1.79	1.53	1.45	2.02	2.73	2.66
K_1	6.0	1.31	2.02	1.22	1.39	1.98	2.11	2.08
K_2	5.9	1.06	1.68	1.15	1.62	1.95	3.69	3.52
K_3	5.9	1.18	1.50	1.03	1.51	2.11	2.12	2.07
K_4	5.8	1.28	1.02	0.96	1.41	1.73	1.48	1.47
LSD 1%		0.14	0.10	0.13	0.15	0.19	0.20	0.47
0.1%		0.19	0.13	0.18	0.21	0.28	0.28	0.61

carbonate deposit ($Ca_{opt.}$) and the other combined products (K_{2-4}) were not significant. The treatment with the combined product K_2 (1:8) had a significant positive effect on the II cut production. A statistically significant maximal production from the next cuts (III–VII cut) was obtained at carbonate deposit and coal powder applied in a ratio 1:8 (K_2). A decrease of the biomass amount from all cuts was observed in the variants K_3 and K_4 containing 30 and 40 g coal powder per kg soil, respectively.

Table 2. Copper and zinc content in alfalfa biomass (mg.kg^{-1} DW) depending on the organo-mineral treatment of acid soils polluted with Cu, Zn and Cu/Zn.

Treatment	I cut		II cut	
	Cu	Zn	Cu	Zn
Soil contaminated with Cu				
Control	35	57	37	51
$Ca_{opt.}$	17	64	22	47
K_1	20	49	25	44
K_2	19	62	24	52
K_3	19	54	23	47
K_4	18	54	23	43
Soil contaminated with Zn				
Control	10	820	16	990
$Ca_{opt.}$	9	650	8	660
K_1	7	710	7	720
K_2	9	670	11	690
K_3	7	760	12	690
K_4	9	670	11	740
Soil contaminated with Cu/Zn				
Control	34	870	35	1340
$Ca_{opt.}$	16	630	26	610
K_1	15	660	21	470
K_2	15	720	22	660
K_3	18	720	28	640
K_4	19	580	30	590

The combined products K_{1-4} applied in the copper polluted soil form according to their effectiveness on alfalfa production the following orders (LSD 1%):

I cut: $K_1 \approx K_2 > K_3 \approx K_4$; II cut: $K_2 > K_1 > K_3 \approx K_4$; III cut: $K_2 > K_1 > K_3 \approx K_4$; IV cut: $K_2 > K_1 > K_3 \approx K_4$; V cut: $K_2 > K_1 > K_3 \approx K_4$; VI cut: $K_2 > K_1 > K_3 > K_4$; VII cut: $K_2 > K_1 > K_3 > K_4$

A higher depression of plant growth was observed in the variant of zinc polluted soil compared to the copper polluted soil. This is probably due to the toxic effect of the high zinc concentration in the soil as well as to the lower stability of the ligands binding zinc than that of the ligands binding copper (Alloway and Ayres, 1994). A maximal alfalfa production from the I–IV cuts was obtained after treatment with carbonate deposit and coal powder applied in a ratio 1:8 (K_2). The combined product K_3 (1:12) had a significant positive effect on the production of the next cuts (V–VII cuts) unlike its effect observed in the variant of copper polluted soil, although the soil pH value was lower (pH 5.9).

In the variant of zinc polluted soil the positive effect of the combined treatments K_{1-4} on plant production is expressed in the following orders (LSD 1%):

I cut: $K_2 > K_3 \approx K_4 \approx K_1$; II cut: $K_2 > K_3 \approx K_4 \approx K_1$; III cut: $K_2 > K_1 > K_4 > K_3$; IV cut: $K_2 > K_1 \approx K_3 > K_4$; V cut: $K_3 > K_2 > K_1 > K_4$; VI cut: $K_3 > K_2 > K_1 > K_4$; VII cut: $K_3 \approx K_2 > K_1 > K_4$.

The soil contamination with copper and zinc added in equivalent amounts increased twice the concentration of heavy metals in comparison to the variants with the individual pollutants. The fact does not change the course of the evaluated parameters – soil pH and alfalfa production. It must be noticed that under conditions of complex copper–zinc pollution of the soil the depressive effect of zinc toxicity on plant growth was more weakly expressed than in the zinc polluted soil, probably due to Cu/Zn antagonism. The alfalfa productivity, however, was lower compared to that on the copper polluted soil. The biomass amount from the I and III cuts was highest at the optimal liming ($Ca_{opt.}$). The combined product of carbonate deposit and coal powder in a ratio 1:4 (K_1) had a significant effect on the II cut production, while after the treatment K_3 (1:12) a higher biomass production from the V cut was obtained, but the differences with the biomass content after the combined treatments K_1 and K_2 were not significant. The alfalfa production from the IV, VI and VII cuts was maximal at carbonate deposit and coal powder applied in a ratio 1:8 (K_2), but only the production from the VI and VII cuts was statistically significant. The biomass content from later cuts (V–VII) decreased in the presence of the combined product K_3 similarly to the variant with the individual copper pollution of the soil. The plant growth depression as a result of the treatment of Cu/Zn polluted soil with the product K_4 (1:16) was strongly expressed.

The orders formed by the combined products K_{1-4} applied in Cu/Zn polluted soil according to their positive effect on alfalfa production are as follows (LSD 1%):

I cut: $K_1 \approx K_4 \approx K_3 \approx K_2$; II cut: $K_1 > K_2 > K_3 > K_4$; III cut: $K_1 \approx K_2 \approx K_3 \approx K_4$; IV cut: $K_2 \approx K_3 \approx K_4 \approx K_1$; V cut: $K_3 \approx K_1 \approx K_2 > K_4$; VI cut: $K_2 > K_3 > K_1 > K_4$; VII cut: $K_2 > K_1 \approx K_3 > K_4$.

In all variants of the soil pollution the treatment with carbonate deposit and coal powder in a ratio 1:8 (K_2) had a higher effectiveness and better time-effect on alfalfa production from almost all cuts compared to the optimal liming ($Ca_{opt.}$) and the other combined treatments during the two years period of vegetation.

The highest coal powder content (40 g.kg^{-1}) during the treatment K_4 caused a decrease of alfalfa production from all cuts, most probably due to the relative excess of acidic groups (-COOH) of the humic acids, which bind nutrients in the soil thus eliminating them from the cation exchange with the plant roots.

The effect of organo-mineral treatment of polluted soils on the total biomass production (sum of seven cuts) is presented in Fig. 1. The combined treatment K_2 had a

Contamination with Cu

Contamination with Zn

Contamination with Cu/Zn
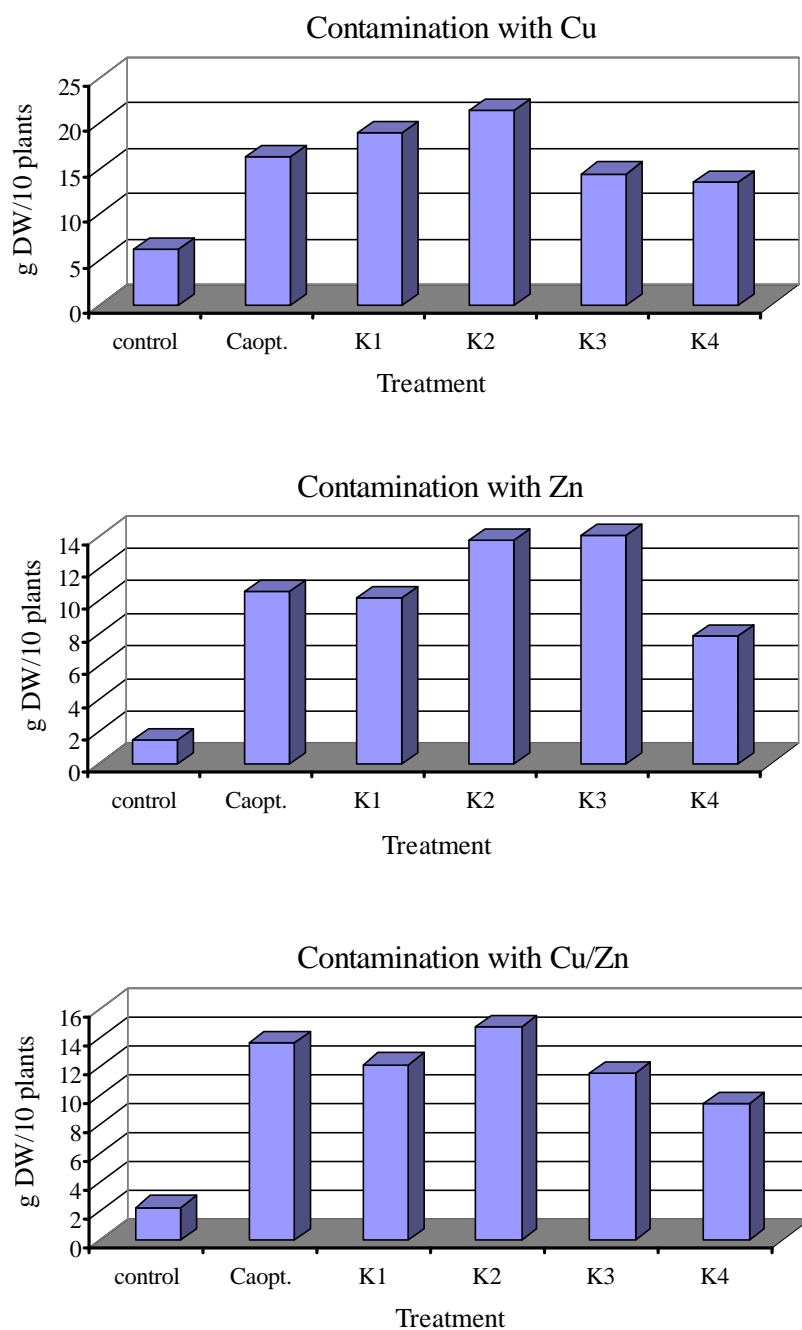
Fig.1. Total alfalfa production from seven cuts (g DW/10 plants) depending on the organo-mineral treatment of acid soils polluted with Cu, Zn and Cu/Zn

maximal effect on the total alfalfa production in all variants of soil pollution. In the zinc polluted soil an almost equal total production was observed in the treatments K_2 and K_3. Obviously, the increased coal powder content in the treatment K_3 (1:12) was favorable for plant growth under zinc toxicity conditions. In the variants of copper and copper/zinc pollution the high coal powder doses (30 and 40 g.kg^{-1}) applied in the soil (treatments K_3 and K_4) reduced the total amount of biomass.

It could be assumed that the treatment with the combined product K_2 of carbonate deposit and coal powder in a ratio 1:8 is the most appropriate for realizing a maximal effect on alfalfa productivity according to the proposed experimental scheme. Therefore, the amount of 2.3 g carbonate deposit and 20 g coal powder per 1 kg soil polluted with copper, zinc and copper/zinc could be accepted as an optimal dose for plant growth, allowing also an ecological utilization of the waste products. The sorption capacity of the coal powder, calculated on the basis of the optimal amount is $T(B) = 250$ mequ per 100 g coal powder containing 85% humic acids, or $T_{HA} \approx 300$ mequ per 100 g humic acids.

The acidic conditions in the soil are decisive for heavy metals' uptake by plants which decreases with the pH increase due to the transformation of their ionic forms in non-available compounds. The effect of organo-mineral treatment of polluted soils on copper and zinc content in the biomass (I and II cuts) is shown in Table 2. It is well known that the normal copper content in plant leaves is about 5–25 mg.kg^{-1}, while the toxic concentrations are 20–100 mg.kg^{-1}. The normal zinc content is 1–400 mg.kg^{-1} and the toxic one is more than 400 mg.kg^{-1} (Alloway and Ayres, 1994).

In the variants with Cu and Cu/Zn pollution the copper content in the biomass from the I and II cuts decreased to almost normal limits (15–30 mg.kg^{-1}) after treatment with carbonate deposit and coal powder (Ca$_{opt.}$, $K_{1–4}$) compared to the control (34–37 mg.kg^{-1}).

The organo-mineral treatment of the soil contaminated with Zn and Cu/Zn decreased the zinc content in alfalfa biomass from the I and II cuts (470–740 mg.kg^{-1}) compared to the control (820–1340 mg.kg^{-1}), although being above the normal limits, probably caused by the depressive effect of the toxic zinc excess in the soil on plant growth.

There were not significant differences between copper and zinc content in alfalfa biomass upon treatment with carbonate deposit applied separately (Ca$_{opt.}$) and in combination with coal powder ($K_{1–4}$). The fact is due mainly to the soil pH buffered in the relatively stable optimal range (pH 5.8–6.2) during the whole vegetation excluding the possibility of some particular influence of the increasing coal powder amount on copper and zinc mobility. Therefore, the treatment of the heavy metal polluted soils with carbonate deposit and coal powder (Ca$_{opt.}$, $K_{1–4}$) causes an immobilization of Cu^{2+} and Zn^{2+} ions because of their association in hydroxides and organo-mineral complexes under optimal soil pH conditions.

Conclusions

Organo-mineral treatment of Cu, Zn and Cu/Zn contaminated soils with carbonate deposit and anthracite coal powder applied in a ratio 1:8 provides maximal effectiveness on alfalfa productivity. The optimal dose of the waste products applicable for soils with copper–zinc pollution is 2.3 g and 20 g per kg soil, respectively. The increase of coal powder content in the combined products causes unbalanced mineral nutrition and depressed plant growth.

The sorption capacity of the humic acids determined on the basis of the optimal amount of carbonate deposit and coal powder is $T_{HA} \approx 300$ mequ/100 g.

Treatment of the soil with carbonate deposit and coal powder decreases both the copper and zinc content in alfalfa biomass. The fact is due to the immobilization of Cu^{2+} and Zn^{2+} ions bound in organo-mineral complexes and hydroxides under optimal soil pH conditions (pH 5.8–6.2) during the whole vegetation period.

References

Alloway, J., D. Ayres, 1994. Chemical principles of environmental pollution. Blackie Academic & Professional, Glasgow.

Arsova, A., 1998. Bioecological testing of carbonate deposit designed for liming copper polluted acid soil. J. Balkan Ecology, 1(2), 86–90.

Arsova, A., T. Raychev, 1999. Bioecological effect of waste materials used for amelioration of copper and arsenic polluted soil located in Kremikovtsi region of Bulgaria. J. Balkan Ecology, 2(2), 47–52.

Che, M., T. Logan, S. Traina, J. Bigham, 1998. Properties of water treatment lime sludge and their effectiveness as agricultural limestone substitutes. J. Water Pollut. Control Fed., 60(5), 674–680.

Dimitrova, N., M., Mihailova, A. Arsova, P. Penchev, 1992. Results of study on the utilization of waste carbonate deposits. In: Proceeding Scientific Papers of International Symposium "Ecology' 92", Burgas, Sept. 1992, 89–92 (In Bulg.).

Ganev, S., A. Arsova, 1980. Methods for determination of strongly acidic and weakly acidic cation exchange in soils. Soil Sci. Agrochem., 15(3), 22–33 (In Bulg.).

Ganev, S., 1987. Strongly acidic and weakly acidic nature of soil acidity and determining the liming rate of acid soils. Forestry, 1, 19–25 (In Bulg.).

Gonzalez, P., R. Espejo, R. Ordonez, J. Santano, 1999. Barley response to several lime and gypsum treatments in nine western Spain palexerult soils. In: Proceeding Scientific Papers of 6th International Meeting on Soils with Mediterranean type of climate, Barcelona, July 1999, 250–253.

Marschner, B., U. Henke, G. Wesselek, 1995. Effects of meliorative additives on the adsorption and binding forms of heavy metals in a contaminated top soil from a former sewage farm. Z. Planzenernahrung and Bodenkunde, 158(1), 9–14.

Munoz, M., L. Pena, J. O'Hallorans, 1994. Use of an industrial by-product as a liming source. J. Agriculture of the Univ. of Puerto Rico, 78(3–4), 73–86.

Orlov, D., 1985. Soil chemistry. Univ. of Moscow, Moscow (In Russ.).

Raychev, T., 1996. Influence of organo-mineral interactions on colloid-chemical state of the soil adsorbent. D. Sci. Thesis, N. Poushkarov Inst., Sofia (In Bulg.).

Raychev, T., A. Arsova, 1998. Regulation of soil adsorbent properties in copper polluted acid soil. Bulg. J. Agricultural Sci., 4, 25–30.

Raychev, T., A. Arsova, S. Pishmanova, 1999. Meliorant for acid soils polluted with copper and method for its application. Patent N 327 Y1 BG, 30. 07. 99 (In Bulg.).

Sajwan, K., W. Ornes, T. Youngblood, 1995. Effect of fly ash/sewage sludge mixture and application rates on biomass production. J. Environ. Sci. Health, 30(6), 1327–1337.

Shestopalov, A., S. Gorbov, 1998. Soil pollution by heavy metals in Rostov-on-Don and the brown coal use as a detoxicant. In: Proceeding Scientific Papers of 16th World Congress of Soil Science, Montpellier, Aug. 1998, vol. 2, 704–705.

Shamshuddin, J., 1998. Soil acidity neutralization by limestone and gypsum application. In: Procceding Scientific Papers of 16th World Congress of Soil Science, Montpellier, Aug. 1998, vol 2, 738–739.