PHYSICOCHEMICAL MANAGEMENT OF ACID SOILS POLLUTED WITH HEAVY METALS

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PREFACE

Soil is the most important part of our living space and our primary duty is to keep its proper functioning for harmonized use of the environment. Therefore much attention has been paid to find environmental friendly measures to cure polluted soils and protect them against degradation.

Sols in Europe are among most polluted and degraded in the world due to long time industrial and traffic activity, large-scale historical events (wars), as well as to intensive agriculture. Knowledge on soil physicochemical properties is necessary for proper undestanding of soil properties and processes that are necessary to design correct solutions to fight against soil pollution and degradation caused by acidification, alkalization, soil organic matter leaching and oxidation.

In a frame of a cooperation between Polish and Bulgarian Academies of Sciences involving Institute of Agrophysics PAS in Lublin and Nikola Poushkarov Institute of Soil Science in Sofia, some scientists have been dealing with the above problems for a long time. This cooperation has been strengthen and enlarged as a result of the activity of a Polish-Bulgarian workgroup organized in a frame of the activity of the Centre of Excellence for Applied Physics in Sustainable Agriculture AGROPHYSICS and with financial support of European Commission and Polish State Committee for Scientific Research.

This issue shows some results obtained by this workgroup in a field of soil physicochemical protection with special attention placed on heavy metal pollution.

THE EDITORS

CONTENTS

ALFALFA YIELD DEPENDENCE ON ORGANO-MINERAL LIMING of HEAVY METAL POLLUTED SOIL

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Abstract

The main problem of liming acid soils polluted with heavy metals soils is the short-term effect of lime materials because of bicarbonates leaching by vertical and lateral water flow. An addition of organic compounds should have a positive chemical melioration effect on polluted soils. According to our theoretically elaborated scheme a 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 the HM ions (Cu^{2+}, Zn^{2+}) in stable organo-mineral complexes. The aim of this study is to test the effect of such organo-mineral amelioration on alfalfa yield under combined Cu/Zn pollution of the soil. A two-year-long pot experiment was carried out with alfalfa grown on a light gray forest soil (Albic Luvisol) polluted with Cu/Zn (pH (H_2O) 5.1; Cu = 300 mg/kg and Zn = 300 mg/kg added as CuO and ZnO). The soil was treated with waste mixture of carbonate deposit and anthracite coal powder applied in the following ratios 1:4, 1:8, 1:12, 1:16. The content of the carbonate deposit was constant, corresponding to the optimal liming rate for acid soils, while the coal powder content in the mixture increased in the range 10, 20, 30 and 40 g per kg soil. The effect of the organo-mineral treatments on alfalfa yield and Cu and Zn uptake by plants was studied. The maximal biomass production from seven cuts was obtained at optimal dose of 2.3 g/kg carbonate deposit and about 20 g/kg coal powder (1:8) applied in the copper/zinc polluted soil. The high coal powder content (40 mg/kg) in the combined mixture caused unbalanced mineral nutrition and depressed plant growth. Treatment of the soil with carbonate deposit and coal powder decreased both the copper and zinc content in alfalfa biomass. The fact was 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.

INTRODUCTION

The main problem of liming acid soils polluted with heavy metals is the short-term effect of lime materials because 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; Gonzalez et al., 1999). 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 (Raytchev, 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.

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 Raytchev, 1999). A compost of carbonate deposit and anthracite coal powder was patented as a meliorant for copper polluted acid soils (Raytchev et al., 1999).

It is of interest to study the effect of the organo-mineral liming on plant growth under conditions of combined copper/zinc pollution of the soils.

Our aim is to establish the maximal effectiveness on alfalfa yield of ameliorating Cu/Zn polluted soil with lime material and coal powder.

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_2O) 5.1; exch. Al = 2.4 mequ/100 g; exch.(Ca^{2+} + Mg^{2+}) = 16.8 mequ/ 100 g; CEC = 24.6 mequ/100 g.

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

- Cu = 300 mg/kg added as CuO = 0.375 g/kg;
- Zn = 300 mg/kg added as ZnO = 0.460 g/kg;

The soil pollution exceeded several times the permissible contaminant levels, which were 40 mg/kg and 60 mg/kg for Cu and Zn, respectively, at pH = 5.0.

The following waste products were used for the organo-mineral liming:

Carbonate deposit ($Ca_{opt.}$) – a product of lime decarbonization and water coagulation in a power station near Burgas, containing 74.3% $CaCO_3$.

Anthracite coal powder (B) – a waste product from the "Svoge" coalmine, containing 85% (relatively to total C) humic acids (HA).

In all treatments the amount of carbonate deposit was constant ($Ca_{opt.}$ = 0.23 g/ 100 g), calculated according to the optimal liming rate of acid soils (Ganev, 1987).

The coal powder (B) was added in increasing amounts – 10, 20, 30 and 40 g/kg.

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

- Control – Cu/Zn polluted soil;
- $Ca_{opt.}$ – carbonate deposit added in an amount corresponding to the optimal liming rate ($Ca_{opt.}$ = 2.3 g/kg);
- 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;
- 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;
- 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;
- 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;

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 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 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 (LSD – least significant difference) was performed to evaluate the alfalfa production.

RESULTS AND DISCUSSION

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

Table 1. Alfalfa yield depending on the applied meliorants on Cu/Zn polluted soil

Variant	pH (H_2O)	I cut	II cut	III cut	IV cut	V cut	VI cut	VII cut
		Dry weight g / 10 plant						
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

Table 2. Copper and zinc content in alfalfa depending on the organo-mineral liming Cu/Zn polluted soil

variant	control	$Ca_{opt.}$	K_1	K_2	K_3	K_4
Cu mg/kg						
I cut	24	16	15	15	18	19
II cut	35	26	21	22	28	30
Zn mg/kg						
I cut	870	630	660	720	720	580
II cut	1340	610	470	660	640	590

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.

The soil contamination with copper and zinc added in equivalent amounts increased twice the concentration of heavy metals (600 mg/kg). It must be noticed that under conditions of complex copper/zinc pollution of the soil the strong depressive effect of zinc toxicity on plant growth was more weakly expressed, probably due to Cu/Zn antagonism. 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. 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.

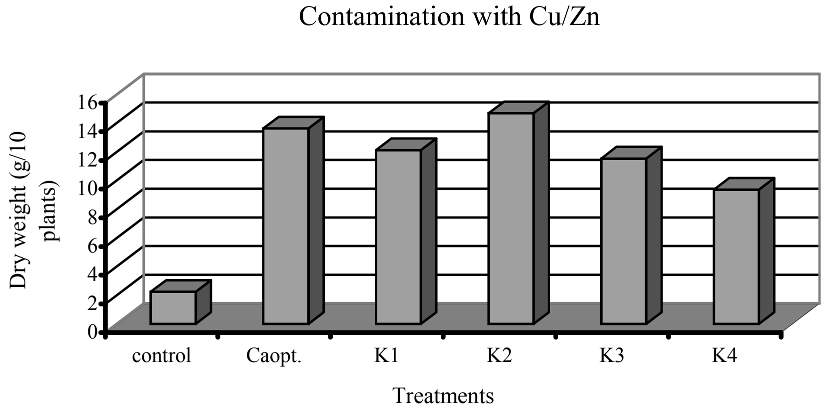

Figure 1. Total production of alfalfa (dry weight g / 10 plants - sum of all cuts) depending on the organo-mineral treatments of acid soil polluted with Cu/Zn

The orders formed by the mixed meliorants K_{1-4} applied in Cu/Zn polluted soil according to their positive effect on alfalfa yield 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: $K_2 > K_1 \approx K_3 > K_4$.

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) during the treatment K_4 caused a decrease of alfalfa yield 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 the Cu/Zn polluted soil on the total biomass production (sum of seven cuts) is presented in fig.1. The combined treatment K_2 had a maximal effect on the total alfalfa production. The higher coal powder doses (30 and 40 g/kg) 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 effectiveness on alfalfa yield 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 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 the 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, while the toxic concentrations are 20 – 100 mg/kg. The normal zinc content is 1 – 400 mg/kg and the toxic one is more than 400 mg/kg (Alloway and Ayres, 1994).

The copper content in the biomass from the I and II cuts decreased to almost normal limits (15 – 30 mg/kg) after treatment with carbonate deposit and coal powder ($Ca_{opt.}$, K_{1-4}) compared to the control (24 –35 mg/kg).

The organo-mineral treatment of the soil contaminated with Cu/Zn decreased the zinc content in alfalfa biomass from the I and II cuts (470 – 720 mg/kg) compared to the control (820 – 1340 mg/kg), 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 soil 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 liming Cu/Zn contaminated soil with carbonate deposit and anthracite coal powder applied in a ratio 1:8 provides a maximal effectiveness on alfalfa yield. 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.

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.

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EFFECT OF COMPOSTING PERIOD OF PEAT AND MANURE ON PHYSICOCHEMICAL PROPERTIES OF DYSTRIC FLUVISOL POLLUTED WITH COPPER

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Abstract

This paper presents investigation on the possibility of changing of chemical state of copper contaminant in strongly acid Alluvial-Delluvial soil (Dystric Fluvisol, FAO) by treating with peat and farmyard manure. It is aimed with application of organic acids causing part of copper cationic forms to be transferred into colloid ones. This process could be accepted as an initial stage of neutralization of exchangeable acidity, when copper toxicity would be determined with its hydroxide forms.

Changes established in physico-chemical parameters of the studied soil after treating with farmyard manure (**FM**) or peat (**P**) could be explained with the full precipitation of amphoteric elements hydroxides. Positively charged hydroxide gels interact with the negatively charged clay minerals forming stable colloid-chemical complex. Colloid binding is preferable over the adsorption interaction between ions.

As a result of positively charged hydroxide polymetal polymers passing into the intra layer spaces of clay structures, blocking of negatively charged cation exchange basal surfaces (decreasing of T_{SA} values) occurs.

It could be concluded that treating with farmyard manure is effective, because it leads to activation of colloid chemical interactions and facilitates formation of "sandwich" clay-humus - adsorption complexes.

Keywords: colloid-chemical interactions, soil adsorbent, peat, farmyard manure

Introduction

Conditions where double electrical layer of permanent and variable charges arises on soil surfaces determine to a great extent the chemical state and behavior of heavy metals in the soil. Tendency of cations to form oxygen-hydroxide co-ordination is well expressed in their ability to form complexes both with clay minerals and anions of humus acids. Unoccupied d-orbitals take part in the process of complex formation. These orbitals undergo considerable changes influenced by the symmetrical filed, which ligands create. Essentially this is a colloid chemical interaction between two types of charges, inherent in components of soil adsorbent and variable charges of hydrophobic colloid forms of heavy metals. Prevailing one or another depends on the quantitative ratio of their charges (Uehara and Gillman, 1981; Uhera, 1995). Heavy metal contaminants could undergo considerable changes in their chemical behavior: hydroxide co-precipitation, adsorption association, ionic incorporation on fresh formed gels, octahedral coordination in alumo-silicate minerals, stable complex formation with soil organic matter etc.

In strongly acid soils, where acid destruction of soil adsorbent in surface horizons is realized, the polyvalent elements occur in their cationic forms. Cation exchange bonding between adsorption positions dominates over complex forming reactions (Harter, 1977; Schnitzer, 1991; Shuman, 1975; Stevenson, 1982). Activation of colloid chemical interactions, in the media where these ionic forms are generated, provokes processes, leading to formation of structural associations with opposite charged surfaces (Raytchev and Benkova, 2004).

It could be accepted that originated colloidal charged zones would determine the possibility for interactions between soil colloids, applied amendments and heavy metals for their efficient immobilization. Their presence depends to a great extent on the conditions where hydroxide polymers are formed on the clay minerals basal surfaces.

The aim of this paper is to study the possibility of changing of chemical state of copper contaminant in strongly acid Alluvial-Delluvial soil (Dystric Fluvisol, FAO) by treating with peat and farmyard manure. It is aimed with application of organic acids part of copper cationic forms to be transferred into colloid ones. This process could be accepted as an initial stage of neutralization of exchangeable acidity, when copper toxicity would be determined with its hydroxide forms.

The dynamics of heavy metals under organic substances influence is discussied, because of the possibility of generation of the easily dissolved organo-metal complexes, which mobility increases with the neutralization of soil acidity. Preliminary experiment was conducted in order to verify this possibility.

Materials and methods

Preliminary experiment

Micro pot experiment with acid soil - Light Grey pseudo podzolic forest soil (Eutric Planosol, FAO), Dushevo village, was carried out. The physico - chemical characteristics of the investigated soil are as follows: pH (H_2O) - 4.4; organic carbon - 1 %, fulvic type of humus; CEC ($T_{8.2}$) - 18.2 cmol/kg; total acidity - 7.2 cmol/kg; exchangeable Al - 2.5 cmol/kg; degree of base saturation - 57 %. The physico - chemical properties were determined according to the method of Ganev & Arsova (1980). During the process of oxidizing thermo- destruction of humus components (Raytchev, 1992) had been determined the following parameters: the amount of C in the composition of easily oxidizable fraction **A** (C_A = 0.82 %) and the quantity of C - in hardly oxidizable fraction **B** (C_B = 0.18 %), respectively. Three levels of pollution with copper (as CuO) were studied: Cu_1 - 100 mg/kg; Cu_2 - 300 mg/kg; Cu_3 - 900 mg/kg. Micro pot experiment with barley as plant - indicator was carried out in three replications, in plastic pots (100 g soil).

The following agents (Table 1) were studied:

- organic material, contains humus substances in initial stage of humification (**FM**)*;
- organic material (**FM**), composted for 20 days with $CaCO_3$ (**FM** + Ca) - 89.7 g (**FM)** with moisture 44.3% + 25 ml distil water;
- organic material, contains humus substances in advanced stage of humification (**C**)*;
- organic material **C**, composted for 20 days with $CaCO_3$ (**C** + Ca) - 50 g **C** + 12.5 g $CaCO_3$ + 62.5 ml distil water;
- calcium tartarate (**CaT**);
- $CaCO_3$ (**Ca**);
- farmyard manure (C% - 18.6; N% - 2.3; C/N - 8.1; degree of humification - 43.3%) - (**FM)**
- ** - coal dust (C% - 7.0) (**C**).

Table 1. Yield and Copper content in plants

Treatment↓	Level of contamination→	Cu_0	Cu_1 (100 mg/kg)	Cu_2 (300 mg/kg)	Cu_3 (900 mg/kg)
Control	Yield g/pot→	0.74	0.59	0.52	0.41
	Cu in plants, ppm-biomass	9.0	17.0	18.6	22.1
	Cu in plants, ppm-roots	17.0	110.4	350.0	445.0
$CaCO_3$ (2.5g/kg) (**Ca**)	Yield g/pot→	0.86	0.78	0.7	0.58
	Cu in plants, ppm-biomass	7.2	13.1	13.6	15.7
	Cu in plants, ppm-roots	8.4	41.0	60.2	157.0
Antracite (10 g/kg) (**C**)	Yield g/pot→	0.7	0.56	0.5	0.48
	Cu in plants, ppm-biomass	8.0	16.9	19.0	21.0
	Cu in plants, ppm-roots	8.1	192.1	311	423.0
Compost:$CaCO_3$ + antracite (12.5 g/kg) (**C+Ca**)	Yield g/pot→	0.84	0.8	0.78	0.76
	Cu in plants, ppm-biomass	6.3	11.8	11.3	12.8
	Cu in plants, ppm-roots	7.2	30.0	29.5	66.6
Farmyard manure (9 g/kg) (**FM**)	Yield g/pot→	0.71	0.68	0.55	0.5
	Cu in plants, ppm-biomass	6.1	17.2	16.4	16.1
	Cu in plants, ppm-roots	8.5	163.3	190.0	379.0
Compost:$CaCO_3$ + FM[1] (11.5 g/kg) (**FM +Ca**)	Yield g/pot→	0.85	0.8	0.75	0.55
	Cu in plants, ppm-biomass	7.2	14.7	14.99	17.9
	Cu in plants, ppm-roots	8.8	127.2	205.0	376.0
Ca tartarat (2.5g/kg $CaCO_3$ + 7.6 g/kg TA[2]) (**CaT**)	Yield g/pot→	0.71	0.62	0.58	0.57
	Cu in plants, ppm-biomass	6.4	15.0	16.1	18.7
	Cu in plants, ppm-roots	9.5	59.5	112.0	350.0
Generally average		0.77	0.69	0.62	0.55
Precise index, %		1.81	3.69	4.96	5.5
GD 1 %		0.073	0.13	0.16	0.16
0,1 %		0.12	0.21	0.26	0.25

1 – Farmyard manure, 2 - Tartaric acid

The calculated rate of optimal liming is 0.25 g $CaCO_3$/100 g soil (Ganev, 1987). The studied agents and the respective composts were mixed with the investigated soil and incubated for 20 days (60% - moisture) and seeded (12 seeds per pot). The experiment were carried out with fertilization as follows: NH_4NO_3 - 0.0219 g/100g; Ca $(H_2PO_4)_2$ - 0.0344 g/100g; KH_2PO_4 - 0.0370 g/100g; $MgSO_4$ - 0.0066 g/100g

As indices of remediation efficiency both, biomass and roots weigh; and the copper content were determined.

Experimental scheme:

- Cu_0Ca_0; Cu_1Ca_0; Cu_2Ca_0; Cu_3Ca_0.
- Cu_0Ca; Cu_1Ca; Cu_2Ca; Cu_3Ca.
- Cu_0**FM**; Cu_1 **FM**; Cu_2 **FM**; Cu_3 **FM**.
- Cu_0(**FM** +Ca); Cu_1(**FM** +Ca); Cu_2(**FM** +Ca); Cu_3(**FM** +Ca).
- Cu_0**C**; Cu_1**C**; Cu_2**C**; Cu_3**C**.
- Cu_0(**C**+Ca); Cu_1(**C**+Ca); Cu_2(**C**+Ca); Cu_3(**C**+Ca).
- Cu_0**CaT**; Cu_1**CaT**; Cu_2**CaT**; Cu_3**CaT**.

The quantities of the studied amendments are presented in Table 1.

Investigation on the possibility for colloid interactions acceleration was carried out with surface horizon (0-20 cm) of loamy sand Alluvial-Delluvial soil (Dystric Fluvisol, FAO), technologic contaminated with copper (845 mg/kg). This soil is strongly acid (pH 4.0), with toxic exchangeable (mainly presented as exchangeable Al) and hydrolytic soil acidity (Table 2).

According to the classification of Orlov and Grishina's (Orlov, 1985) it is described as soil with: low humus content (1.38 %), humic-fulvic type of humus (C_h/C_f – 0.71), average content of Ca bounded humic acids, and low degree of humification.

Semi-quantitative analysis of minerals (in % of integral intensity of mineral phases) showed presence of mica (muscovite) - 55.4 %, chlorite - 25.8 %, kaolinite - 13.9 % and quartz - 4.9 %.

Farmyard manure as organic substances was applied. The main characteristics are as follows: pH = 6.50, N – 5.0 %; P_2O_5 – 2.8 %; K_2O – 3.4 %; CaO – 4.9 %; MgO – 0.7 %; SiO_2 – 3.2 %; H_2O – 8.0 %; ash – 28.0 %. It is established considerable content of low molecular organic acids (fraction 1^a – extracted with 0.1 N H_2SO_4), humic-fulvic type of humus and 90 % of humic acids are presented as "free" and R_2O_3 complexed forms.

Exchangeable forms of heavy metals were determined after extraction with 1n $CaCl_2$ according to the analytical procedure of Ganev and Arsova (1980) and AAS measured.

Table 2. Influence of composting duration of lime materials on the sorption properties of treated soil

Treatment Pot, №	period, months	pHH_2O	$T_{8.2}$	T_{SA}	T_A	$H_{8.2}$	Al exch.	Ca$^{exch.}$	Mg exch.	Cu$^{exch.}$	Zn exch.
			cmol/kg							mg/kg	
Control	1.5	4.0	22.8	15.5	7.3	11.2	3.7	9.5	2.2	555.0	12.8
1. Backgr.	1.5	4.5	22.4	15.4	7.0	10.0	2.8	10.6	2.1	203.0	17.5
	2.5	5.2	21.5	15.0	6.5	8.6	1.8	10.8	2.2	80.5	5.0
	12	5.0	20.8	14.0	6.8	8.5	1.5	10.5	2.2	125.0	12.5
2. **Ca**$^{0.5}$	1.5	6.1	21.8	16.3	5.5	5.4		14.3	2.1	6.8	6.8
	2.5	6.5	21.7	17.2	4.5	4.2		15.1	2.2	8.0	5.3
	12	6.8	21.8	19.2	2.0	2.0		17.5	2.2	12.5	5.0
3. **Ca**	1.5	7.1	21.6	19.6	2.0	1.8		17.7	2.1	6.8	4.8
	2.5	6.9	21.5	19.1	2.4	2.5		16.6	2.3	7.0	5.0
	12	7.3	22.0	21.1	1.0	0.8		19.1	2.2	7.0	3.8
4. **Ca**$^{1.5}$	1.5	7.6	22.0					19.8	2.2	8.5	5.3
	2.5	7.4	21.0					18.8	2.2	7.3	5.3
	12	7.5	22.2					19.1	2.3	5.5	3.0
5. **Ca**^{2}	1.5	7.9	21.8					19.5	2.2	11.8	6.0
	2.5	7.5	21.9					19.7	2.2	8.3	5.3
	12	7.7	22.3					20.0	2.3	6.0	4.3

Abbreviations:
$T_{8.2}$ – The sum of the negative charge on the surface of the colloids, determined by the amount of exchangeable cations at pH 8.2 – total cation exchange capacity (CEC) (Ganev and Arsova, 1980):
T_{SA} – the amount of the permanent negative charge – CEC of strongly acidic exchange complex;
T_A – the amount of the variable negative charge - CEC of weakly acidic exchange complex.
$H_{8.2}$ - total acidity

Ganev and Arsova (1980) method was used for determination of physico-chemical properties.

Scheme 1 presents both, treatments and amount of applied amendments to the studied soil in the carried out pot experiment.

Scheme 1. Amount of amendments applied to polluted with heavy metals acid soil (Zlatitsa region)

№	Treatments
Control	Initial soil – 2 kg/pot
1	background - control + 5 g granulated farmyard manure (**FM**)/kg soil
2	**Ca**$^{0.5}$ – background + 2.3 g CaO/kg soil
3	**Ca** – background + 3.4 g CaO/kg soil
4	**Ca**$^{1.5}$ - background + 5.1 g CaO/kg soil
5	**Ca**^{2} – background + 6.8 g CaO/kg soil
7	**P**$^{0.5}$ – background + 5.5 g peat (**P**)/kg soil
8	**P** – background + 11.0 g peat /kg soil
9	**P**$^{1.5}$ – background + 16.0 g peat /kg soil
10	**P**^{2} – background + 22.0 g peat /kg soil
15	**PFe**^{1} – background + [11.0 g peat + 1 g Fe]/kg soil
16	**P**^{2}**Fe**^{1} – background + [22.0 g peat +1 g Fe]/kg soil
17	**PFe**^{2} – background + [11.0 g peat + 4 g Fe]/kg soil
18	**P**^{2}**Fe**^{2} – background + [22.0 g peat + 4 g Fe]/kg soil

Results and discussions

1. Preliminary experiment

The investigation is based on the hypothesis as follows: association of heavy metals in organo - mineral compounds with the humus fraction **B** which is more stable to oxidizing thermo destruction greatly decreases the possibility of their transformation from solid to liquid phase of soil system and their uptake by plants. The phenology observations presented a significant effect in the treatment with compost (**C** + **Ca**) where the pollution with copper is over 300 mg/kg. The results obtained in the lower concentrations (100-300 mg) manifested similar effect for the two studied agents - (**Ca**) and (**FM**+**Ca**). It has been established a significant remediation effect of the studied agent (**C**+ **Ca**) in the investigated three levels of pollution (30 - 40 % copper in the biomass compare to the control). The results are presented in Figure 1.

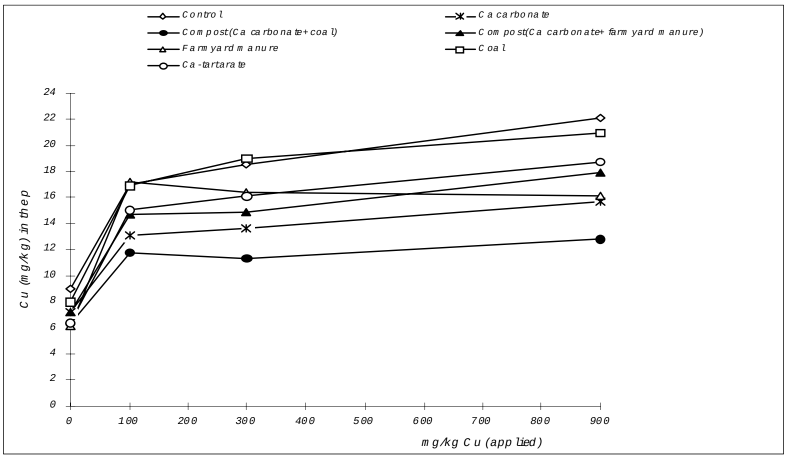

Figure 1. Copper content in the plants corresponding to the studied treatments

The similar tendency is observed for the copper content in the roots, but the decreasing there is in a higher degree and in the wider limits (73 - 92 %) (Table 1).

The studied agent $CaCO_3$ (**Ca**) is manifested efficiency following the compost (**C**+ **Ca**). The copper content (compare to control) decreases in the biomass and roots, 23 - 29 % and 63 - 83 %, respectively.

The copper uptake by plants increases in the cases of remediation with agents: farmyard manure (**FM**), compost farmyard manure + $CaCO_3$ (**FM** + **Ca**) and Ca - tartrate (**CaT**) in comparison with independently liming. Copper accumulation in roots is similar, but the quantity is much higher. This can be explained by the fact that some heavy metals (Cu, Zn) are located on the ion - exchange positions in the basal surface of clay minerals (Ganev, 1990). The other part of them presents as soluble metal hydroxides, which are able to form organo - mineral complexes with humus compounds (Evdokimova et al., 1989; Filcheva, 1976; Chuldjian, 1978; Drozd et al., 1992; Ganev et al., 1993; Jakubus et al., 1996; Takacs et al., 1996). In addition the fulvic acids take part in one of the first places of the groups which provoke dispertion: phosphate ions, fulvic acids > citrate ions, oxalate, tartarate ions > salicylate ions (Edwards et al., 1992). The fulvic complexes, which dominate in the easily oxidizable fraction A, are distinguished for their lower stability compare to the humic acids complexes. The latest ones are the main component of fraction **B** (Savrova et al., 1996).

The investigated soil is characterized with fulvic type of humus according to the classification of Orlov (Orlov, 1985). Heavy metals form mainly intra-molecular complex salts with such type of compounds. The last one leads to formation of unstable organo - mineral structures. The evidence of that opinion is the fact that copper forms easily soluble intra-molecular complex salts with alkali tartrate (Nekrasov, 1962).

2. Changes in physico-chemical parameters of Dystric Fluvisol after application of farmyard manure (FM)

It is established that total acidity ($H_{8.2}$) value is higher (11.2 cmol/kg) compared to that corresponds to weakly acidic exchangeable positions (T_A = 7.3 mequ/100g), and exchangeable bases (11.7 cmol/kg) are lower than the strongly acidic positions (T_{CA} = 15.5 cmol/kg) (Table 2). This means that weakly acidic positions on the external surfaces of clay minerals are changed to H-form. This process is affected also the strongly acidic positions, and it is partly neutralized with bases. Eliminated from the strongly acidic system Al and heavy metals' cations are included in the composition of exchangeable ions on the clay minerals basal surface and because of that $\Sigma(\text{bases} + Al^{ech.}) \approx T_{CA}$ (15.3 – 15.5).

After 1.5 months of composting applied to the control treatment farmyard manure (background) exchangeable acidity decrease with 25 % (from 3.7 cmol/kg to 2.8 cmol/kg), and hydrolytic ones - with 10 % (from 11.2 cmol/kg to 10.0 cmol/kg), respectively. It is observed that the "exchangeable" Cu decrease from 555 mg/kg to 203 mg/kg, while “exchangeable” Zn increases from 12.8 to17.5 mg/kg (Table2).

If exchangeable copper is presented as Cu^{2+} (most likely in pH 4.0), and after transformation in cmol/kg, value of 1.75 cmol/kg is calculated. This means that after discharging of its contribution to the exchangeable acidity (marked as $Al^{exch.}$), than 1.95 cmol/kg (3.7 – 1.75) are correspond to the exchangeable Al and Mn, considered as its main participants.

The results obtained show that the amount of exchangeable copper decreases to 20.3 cmol/kg and this means that 0.64 cmol/kg (20.3/31.75 = 0.64; 31.75 - equivalent weight of Cu^{2+}) is distributed on the exchangeable position. Consequently exchangeable acidity, expressed via $Al^{exch.}$, has to decrease from 3.7 cmol/kg to 2.6 cmol/kg [1.95 + 0.64]. This value is rather similar to the experimental ones (2.8 cmol/kg).

This is received under circumstances where exchangeable Al does not change chemically, but that contradict to the lower pH-values for precipitation of the discussed element. Probable explanation of the apparent anomaly is the influence of pH on the adsorbed amount of copper by both, kaolinite and illite. It is well expressed through the fact that total absorption from solution is realized in lower pH-values compared to these corresponding to precipitation as copper hydroxide in conditions of clay absences.

Furthermore high content of organic matter (farmyard manure - **FM)** additionally decreases zero point of charges (ZPC). Exothermal character of copper sorption is explained with the thin layer of this metal with an adsorbent. The result of this is its strong association compared for both alkali and alkali earth metals (Assaad and Nielsen, 1984).

After 2.5 months of composting exchangeable copper content decreases up to 0.27 cmol/kg and Al^{exch} would expect to decline from 2.6 cmol/kg to 2.2 cmol/kg [1.95 + 0.27]. But the experimental obtained value for $Al^{exch.}$ (1.8 cmol/kg) is distinguished with 0.4 cmol/kg

According to the experimental results of exchangeable copper after 12 months of composting, Al^{exch} has to read 2.34 cmol/kg [1.95 + 0.39], which is considerably different from the data received - 1.5 cmol/kg. This could be explained with the affect of exchangeable forms of Al and Mn, ratter probably after the arising of pH value from 4.5 for the initial point up to 5.2 - 5.0 in the end point of the experiment.

The evidence for similar possibility is decreasing of T_{SA} from 15.5 cmol/kg to 14.0 cmol/kg with negligible change of T_A (7.3 cmol/kg - 6.8 cmol/kg). This could be explained by blocking mainly of strongly acidic positions with positively charged colloid forms of heavy metals. Possible explanation of this behaviour is formation of polymer hydroxide ions, adsorbed of specific positions (Farrah and Pickering, 1976).

3. Changes in physico-chemical parameters of Dystric Fluvisol after application of peat (P)

Copper behaviour is similar in the treatments, where 4 doses of peat (**P**) in combination with farmyard manure are applied (**FM**) (Table.3).

It is observed the same pH-value in the treatment after 1.5 months of composting of applied farmyard manure as in the control variant. Exchangeable acidity ($Al^{exch.}$) decreases from 3.7 cmol/kg to 2.4 cmol/kg, and hydrolitic - from

11.2 cmol/kg to 10.0 cmol/kg. The results obtained show that "exchangeable" copper content decreases from от 555 mg/kg to 145 mg/kg, while "exchangeable" Zn increases from 12.8 mg/kg to 18.8.

Table 3. Influence of peat composting duration on the sorption properties of treated soil

Treatment Pot, №	Period, months	pHH_2O	$T_{8.2}$	T_{SA}	T_A	$H_{8.2}$	Al exch.	Ca exch	Mg exch.	Cu exch.	Zn exch
			cmol/kg							mg/kg	
Control	1.5	4.0	22.8	15.5	7.3	11.2	3.7	9.5	2.2	555.0	12.8
1.Background	1.5	4.5	22.4	15.4	7.0	10.0	2.8	10.6	2.1	203.0	17.5
	2.5	5.2	21.5	15.0	6.5	8.6	1.8	10.8	2.2	80.5	5.0
	12	5.0	20.8	14.0	6.8	8.5	1.5	10.5	2.2	125.0	12.5
7. $\mathbf{P}^{0.5}$	1.5	4.6	22.5	14.8	7.7	10.0	2.4	10.6	2.1	145.0	18.8
	2.5	5.4	20.9	14.9	6.0	8.1	1.8	10.8	2.1	140.0	7.5
	12	5.0	19.9	14.2	5.7	7.4	1.6	10.5	2.1	230.0	14.5
8. **P**	1.5	4.6	22.6	15.0	7.6	10.1	2.4	10.6	2.1	108.0	15.3
	2.5	5.4	21.5	15.4	6.1	8.1	1.8	11.1	2.3	91.5	8.0
	12	5.0	20.9	15.4	5.5	7.5	1.5	11.5	2.2	180.0	15.8
9. $\mathbf{P}^{1.5}$	1.5	4.8	22.3	15.3	7.0	9.6	2.4	10.8	2.2	83.5	14.8
	2.5	5.5	22.1	15.8	6.3	7.6	1.0	12.4	2.3	50.0	8.0
	12	5.7	21.6	17.1	4.5	5.2	0.6	14.2	2.3	90.0	10.0
10. $\mathbf{P}^2$	1.5	5.2	22.4	16.9	5.5	6.8	1.4	13.5	2.2	60.3	16.8
	2.5	6.0	21.5	15.8	5.7	6.0		13.4	2.4	46.3	8.2
	12	6.1	21.5	17.5	4.0	3.8		15.0	2.3	64.3	9.0

Abbreviations:
T8.2 – The sum of the negative charge on the surface of the colloids, determined by the amount of exchangeable cations at pH 8.2 – total cation exchange capacity (CEC) (Ganev and Arsova, 1980):
TSA – the amount of the permanent negative charge – CEC of strongly acidic exchange complex;
TA – the amount of the variable negative charge - CEC of weakly acidic exchange complex.
H8.2 - total acidity

As it is reported above, after discharging of its contribution to the exchangeable acidity (marked as $Al^{exch.}$), corresponding to exchangeable Al and Mn remain 1.95 cmol/kg (3.7 – 1.75).

After combination of farmyard manure with low dose peat (treatment $P^{0.5}$), exchangeable copper content decreases to 14.5 mg/100g, that means 0.46 cmol/kg (14.5/31.75 = 0.46; 31.75 - equivalent of Cu^{2+}) occupy exchangeable position. Therefore, exchangeable acidity, expressed as Al^{exch} must lower from 3.7 cmol/kg to 2.41 cmol/kg [1.95 + 0.46]. This calculated value is equal to the experimental result - 2.4 cmol/kg. After 2.5 months of composting quantity of exchangeable copper decreases to 0.44 cmol/kg and Al^{exch} has to change from 2.41 cmol/kg to 2.39 cmol/kg [1.95 + 0.44]. But, the experimental result for Al^{exch} is distinguished with 0.6 cmol/kg. In accordance with experimental results for "exchangeable" copper after 12 months of composting, $Al^{exch.}$ has to arise up to 2.67 cmol/kg [1.95 + 0.72], which is considerably differ from the obtained value - 1.6 cmol/kg. It is established that after combined application of farmyard manure and high dose peat (treatment (**P**), the exchangeable copper content decreases to 10.8 cmol/kg (0.34 cmol/kg occupied exchangeable positions). Consequently, exchangeable acidity has to decrease to 2.29 cmol/kg (1.95+0.34), and the experimental result is - 2.4 cmol/kg. After 2.5 months of composting of this mixture, exchangeable acidity value is 1.23 and the experimental ones - 1.8.The results obtained show significant differences in the treatments with high level of peat and long term of composting, due to the neutralizing ability of this material.

It is observed considerable decreases of T_A values with extending of composting period. This could be explained with the size of Cu^{2+} ion, which allow octahedral coordination via hydroxyl or oxygen ions. On the crystal surface of clay mineral, coordination of both, three $O^{2-}$from the mineral and three - hydrate water of Cu^{+2} is possible. Take H^+ off the molecule' hydrate water or involve via clay surface, or release in the solution, allow strongly packaged oxygen atoms around Cu^{+2} and leads to adsorption of $CuOH^+$. In case Cu^{2+}get into octahedral hole of the edge of clay minerals' particles, one OH^- could be enough in generation of octahedral and to facilitate incorporation in the intra layer spaces under form of "clatrat" compound (Figure 2). Since 4 is a normal coordination number for copper, the real structure around adsorbed CuOH+ ion could be deformed tetrahedral instead octahedral. This mechanism explains affect on the weakly acid position of clay minerals.

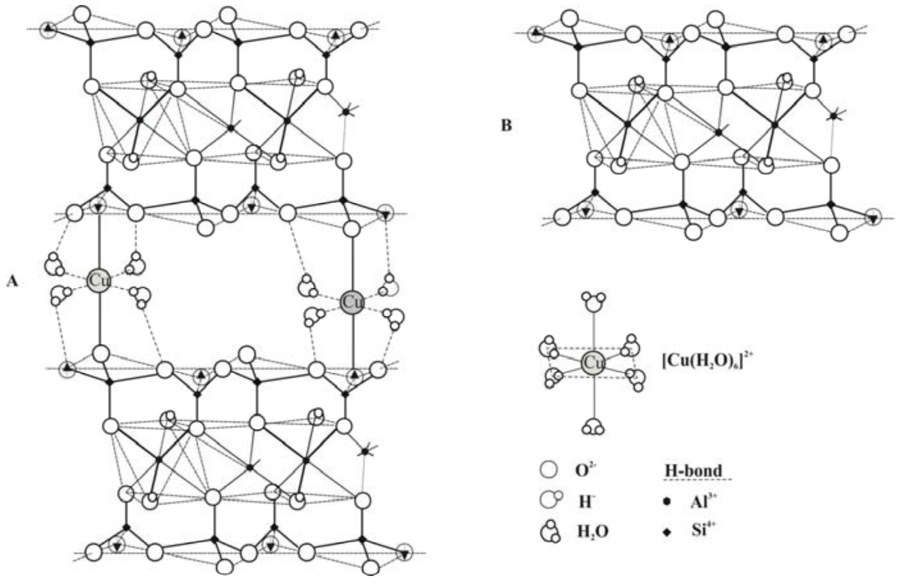

Figure 2. Including of copper hydroxide forms as "clatrate" compounds of interlayer area (A) of clay minerals - montmorilonite type (B)

Data obtained show increasing of total carbon in the treatment with high dose of peat alone (**P**^{2}) after 45 days of composting. Type of humus changes from humic-fulvic to humic in all studied treatments compared to the control. Humic acids are characterized with low degree of condensation and aromatization. Negligible variation is observed in the treatment of middle dose peat (**P**$^{1.5}$). There humic acids are presented as "free" and bonded with mobile forms of R_2O_3. This determines treatment (**P**$^{1.5}$) as unfavourable in respect to these indexes. Extending the composting period - up to 12 months leads to increasing of organic carbon content. The type of humus in the variants is fulvic-humic that is a result of fulvic character of this material. The optimal in the respect to humus state are variants with the lowest content of peat (**P**$^{0.5}$) (Table 4).

Table 4. Influence of composting duration of peat + iron hydroxide on the sorption properties of treated soil

Treat. Pot, №	Mont.	PH H_2O	$T_{8.2}$	T_{SA}	T_A	$H_{8.2}$	$Al^{exch.}$	Ca^{exch}	$Mg^{exch.}$	$Cu^{exch.}$	$Zn^{exch.}$
			cmol/kg							mg/kg	
1.Backgr.	1.5	4.5	22.4	15.4	7.0	10.0	2.8	10.6	2.1	203.0	17.5
	2.5	5.2	21.5	15.0	6.5	8.6	1.8	10.8	2.2	80.5	5.0
	12	5.0	20.8	14.0	6.8	8.5	1.5	10.5	2.2	125.0	12.5
8. **P**	1.5	4.6	22.6	15.0	7.6	10.1	2.4	10.6	2.1	108.0	15.3
	2.5	5.4	21.5	15.4	6.1	8.1	1.8	11.1	2.3	91.5	8.0
	12	5.0	20.9	15.4	5.5	7.5	1.5	11.5	2.2	180.0	15.8
10. **P**^{2}	1.5	5.2	22.4	16.9	5.5	6.8	1.4	13.5	2.2	60.3	16.8
	2.5	6.0	21.5	15.8	5.7	6.0		13.4	2.4	46.3	8.2
	12	6.1	21.5	17.5	4.0	3.8		15.0	2.3	64.3	9.0
15. PFe^1	1.5	5.0	22.1	15.1	7.0	9.4	2.5	10.2	2.2	77.5	13.8
	2.5	5.3	22.1	15.1	7.0	8.6	1.4	11.6	2.2	68.8	6.5
	12	4.9	21.4	14.5	6.9	8.5	1.4	10.8	2.2	123.0	11.0
17. PFe^2	1.5	5.2	22.0	14.9	7.1	9.2	2.0	10.5	2.1	120.0	16.8
	2.5	5.4	22.0	14.9	7.1	8.1	1.4	12.2	2.1	140.0	7.5
	12	4.7	21.6	15.0	6.6	8.9	2.4	10.4	2.3	233.0	15.5
16. **P**^{2}Fe^1	1.5	5.4	21.8	15.0	6.8	9.0	2.0	11.5	2.3	32.0	10.5
	2.5	5.5	21.8	15.0	6.8	8.0	1.5	12.5	2.3	89.0	10.0
	12	5.0	21.3	14.8	6.5	8.0	1.4	11.2	2.2	180.0	13.8
18. **P**^{2}Fe^2	1.5	5.6	22.4	15.4	7.0	9.0	1.5	11.9	2.2	48.3	15.3
	2.5	5.6	22.4	15.4	7.0	7.8	1.4	13.0	2.2	160.0	10.7
	12	5.2	21.4	14.9	6.5	8.0	1.6	11.3	2.1	180.0	12.5

Abbreviations:

$T_{8.2}$ – The sum of the negative charge on the surface of the colloids, determined by the amount of exchangeable cations at pH 8.2 – total cation exchange capacity (CEC) (Ganev and Arsova, 1980):

T_{SA} – the amount of the permanent negative charge – CEC of strongly acidic exchange complex;

T_A – the amount of the variable negative charge - CEC of weakly acidic exchange complex.

$H_{8.2}$ - total acidity

4. Changes in physico-chemical parameters of Dystric Fluvisol after application of peat (P) and iron

There are no any changes found in the studied physico-chemical parameters after combined application of farmyard manure and Fe in the treatment **PFe**^{1} compared to variant **P** after 1.5 months of composting. But exchangeable copper content decreases from 0.34 cmol/kg to 0.24 cmol/kg (Table 4). This could correspond to 2.19 cmol/kg (1.95+0.24=2.19), and measured value is 2.5 cmol/kg, respectively. 2.5 months the respective values are as follows: 2.17 towards measured – 1.4. In the end of the experiment exchangeable copper content increases to края на 0.39 cmol/kg. This corresponds to 2.34 cmol/kg, but measured value is1.4 cmol/kg. It is observed increasing of exchangeable copper almost twice with the increasing of Fe at each peat dose. Exchangeable acidity does not change in these cases. This is read to pH range 5.4-5.5. It is possible close to this values considerable part of Al ions to be excluded from exchangeable positions. The last one could be explained with the pH interval (5.2-7.8) where Al $(OH)_3$ exist in the solution. It is different in respect to copper hydroxide - the final pH- value is 7.6. After 12 months of composting of this mixture soil pH sharply decreases to 4.7. Exchangeable copper logically increases as exchangeable acidity enhanced with 1 cmol/kg (PFe^2-12 months). Measured value (2.4 cmol/kg) reaches the calculated ones (2.68 cmol/kg).

Conclusions

Changes established in the studied soil physico-chemical parameters after treating with farmyard manure (**FM**) or peat (**P**) could be explained with the fully hydroxide precipitation of amphoteric elements. Positively charged hydroxide gels interact with the negatively charged clay minerals forming stable colloid-chemical complex. Colloid binding is preferable to the adsorption interaction between ions.

As a result of positively charged hydroxide polymetal polymers in the intra layer spaces of clay structures and blocking negatively charged basal charges for cation exchange passing there (decreasing of T_{SA} values– Table3).

It could be concluded that treating with farmyard manure is effective, because it leads to activation of colloid chemical interactions and facilitates formation of "sandwich" clay-humus - adsorption complexes.

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IMPACT OF DIFFERENT AMELIORANTS ON AGGREGATE STABILITY OF ACID SOIL POLLUTED WITH HEAVY METALS

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Abstract

Based on samples from acid Dystric Fluvisol polluted with heavy metals, greenhouse experiments were carried out to test the effect of different organic and mineral melioration materials on soil aggregation. Peat, coal and manure have been considered as organic components and lime, iron hydroxide, and zeolite – as mineral ones to prepare different amelioration mixtures containing one, two or three components. There were 49 combinations tested in these experiments along with a reference – the untreated soil. The influence of the treatments on the soil aggregate stability has been studied after 12 months of composting and harvesting the crops, while the aggregate stability was assessed by indices based on aggregate-size distribution.

It was found that amendment containing lime-peat composites have the most favorable effect on soil aggregation. This may be caused by that the electric charge of the humus substances is activated in these composites enabling formation of sandwich charged colloids between the negatively charged colloids of the clay minerals and the humus substances as well as positively charged ions or hydroxide forms of the polyvalent elements.

The organo-mineral mixtures combining high dose of lime, both peat doses and low dose of iron hydroxide affect most favorably the soil aggregate stability. The reason of this is that the saturation of the soil adsorbent with bivalent and trivalent cations, being a prerequisite for development of stable aggregates, is obtained at these optimal treatments by amendments of high dose of Ca and low dose of Fe combined with peat.

It is concluded that treatment of polluted soils with organo-mineral composites not only decreases the toxic impact of the heavy metals but enables

formation of stable adsorption organo-clay formations and also improves significantly the soil macro-structure.

Introduction

Some ameliorants (lime materials, zeolites or iron enriched supplements) applied for detoxication of polluted with heavy metals soils serve not only as immobilization materials but their application improves also the soil structure (Hooda and Alloway, 1996; Czupyrna et al., 1989; Gworek, 1992; Edwards et al., 1999; Warren and Alloway, 2003; Lombi et al., 2004; Chlopecka and Adriano, 1997). Availability of sufficient amount of colloid matter is considered as a necessary condition for development of stable soil structure considering the role of the colloids as an active component for binding the soil particles and macro-structure formation. Introduction o mineral and organic amendments in colloid state or their activation result to formation of organo-mineral complexes, possessing high stability and sorption properties.

Natural zeolites have been used for a long time in Japan to improve the soil quality (Dwyer and Dyer, 1984; Zamzow et al., 1990). Results of the studies of Rousseva (1998) show that coal ashes used as liming agent can also improve the soil properties and to raise the production. It has been assumed that some organic substances (sewage sludge, manure composites, peat), which are balanced with respect to pH, can react like $CaCO_3$ at sedimentation of Al or Fe or to form humic complexes with them (Iyamuremye et al., 1996; Sappin-Didier et al.,1997; Hue, 1992; Hue et al., 1999; Warren and Fonteno, 1993; O'Hallorans et al., 1997; Wong et al., 1998; Whalen et al, 2000; Cooper and Warman, 1997; Eghball, 1999). Among the possible mechanisms for constituting compounds between the humus substances and the layered aluminous silicons, the main role belongs to the polyvalence cations and their positively charged oxide-hydroxide forms, being able to develop bonds with the anions of the humus acids as well as with the negatively charged groups of the surface of the aluminous silicones transforming them to stable compounds.

The aim of this work is to study the influence of different organo-mineral composites on the aggregate stability of acid soil polluted with heavy metals.

Materials and methods

Soil

The studied soil was sampled from heavy metal polluted (Cu – 845.0 mg/kg; Zn – 87.0 mg/kg) region, close to the Umicor Copper smelter AD, Pirdop. This soil, classified as Dystric Fluvisol (FAO, 1997), is strongly acid (pH 4.0), with toxic exchangeable (exch. Al = 7.3 mequ/100g) and hydrolytic ($H_{8.2}$=11.2 mequ/100 g) soil acidity.

The studied soil has a relatively high gravel content – 23,1 % particles with sizes from 2 to 10 mm, clay content of 13 % and 19.4 % particles finer than 0.01 mm (Tab. 1). The soil texture is loamy sand. The soil structure is very fine and unstable, proved by the very low value (0,12) of the index of aggregate stability (Tab. 2). The semi-quantitative analysis shows the following distribution of clay minerals in the studied soil: mica (muscovite) 55.4 % > chlorite (25.8 %) > kaolinite (13.9 %) > > quartz (4.9 %)

Table 1. Soil particle-size distribution, in % of air-dry initial soil sample from acid Dystric Luvisol polluted with heavy metals

Gravel > 2 mm	Fine earth < 2 mm				
	2-0,2 mm	0,2-0,02 mm	0,02-0,002 mm	< 0,002 mm	< 0, 01 mm
23,1	41,7	31,1	14,2	13,0	19,4

Table 2. Aggregate-size distributions and mean-weight diameters and of dry (D_d) and water-stable (D_w) structural aggregates of initial soil sample from acid Dystric Luvisol polluted with heavy metals. (K)

Dry structural aggregates, mm				Water-stable aggregates, mm				K= D_w/D_d
>0,25	>1	>5	D_d	>0,25	>1	>5	D_w	
19,7	19,4	13,2	1,26	3,2	0,6	0,0	0,15	0,12

Mineral ameliorants

- Lime material: CaO – neutralizing ability of 3500 mequ per 100g material (nBM = 100/3500 ≈ 0.03 g / 1 mequ);
- Iron-containing adsorbent: Iron hydroxide – waste product, containing 55% $Fe(OH)_3$ or 25 g Fe/100 g
- Aluminous silicon adsorbent: Zeolite – clinoptilolite from the area of the town of Kardzhali.

Organic ameliorants

- Coal powder – anthracite waste from mine "Svoge";
- Peat – from deposit in the area of Venets village containing humus substances with lower degree of condensation compared to that of the anthracite coal. Humic acids dominate in the composition of the organic matter, which determines the humic type of the humus (Orlov, 1985).
- Organic fertilizer – manure containing: N – 5.0%; P_2O_5 – 2.8%; K_2O – 3.4%; CaO – 4.9%; MgO – 0.7%; SiO_2 – 3.2%; H_2O – 8.0%; ash – 28.0%. Its introduction aims at activating the colloid state of a part of the heavy metal cations and enabling their interaction with the components of the applied ameliorative composites. The degree of condensation of the humic acids in the manure is much lower than that in the peat.

Green house experiments have been carried out to test 49 combinations of the studied ameliorants along with a reference – the untreated soil (Tab. 3). The experiments have been accomplished in pots of 2 kg soil at field capacity in three replicates. The influence of the tested ameliorants on the soil aggregate stability has been studied after 12 months of composting and harvesting the crop grown.

Soil texture was determined after dispersing the soil samples by sodium pyrophosphate and measuring the particle-size distribution by pipette (Robinson, 1922). Aggregate-size distribution was determined following the method of Savinov as modified by Vershinin and Revut (Revut and Rode, 1969). It is accomplished in two stages: Dry sieving to establish the size distribution of the macro-aggregates at air-dry state among the size fractions: >5, 5-3, 3-1, 1-0,25 and 0,25mm; Wet sieving to establish the size distribution of the water-stable aggregates. Mean-weight diameters (D) of the dry and the water-stable aggregates have been calculated on the basis of the obtained aggregate-size distribution using the formula:

$$D = \frac{(7{,}5a_1 + 4a_2 + 2a_3 + 0{,}625a_4 + 0{,}125a_5)}{100}, \qquad (1)$$

where a_1, a_2, a_3, a_4 and a_5 are the percentage contents of aggregate fractions with equivalent diameters respectively >5, 5-3, 3-1, 1-0,25 and < 0,25 mm.

The soil aggregate stability was then assessed by the absolute (K_n) and the relative (K_r) indices of aggregate stability:

$$K_n = \frac{D_w}{D_d},\ K_r = \frac{K_n - K_r}{K_k}, \qquad (2)$$

where D_d and D_w are respectively the values of the mean-weight diameters of dry and water-stable structural aggregates and n = 1, 2, 3, … , 49 is the number of the treatment; K_r is the index of aggregate stability of the untreated soil (reference).

Table 3. Designations and descriptions of the tested treatments for amelioration of acid Dystric Fluvisol polluted with heavy metals

No	Name	Description
1	R	Reference: Untreated soil – 2 kg / pot
2	$Ca^{0.5}$	Soil + 2.3 g CaO / kg soil
3	Ca	Soil + 3.4 g CaO / kg soil
4	$Ca^{1.5}$	Soil + 5.1 g CaO / kg soil
5	Ca^{2}	Soil + 6.8 g CaO / kg soil
6	M	Soil + 5 g granulated manure / kg soil
7	$P^{0.5}$	Soil + 5.5 g peat / kg soil
8	P	Soil + 11.0 g peat / kg soil
9	$P^{1.5}$	Soil + 16.0 g peat / kg soil
10	P^{2}	Soil + 22.0 g peat / kg soil
11	CaFe	Soil + [3.4 g CaO + 1 g Fe] / kg soil
12	$Ca^{2}Fe$	Soil + [6.8 g CaO + 1 g Fe] / kg soil
13	$CaFe^{2}$	Soil + [3.4 g CaO + 4 g Fe] / kg soil
14	$Ca^{2}Fe^{2}$	Soil + [6.8 g CaO + 4 g Fe] / kg soil
15	PFe	Soil + [11.0 g peat + 1 g Fe] / kg soil
16	$P^{2}Fe$	Soil + [22.0 g peat +1 g Fe] / kg soil
17	PFe^{2}	Soil + [11.0 g peat + 4 g Fe] / kg soil
18	$P^{2}Fe^{2}$	Soil + [22.0 g peat + 4 g Fe] / kg soil
19	CaP	Soil + [3.4 g CaO + 11.0 g peat] / kg soil
20	$Ca^{2}P$	Soil + [6.8 g CaO + 11.0 g peat] / kg soil
21	CaP^{2}	Soil + [3.4 g CaO + 22.0 g peat] / kg soil
22	$Ca^{2}P^{2}$	Soil + [6.8 g CaO + 22.0 g peat] / kg soil
23	CaC	Soil + [3.4 g CaO + 11.0 g coal] / kg soil
24	$Ca^{2}C$	Soil + [6.8 g CaO + 11.0 g coal] / kg soil
25	CaC^{2}	Soil + [3.4 g CaO + 22.0 g coal] / kg soil
26	$Ca^{2}C^{2}$	Soil + [6.8 g CaO + 22.0 g coal] / kg soil
27	CaPFe	Soil + [3.4 g CaO + 11.0 g peat + 1 g Fe] / kg soil
28	$CaP^{2}Fe$	Soil + [3.4 g CaO + 22.0 g peat + 1 g Fe] / kg soil
29	$Ca^{2}PFe$	Soil + [6.8 g CaO + 11.0 g peat + 1 g Fe] / kg soil
30	$Ca^{2}P^{2}Fe$	Soil + [6.8 g CaO + 22.0 g peat + 1 g Fe] / kg soil
31	$CaPFe^{2}$	Soil + [3.4 g CaO + 11.0 g peat + 4 g Fe] / kg soil

Table 3 cd.

No	Name	Description
32	CaP^2Fe^2	Soil + [3.4 g CaO + 22.0 g peat + 4 g Fe] / kg soil
33	Ca^2PFe^2	Soil + [6.8 g CaO + 11.0 g peat + 4 g Fe] / kg soil
34	$Ca^2P^2Fe^2$	Soil + [6.8 g CaO + 22.0 g peat + 4 g Fe] / kg soil
35	CaCFe	Soil + [3.4 g CaO + 11.0 g coal + 1 g Fe] / kg soil
36	CaC^2Fe	Soil + [3.4 g CaO + 22.0 g coal + 1 g Fe] / kg soil
37	Ca^2CFe	Soil + [6.8 g CaO + 11.0 g coal+ 1 g Fe] / kg soil
38	Ca^2C^2Fe	Soil + [6.8 g CaO + 22.0 g coal + 1 g Fe] / kg soil
39	$CaCFe^2$	Soil + [3.4 g CaO + 11.0 g coal + 4 g Fe] / kg soil
40	CaC^2Fe^2	Soil + [3.4 g CaO + 22.0 g coal + 4 g Fe] / kg soil
41	Ca^2CFe^2	Soil + [6.8 g CaO + 11.0 g coal + 4 g Fe] / kg soil
42	$Ca^2C^2Fe^2$	Soil + [6.8 g CaO + 22.0 g coal + 4 g Fe] / kg soil
43	CaPZ	Soil + [3.4 g CaO + 11.0 g peat + 5 g zeolite] / kg soil
44	CaP^2Z	Soil + [3.4 g CaO + 22.0 g peat + 5 g zeolite] / kg soil
45	Ca^2PZ	Soil + [6.8 g CaO + 11.0 g peat + 5 g zeolite] / kg soil
46	Ca^2P^2Z	Soil + [6.8 g CaO + 22.0 g peat + 5 g zeolite] / kg soil
47	CaCZ	Soil + [3.4 g CaO + 11.0 g coal + 5 g zeolite] / kg soil
48	CaC^2Z	Soil + [3.4 g CaO + 22.0 g coal + 5 g zeolite] / kg soil
49	Ca^2CZ	Soil + [6.8 g CaO + 11.0 g coal + 5 g zeolite] / kg soil
50	Ca^2C^2Z	Soil + [6.8 g CaO + 22.0 g coal + 5 g zeolite] / kg soil

Results and discussion

The results from the aggregate stability analyses show (Tab. 4) that the mean-weight diameters and the size distributions of the air dry and the water-stable structural aggregates vary significantly depending on the applied treatment. The values of the mean-weight diameter of dry aggregates ranges from 0,28 (Ca^2PFe) to 1,26 mm (reference). The mean-weight diameters of the water-stable aggregates vary in relatively narrow limits from 0,15 (R and Ca) to 0,29 (Ca^2P^2Fe). High value (0,26) is obtained also without amendment of iron hydroxide but with amounts of the lime material and the peat Ca^2P^2 like these at treatment No 30 (Ca^2P^2Fe). Treatments with a composite of lime, coal powder and zeolite result in larger mean-weight aggregate diameters compared to the reference. For the rest of the treatments, the values of the mean-weight diameters of the dry aggregates vary in the mentioned limits and it is hard to define any regularity for a specific organo-mineral composite.

Table 4. Grain-size distributions and mean-weight diameters of dry (D_d) and water-stable (D_w) structural aggregates depending on the tested treatments for amelioration of acid Dystric Fluvisol polluted with heavy metals

Treatment		Dry structural aggregates				Water-stable aggregates				K = D_w/D_d
		Grain-size [mm] distribution, %			D_d, mm	Grain-size [mm] distribution, %			D_w, mm	
No	Name	>0,25	>1	>5		>0,2	>1	>5		
1	R	19,7	19,4	13,2	1,26	3,2	0,6	0,0	0,15	0,12
2	$Ca^{0.5}$	15,1	15,0	11,3	1,07	3,5	2,1	0,1	0,18	0,17
3	Ca	11,9	9,8	5,7	0,67	1,4	0,9	0,0	0,15	0,22
4	$Ca^{1.5}$	11,7	10,0	4,3	0,59	1,8	1,4	0,0	0,16	0,27
5	Ca^2	13,5	9,8	3,9	0,58	3,4	1,8	0,0	0,17	0,29
6	M	11,2	6,7	0,3	0,31	2,3	1,4	0,1	0,16	0,51
7	$P^{0.5}$	14,8	13,6	6,0	0,77	3,9	2,2	0,1	0,18	0,24
8	P	18,3	16,5	9,6	1,02	8,5	1,6	0,2	0,20	0,20
9	$P^{1.5}$	16,6	13,4	11,0	1,02	5,0	1,3	0,1	0,18	0,17
10	P^2	13,7	8,6	5,1	0,61	5,1	0,8	0,1	0,17	0,29
11	CaFe	19,6	14,3	6,2	0,79	7,8	0,5	0,1	0,18	0,23
12	Ca^2Fe	16,4	10,1	2,3	0,51	7,8	1,8	0,4	0,21	0,42
13	$CaFe^2$	18,5	13,0	5,3	0,75	6,2	1,5	0,2	0,19	0,26
14	Ca^2Fe^2	19,9	14,0	5,4	0,77	5,9	1,2	0,1	0,18	0,23
15	PFe	12,3	7,2	1,1	0,37	4,4	1,5	0,1	0,18	0,48
16	P^2Fe	17,1	10,6	3,0	0,56	5,2	2,3	0,2	0,20	0,35
17	PFe^2	11,4	6,7	0,7	0,35	2,2	1,2	0,1	0,16	0,45
18	P^2Fe^2	14,2	9,8	3,6	0,55	2,6	1,1	0,2	0,17	0,30
19	CaP	13,7	6,8	0,2	0,33	3,4	2,5	0,1	0,18	0,56
20	Ca^2P	14,0	11,3	2,3	0,54	1,9	1,1	0,3	0,17	0,32
21	CaP^2	14,1	10,7	3,6	0,57	4,2	2,3	0,2	0,19	0,33
22	Ca^2P^2	15,1	9,6	2,3	0,48	9,4	5,2	0,2	0,26	0,54
23	CaC	17,5	13,6	10,5	0,99	8,3	1,8	0,2	0,21	0,21
24	Ca^2C	17,4	12,6	7,1	0,82	8,2	1,4	0,1	0,19	0,23
25	CaC^2	18,9	15,4	10,1	1,01	11,2	3,7	0,0	0,23	0,23
26	Ca^2C^2	15,1	9,3	4,0	0,57	6,7	1,1	0,1	0,18	0,31
27	CaPFe	19,1	12,7	3,6	0,63	8,7	1,4	0,0	0,19	0,30
28	CaP^2Fe	19,7	13,8	5,6	0,77	7,2	1,2	0,2	0,19	0,25
29	Ca^2PFe	12,4	5,2	1,6	0,28	6,4	1,3	0,1	0,19	0,67
30	Ca^2P^2Fe	22,1	15,7	4,2	0,75	16,5	5,6	0,1	0,29	0,39
31	$CaPFe^2$	22,7	16,8	10,7	1,07	9,2	0,7	0,1	0,19	0,18
32	CaP^2Fe^2	23,9	16,3	5,2	0,80	10,3	1,3	0,1	0,20	0,25
33	Ca^2PFe^2	19,4	11,1	1,9	0,51	6,6	0,2	0,0	0,16	0,32
34	$Ca^2P^2Fe^2$	14,1	6,4	3,1	0,38	8,8	1,9	0,2	0,21	0,55
35	CaCFe	21,9	15,6	6,3	0,85	4,9	1,3	0,0	0,17	0,20

Table 4. cd.

Treatment		Dry structural aggregates				Water-stable aggregates				K = D_w/D_d
		Grain-size [mm] distribution, %			D_d, mm	Grain-size [mm] distribution, %			D_w, mm	
No	Name	>0,25	>1	>5		>0,2	>1	>5		
36	CaC^{2}Fe	18,6	12,5	0,9	0,50	7,4	1,0	0,2	0,19	0,37
37	Ca^{2}CFe	19,8	13,7	3,5	0,67	4,3	0,8	0,0	0,16	0,24
38	Ca^{2}C^{2}Fe	17,9	11,8	3,2	0,60	4,4	1,1	0,0	0,16	0,28
39	CaCFe^2	16,6	10,8	1,4	0,49	7,3	2,3	0,0	0,20	0,40
40	CaC^{2}Fe^2	19,2	13,7	6,6	0,81	7,9	0,9	0,1	0,19	0,23
41	Ca^{2}CFe^2	22,2	15,8	7,5	0,92	8,4	2,4	0,1	0,21	0,23
42	Ca^{2}C^{2}Fe^2	17,6	10,8	1,5	0,50	4,5	0,6	0,1	0,16	0,33
43	CaPZ	17,2	8,8	1,1	0,41	7,5	2,0	0,1	0,20	0,48
44	CaP^{2}Z	14,5	7,4	0,0	0,33	7,9	2,8	0,1	0,21	0,65
45	Ca^{2}PZ	13,5	6,6	2,4	0,42	4,0	1,4	0,0	0,17	0,40
46	Ca^{2}P^{2}Z	15,9	7,9	0,6	0,37	2,9	1,2	0,0	0,16	0,43
47	CaCZ	17,7	12,3	6,6	0,75	11,4	3,3	0,0	0,23	0,31
48	CaC^{2}Z	22,7	16,7	9,0	1,03	11,5	3,3	0,2	0,24	0,23
49	Ca^{2}CZ	21,8	15,8	11,1	1,09	8,9	0,6	0,0	0,18	0,16
50	Ca^{2}C^{2}Z	21,3	16,6	7,2	0,89	8,3	2,8	0,2	0,22	0,24

The values of the index of aggregate stability K_n vary from 0,12 (reference) to 0,67 (Ca^{2}PFe) (Tab.3). There is a gradual increase of the values of K_n from 0.17 to 0.29 at the treatments with increasing amounts of lime material (Ca) as a single ameliorant (treatments Numbers 1-5). Application of peat (P) as a single ameliorant (treatments with numbers 7-10) results also in higher values of K_n compared to the reference, and the best aggregate stability ($K_n = 0.29$) is obtained again at the highest peat rate (P^2).

The influence on the soil aggregate stability of combined amendments of iron hydroxide (Fe and Fe^2) and lime material (Ca and Ca^2), which have been studied by treatments Numbers 11-14, does not differ significantly from the treatments with amendment of lime as a single ameliorant excluding the treatment Ca^{2}Fe where $K_n = 0,42$. Amendments of the organo-mineral composites of lime and peat (treatments Numbers 19-22) result in much higher values of the index of aggregate stability compared to these already discussed: 0,54 at Ca^{2}T^2 and 0,56 at CaT treatment. The values of the index of aggregate stability range from 0,18 to 0,67 at the treatments with numbers 27-34 with amendments of three-component composites of peat (P and P^2), lime (Ca and Ca^2) and iron hydroxide (Fe and Fe_2). The best effect on the aggregate stability is obtained at Ca^{2}PFe (0,67), followed by $Ca^2T^2Fe^2$ (0.55). Amendments of two-component composites of iron hydroxide and peat (treatments with numbers 15-18) result in a relatively well developed aggregate stability since the values of K_n range from 0,25 to 0,48.

Compared to the reference, there is a positive effect on the aggregate stability of treatments including coal powder combined with lime (treatments with numbers 23-26) but this effect is more poorly expressed compared to the treatments already discussed. Addition of iron hydroxide (Fe and Fe^2) to the organo-mineral composite of coal powder (C and C^2) and lime (Ca and Ca^2) studied at the treatments with numbers 35-42 do not result in any significant improvement of the aggregate stability.

The effects on the aggregate stability of addition of zeolite to the organo-mineral composites are better expressed for the composite with peat and lime (treatments Numbers 43-46) compared to the composite with coal and lime (treatments with numbers 47-50). The values of K_n at these three-component composites range from 0.43 to 0.65 with the highest value at CaP^2Z.

The individual effects of the studied ameliorants on the soil aggregate stability are illustrated on Fig. 1. The combined effects on the aggregate stability of peat and lime in both two-components and three-component composites as well as addition of zeolite to the both types of studied organo-mineral composites are proved to be statistically significant.

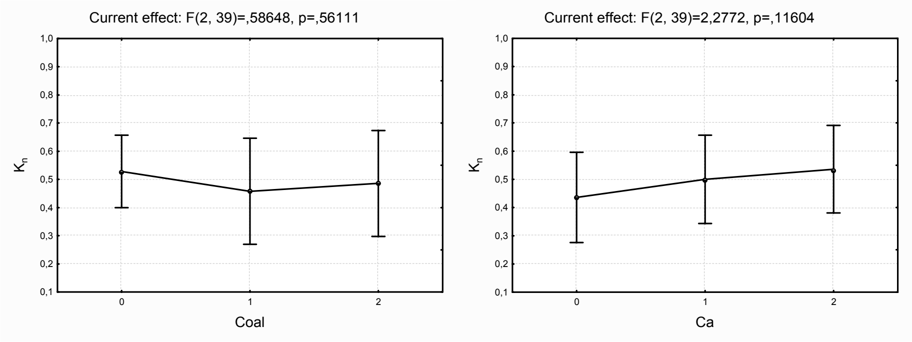

Figure 1. Individual effects of the tested organic and mineral ameliorants on the index K_n of aggregate stability of acid Dystric Fluvisol. The current variate values for the F-distribution and the respective computed p-values are presented for each effect. Vertical bars denote 0.95 confidence intervals.

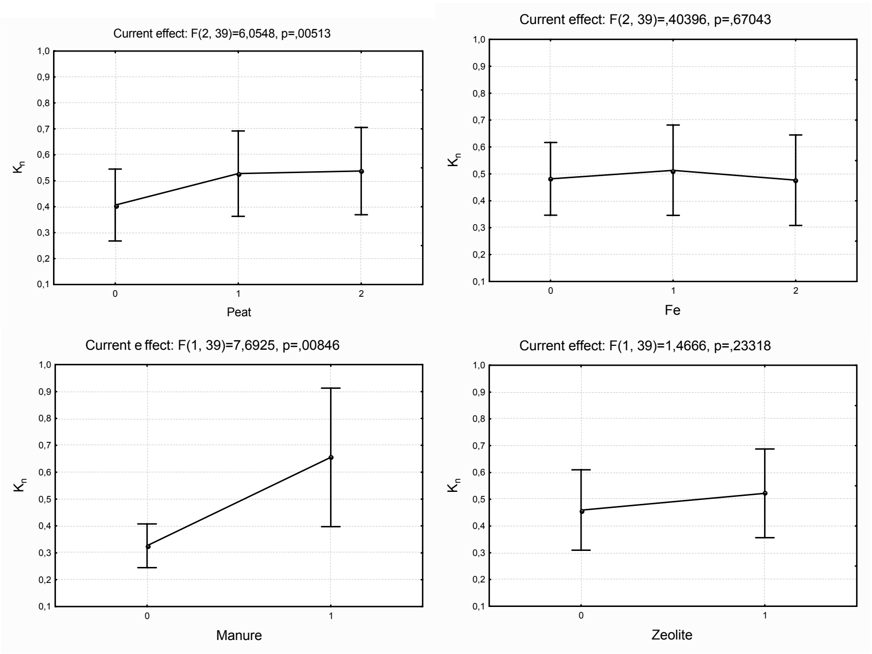

Figure 1. c.d. Individual effects of the tested organic and mineral ameliorants on the index K_n of aggregate stability of acid Dystric Fluvisol. The current variate values for the F-distribution and the respective computed p-values are presented for each effect. Vertical bars denote 0.95 confidence intervals.

The values of the relative index of aggregate stability demonstrate well (Fig. 2) the effects of the different treatments on soil structure. These data show that the composites with numbers 29 (Ca^2PFe), 44 (CaP^2Z), 19 (CaP), 34 (Ca^2T^2Fe) and 6 (M) are outlined for their better aggregative effect followed by the treatments with numbers 22 (Ca^2T^2) and 5 (Ca^2). The organo-mineral composites with high dose of lime, both peat dozes and low dose of iron hydroxide cause the most favorable impact on soil aggregate stability. These findings are reasonable since the saturation of the soil adsorbent with bivalent and trivalent cations, being a prerequisite for development of stable aggregates, is obtained at the optimal treatments by amendments of high dose of Ca and low dose of Fe combined with peat.

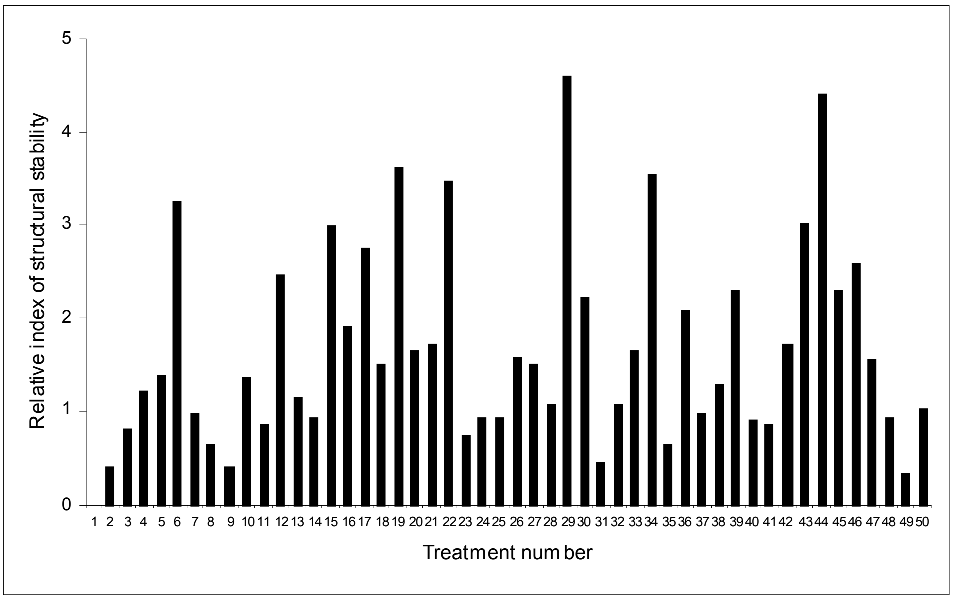

Figure 2. Values of the relative index of aggregate stability of acid Dystric Fluvisol depending on its treatment with different amelioration composites with one, two or three organic and/or mineral components.

Used as an addition, $Fe(OH)_3$ is a subject of specific modifications of the properties of its colloidal mycelium. Principally, the colloid systems of the hydrophobic colloids, such as the iron hydroxide, are thermodynamically unstable. They have highly developed boundary surface and a large surplus of free surface energy. This determines their susceptibility to random self-reduction of this between-phase energy through aggregation (coagulation).

Formation of stable soil structural aggregates is not possible without contribution of organic substances. Amendment of humus substances into the soil increases the concentration of the acid groups, enables binding of the polyvalent ions and formation of humus organo-mineral structures. The peat used in the experiments is most likely to have better binding ability compared to the coal powder since the former contains humus substances of lower degree of condensation compared to the latest. The treatments, which have the most favorable effect on aggregation, are these with lime-peat composites where the electric charge of the humus substances is activated and enables formation of sandwich charged colloids between the negatively charged colloids of the clay minerals and the humus substances as well as positively charged ions or hydroxide forms of the polyvalent elements.

Conclusions

The results from the green house experiments carried out to test the effect on soil aggregation of different organic and mineral materials for meliorating acid Dystric Fluvisol polluted with heavy metals have shown that amendments containing lime-peat composites have the most favorable effect on soil aggregation. These findings are accounted on the understanding that the electric charge of the humus substances is activated in these composites enabling formation of sandwich charged colloids between the negatively charged colloids of the clay minerals and the humus substances as well as positively charged ions or hydroxide forms of the polyvalent elements.

The organo-mineral composites combining high dose of lime, both peat dozes and low dose of iron hydroxide impacts most favorably the soil aggregate stability. The reason of this result can be found in the understanding that the saturation of the soil adsorbent with bivalent and trivalent cations, being a prerequisite for development of stable aggregates, is obtained at these optimal treatments by amendments of high dose of Ca and low dose of Fe combined with peat.

It is concluded that treatment of polluted soils with organo-mineral composites not only decreases the toxic impact of the heavy metals but enabling formation of stable adsorption organo-clay formations it also improves significantly the soil macro-structure.

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IMPACT OF DIFFERENT AMELIORANTS ON HUMUS STATE IN ACID SOIL POLLUTED WITH HEAVY METALS

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Abstract

Greenhouse experiments with heavy metal polluted soil (Dystric Fluvisol, FAO) meliorated with application of organo-mineral compounds were carried out. In the present work peat and coal were taken as melioration components in the following composites: lime material and peat; lime material, peat and ferrous hydroxide; peat and ferrous hydroxide; lime compounds, peat and zeolite; and peat and lime material separately in increasing doses; lime material and coal; lime material, coal and ferrous hydroxide; coal and ferrous hydroxide; lime compounds, peat and zeolite. After 45 days and next after 12 months of composting (soil and tested amendments) the effect of organo-mineral composites on humus state was retraced. After 45 days of composting, more favourable effect on humus state was established for a composite: lime compounds, peat and ferrous hydroxide. After 12 months of composting found was: increase of total carbon; humic acids; and decrease of fulvic acids - precondition for favourable soil physical and physical – chemical properties. Observed increasing of “free” and R_2O_3 complexed humic acids, as a result of peat transformation is most likely due to lower amount of lime material in the respective treatments.

Introduction

In the progress of investigations on the possibilities for increasing the lime effeciency on heavy metal contaminated acid soils by decreasing their availability for biological systems is the enrichment of soil with organic matter. This is based on the stable chelate interaction among metal and humus substances considerable part of which may form stable associates with hydroxides of amphoteric elements and these are eliminated from cation exchange. Both, carboxyl and phenol hydroxyl groups are the basic factor in formation of stable organo mineral bonds. Application of suitable organo mineral mixture to acid polluted soils leads to both hydroxide precipitation of heavy metal contaminants and bonding of their ionic forms in chelate compounds, and including them in organo-mineral adsorptive structures (Raytchev, 1996; Raytchev et al., 1999). Organic acids with carboxyl and phenolic groups have an important role in buffering soil acidity and pH increasing of acid soils. It has been suggested that organic amendments such as plant residues, animal manure and peat may react similar to $CaCO_3$ by precipitating Al and Fe or may form humic complexes with Al and Fe (Iyamuremye et al., 1996).

Peat has been used for improvement of humus state and to immobilize heavy metals in contaminated soils (Teocharov, 1995; Chaney et al., 1993). In addition to the possibility for immobilization of heavy metals, peat (as a component of organo-mineral amendments), on the base of its high biological activity may lead to increasing of total agro-chemical background.

The aim of this paper was to retrace the influence of peat and coal as components of different amendments on the humus state of heavy metals contaminated acid soil.

Material and methods

The studied soil was sampled from heavy metal polluted (Cu – 845.0 mg/kg; Zn – 87.0 mg/kg) region, close to the Umicor Copper smelter AD, Pirdop. This soil, classified as Dystric Fluvisol (FAO, 1997), is strongly acid (pH 4.0), with toxic exchangeable (exch. Al=7.3 mequ/100g) and hydrolytic ($H_{8.2}$ = 11.2 mequ/100 g) soil acidity. According to the classification of Orlov and Grishina's (Orlov, 1985) it is described as soil with low humus content (1.38%), humic-fulvic type of humus (C_h/C_f – 0.71), average content of Ca bounded humic acids, and low degree of humification.

In the present work peat and coal are considered as components in the following composites: lime material and peat; lime material, peat and ferrous hydroxide; peat and ferrous hydroxide; lime compounds, peat and zeolite; and peat and lime material alone in increasing doses lime material and coal; lime material, coal and ferrous hydroxide; coal and ferrous hydroxide; lime compounds, peat and zeolite. The experiments were conducted in three replications with 2-kg soil per pot and moisture 60% of the field capacity. After 45 days and 12 months of composting (soil and testing amendments) the effect of organo-mineral composites on humus state were retraced. To evaluate the changes in humus state of the studied treatments the following parameters: total C, humic to fulvic acids ratio (C_h/C_f) and Ca complexed humic acid were considered.

The peat was collected from the deposit of v.Venets region (pH 7.6; 13.1% C; 1.79% Fe; 45.5 mg/kg Cu; 70.5 mg/kg Zn; 13.5 mg/kg Pb; 14.0 mg/kg Co; 32.0 mg/kg Ni; and 42.5 mg/kg Cr).

The main characteristic of soil organic matter composition is predomination of humic acids over the fulvic acids. This determinates humic type of humus (Orlov, 1985). Part of humic acids (45%) are presented as free and R_2O_3 complexed forms. The amount of two levels of lime material (Ca –3.4g CaO/kg and Ca^2- 6.8g CaO/ kg soil) in organo-mineral mixtures is calculated on the base of formula, which is a modified equation for determining of liming dose for acid soils (Ganev, 1987). Applied amounts of peat (P and P^2) and coal powder (C^1 and C^2) are calculated according to the optimal rate for organo-mineral mixture (Raytchev et al., 2002; Benkova, 2005). The peat and coal powder (anthracite, Svoge coal mine, Sofia region) contain humic acids equivalent to 85 % of total carbon. Two doses of ferrous hydroxide (Fe^1 – 1 g/kg; Fe^2 – 4 g/kg) are examined in a combination with lime material and organic component.

The content and composition of soil organic mater were determined after 45 days and 12 months of composting according to the Turin's modified method (acid-dichromate digestion, 120ºC, 45 min in a thermostat, catalyst Ag_2SO_4) and Kononova-Belchicova's method (Kononova, 1963), respectively. Analytical course was based on the different solubility of humic substances in acid medium. Soil organic matter was fractionated in 2 groups –humic and fulvic acids (extracted with mixed solution of 0.1 M $Na_4P_2O_7$ and 0.1N NaOH). Humic acids were separated in the following groups: a. Ca-complexed and b. "free" and R_2O_3 complexes (extracted with 0.1N NaOH). The most dynamic, low molecular fraction of organic matter, so called "aggressive" fulvic acids was extracted with 0.1 N H_2SO_4.

Results and discussion

After 45 days of composting with increasing doses CaO is proved the favourable effect on soil organic matter composition. The humus type is changed from humic-fulvic to humic ones (from 0.71 for control reach to values >1.5). It is observed decreasing (№ 2 - $Ca^{0.5}$) or absence (№№ 3 - Ca, 4 - $Ca^{1.5}$ and 5 - Ca^2)

of ‘free” and R_2O_3 complexed humic acids after 12 months of composting (Table 1 and 2).

Table 1. Content and composition of organic matter, after 45 days of composting.Designated: a - % of soil sample, b - % of total C, c - % of humic acids total content (h), f – fulvic acids; P - peat; C - coal powder; Fe - Fe hydroxide

№	Treatments and amounts of amendments, g/kg soil	Total C, %	Organic C (%) Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			C_h/C_f	C - in humic acids fractions, (%)	
			total	h	f		“free” R_2O_3, complexed	Ca comlexed
1	Reference	0.78	0.24[a] 30.77[b]	0.10 12.82	0.14 17.95	0.71	0.05 50.0[c]	0.05 50.0
2	$Ca^{0.5}$ 2.3g	0.82	0.28 34.15	0.22 26.83	0.06 7.32	3.67	0.0	100.0
3	Ca 3.4g	0.74	0.30 40.54	0.18 24.32	0.12 16.22	1.50	0.0	100.0
4	$Ca^{1.5}$ 5.1g	0.76	0.28 36.84	0.20 26.32	0.08 10.52	2.50	0.0	100.0
5	Ca^2 6.8g	0.74	0.35 47.30	0.20 27.03	0.15 20.27	1.33	0.0	100.0
11	$CaFe^1$ 3.4g+1g	0.69	0.33 47.83	0.22 31.88	0.11 15.94	2.00	0.0	100.0
12	Ca^2Fe^1 6.8g+1g	0.59	0.32 54.24	0.17 28.81	0.15 25.42	1.34	0.0	100.0
13	$CaFe^2$ 3.4g+4g	0.61	0.32 52.46	0.16 26.23	0.16 26.23	1.00	0.0	100.0
14	Ca^2Fe^2 6.8g+4g	0.61	0.33 54.09	0.16 26.23	0.17 27.86	0.94	0.0	100.0
23	CaC 3.4g+11g	0.74	0.32 43.24	0.16 21.62	0.16 21.62	1.00	0.0	100.0
24	Ca^2C 6.8g+11g	0.70	0.39 55.71	0.21 30.00	0.18 25.71	1.67	0.0	100.0
25	CaC^2 3.4g+22g	0.81	0.33 40.74	0.19 23.46	0.14 17.28	1.36	0.0	100.0
26	Ca^2C^2 6.8g+22g							

Table 1. cd.

№	Treatments and amounts of amendments, g/kg soil	Total C, %	Organic C (%)			C_h/C_f	C - in humic acids fractions, (%)	
35	$CaCFe^1$ 3.4g+11g+1g	0.72	0.22 30.56	0.17 23.61	0.05 6.95	3.40	0.00	100.0
36	CaC^2Fe^1 3.4g+22g+1g	0.89	0.27 30.34	0.22 24.72	0.05 56.18	4.40	0.00	100.0
37	Ca^2CFe^1 6.8g+11g+1g	0.83	0.28 33.73	0.20 24.09	0.08 9.64	2.50	0.0	100.0
38	$Ca^2C^2Fe^1$ 6.8g+22g+1g	1.74	0.30 29.70	0.15 14.85	1.15 14.85	1.00	0.0	100.0
39	$CaCFe^2$ 3.4g+11g+4g	1.57	0.30 32.97	0.20 21.98	0.10 10.99	2.00	0.0	100.0
40	CaC^2Fe^2 3.4g+22g+4g	0.97	0.23 23.71	0.17 17.53	0.06 6.18	2.83	0.12 70.59	0.05 29.41
41	Ca^2CFe^2 6.8g+11g+4g	0.80	0.23 28.75	0.17 21.25	0.06 7.50	2.83	0.00	100.0
42	$Ca^2C^2Fe^2$ 6.8g+11g+4g	0.87	0.26 29.88	0.19 21.84	0.07 8.04	2.71	0.00	100.0
47	CaBZ 3.4g+11g+5g	0.78	0.24 30.77	0.24 30.77	0.00	-	0.00	100.0
48	CaC^2Z 3.4g+22g+5g	0.93	0.25 26.88	0.18 19.35	0.07 7.53	2.57	0.00	100.0
49	Ca^2CZ 6.8g+11g+5g	0.86	0.26 30.23	0.06 6.98	0.20 23.25	0.30	0.00	100.0
50	Ca^2C^2Z 6.8g+22g+5g	0.96	0.27 28.13	0.09 9.38	0.18 18.75	0.50	0.00	100.0

Total C content does not change after treating with organo-mineral mixture of coal powder and CaO. It is observed a favourable effect on both, humus type (treatment № 24 - Ca^2C) and the maturity of humic acids (application of CaO alone) (Table 1 and 2).

It is proved the positive effect on the composition of soil organic matter after 45 days of composting with organo mineral mixture: $Fe(OH)_3$, CaO and coal powder (№№ 35 - 42). The type of humus is changed from humic- fulvic to humic ones in the studied treatments with exception of treatment № 38 - $Ca^2B^2Fe^1$. Humic acids are bonded with Ca (exception for treatment № 40-CaB^2Fe^2) in stable complexes. Almost 70% of humic acids in this treatment (№ 40) were “free" or R_2O_3 complexed. The most favourable in respect to humus status № 36-CaB^2Fe^1 is outlined. There are no significant differences in the treatments with high doses. After 12 months of composting of this mixture, in respect to humus status, the most favourable treatments are as follows: № 42 - $Ca^2C^2Fe^2$ and № 37 - $Ca^2C^1Fe^1$ (Table 1 and 2).

Table 2. Content and composition of organic matter, after 12 months of composting Designated: a - % of soil sample, b - % of total C, c - % of humic acids total content (h), f – fulvic acids; P - peat; C - coal powder; Fe - Fe hydroxide

№	Treatments and amounts of amendments, g/kg soil	Total C, %	Organic C (%)			C_h/C_f	C - in humic acids fractions, (%)	
			Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH				"free" and R_2O_3 complexed	Ca comlexed
			total	H	F			
1	Reference	0.95	0.35a 36.84^b	0.17 17.89	0.18 18.95	0.94	100.00	0.00
2	$Ca^{0.5}$ 2.3g	1.00	0.35 35.00	0.21 21.00	0.14 14.00	1.50	0.16 76.19^c	0.05 23.81
3	Ca 3.4g	0.95	0.35 36.84	0.14 14.73	0.21 22.11	0.67	0.00	100.00
4	$Ca^{1.5}$ 5.1g	0.95	0.31 32.63	0.14 14.74	0.17 17.89	0.82	0.00	100.0
5	Ca^2 6.8g	0.86	0.31 36.05	0.16 18.60	0.15 17.44	1.00	0.00	100.0
11	$CaFe^1$ 3.4g+1g	1.15	0.45 39.13	0.17 14.78	0.28 24.35	0.61	0.00	100.0
12	Ca^2Fe^1 6.8g+1g	1.06	0.34 32.08	0.28 26.42	0.06 5.66	4.67	0.00	100.0
13	$CaFe^2$ 3.4g+4g	1.19	0.49 41.18	0.28 23.53	0.21 17.65	1.34	0.00	100.00
14	Ca^2Fe^2 6.8g+4g	1.24	0.51 41.13	0.26 20.97	0.25 20.16	1.04	0.00	100.0
23	CaC 3.4g+11g	1.05	0.28 26.67	0.16 15.24	0.12 11.43	1.33	0.00	100.0
24	Ca^2C 6.8g+11g	1.16	0.33 28.45	0.20 17.24	0.13 11.21	1.54	0.00	100.0
25	CaC^2 3.4g+22g	0.95	0.30 32.58	0.20 21.05	0.10 10.53	2.00	0.00	100.0
26	Ca^2C^2	1.10	0.45 40.91	0.27 24.54	0.18 16.36	1.50	0.13 48.15	0.14 51.85

Table 2. cd.

№	Treatments and amounts of amendments, g/kg soil	Total C, %	Organic C (%)			C_h/C_f	C - in humic acids fractions, (%)	
35	$CaCFe^1$ 3.4g+11g+1g	1.34	0.50 37.31	0.34 25.37	0.16 11.94	2.12	0.20 58.82	0.14 41.18
36	CaC^2Fe^1 3.4g+22g+1g	1.26	0.36 28.57	0.25 19.84	0.11 8.73	2.27	0.19 76.00	0.06 24.00
37	Ca^2CFe^1 6.8g+11g+1g	1.19	0.36 30.25	0.25 21.01	0.11 9.24	2.27	0.00	100.00
38	$Ca^2C^2Fe^1$ 6.8g+22g+1g	1.11	0.41 36.94	0.25 22.52	0.16 14.41	1.56	0.20 80.00	0.05 20.00
39	$CaCFe^2$ 3.4g+11g+4g	1.53	0.29 18.95	0.10 6.54	0.19 12.41	0.53	0.00	100.00
40	CaC^2Fe^2 3.4g+22g+4g	1.36	0.51 37.50	0.23 16.91	0.28 20.59	0.82	0.00	100.00
41	Ca^2CFe^2 6.8g+11g+4g	1.23	0.28 22.76	0.20 16.26	0.08 6.50	2.50	0.12 60.00	0.08 40.00
42	Ca^2C2Fe^2 6.8g+11g+4g	1.37	0.27 19.71	0.27 19.71	0.00	-	0.00	100.00
47	CaCZ 3.4g+11g+5g	1.12	0.28 25.00	0.17 15.18	0.11 9.82	1.54	0.00	100.00
48	CaC^2Z 3.4g+22g+5g	1.26	0.37 29.36	0.22 17.46	0.15 11.90	1.47	0.00	100.00
49	Ca^2CZ 6.8g+11g+5g	1.32	0.37 28.03	0.25 18.94	0.12 9.09	2.08	0.15 60.00	0.10 40.00
50	Ca^2C^2Z 6.8g+22g+5g	1.23	0.42 34.15	0.34 27.64	0.08 6.51	4.25	0.00	100.00

It is established both, stabilizing the soil organic matter - humic acids are 100 % bonded with Ca, and a tendency of slightly increasing of total carbon in the treatments with organo-mineral composites - zeolite (Z), CaO (Ca) and coal powder (C). Unfavourable effect is observed in the treatments with high dose of Ca, mainly expressed in the type of humus, changed from humic-fulvic to fulvic ones (Table 1).

The established positive effect of peat on the humus state of studied soil allows us to describe in more details those treatments where it is a component of organo-mineral composites.

After 45 days of peat composting to initial soil it is observed increasing of total C only in treatment, treated with the highest dose (P^2). In all other cases the humus type is changed from humic-fulvic to humic in comparison to the background and humic acids are with very low degree of condensation and aromatization. This change is the most insignificantly in the treatment with a middle dose of peat ($P^{1.5}$). There, humic acids are presented of "free"and bonded with mobile forms of R_2O_3, that it determinates as the most unfavourable regard to these indexes. In all studied treatments humic acids are with very low degree of condensation (Table 3). Extension the period of peat composting (12 months) leads to increasing the organic C content. The type of humus in the treatments is fulvic-humic, that is as a result of fulvic character of this material. The optimal in the respect to humus state are treatments with the lowest peat ($P^{0.5}$) content (Table 4).

Table 3. Content and composition of organic matter, after 45 days of composting. Designated: a - % of soil sample, b - % of total C, c - % of humic acids total content (h), f – fulvic acids; P - peat; C - coal powder; Fe - Fe hydroxide

№	Treatments and amounts of amendments, g/kg soil	C_{Tot}, %	Organic C (%) Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			C_h/C_f	C - in humic acids fractions, (%)	
			total	H	F		"free" and R_2O_3 complexed	Ca comlexed
7	$P^{0,5}$ 5.5g	0.78	0.28[a] 35.90[b]	0.16 20.51	0.12 15.38	1.33	0.13 81.25[c]	0.03 18.75
8	P 11g	0.74	0.32 43.24	0.24 32.43	0.08 10.81	3.00	0.15 62.50	0.09 37.50
9	$P^{1,5}$ 16g	0.88	0.28 31.82	0.15 17.04	013 14.77	1.15	100.0	0.00
10	P^2 22g	1.10	0.30 27.27	0.24 21.82	0.06 5.45	4.00	0.10 41.67	0.14 58.33
15	PFe^1 11g+1g	1.48	0.51 34.46	0.23 15.54	0.28 18.92	0.82	0.17 73.91	0.06 26.09
16	P^2Fe^1 22g+1g	1.81	0.68 37.57	0.38 20.99	0.30 16.57	1.27	0.22 57.89	0.16 42.11
17	PFe^2 11g+4g	1.46	0.63 43.15	0.26 17.81	0.37 25.34	0.70	100.0	0.00
18	P^2Fe^2 22g+4g	1.56	0.64 41.03	0.23 14.74	0.41 26.28	0.56	100.0	0.00

Table 3. cd.

№	Treatments and amounts of amendments, g/kg soil	C_{Tot}, %	Organic C (%)			C_h/C_f	C - in humic acids fractions, (%)	
19	CaP 3.4g+11g	0.68	0.36 52.94	0.19 27.94	0.17 25.00	1.12	0.00	100.0
20	Ca^2P 6.8g+11g	0.68	0.43 63.23	0.24 35.29	0.19 27.94	1.26	0.00	100.0
21	CaP^2 3.4g+22g	0.81	0.39 48.15	0.17 20.99	0.22 27.16	0.77	100.0	0.00
22	Ca^2P^2 6.8g+22g	0.88	0.44 50.00	0.27 30.68	0.17 19.32	1.59	0.00	100.0
27	$CaPFe^1$ 3.4g+11g+1g	0.74	0.27 36.49	0.22 29.73	0.05 6.76	4.40	0.00	100.0
28	CaP^2Fe^1 3.4g+22g+1g	0.90	0.36 40.00	0.26 28.89	0.10 11.11	2.60	0.17 65.38	0.09 34.62
29	Ca^2PFe^1 6.8g+11g+1g	0.67	0.31 46.27	0.24 35.82	0.07 10.45	3.43	0.00	100.0
30	$Ca^2P^2Fe^1$ 6.8g+22g+1g	0.95	0.39 41.05	0.33 34.74	0.06 6.31	5.50	0.00	100.0
31	$CaPFe^2$ 3.4g+11g+4g	0.72	0.25 34.72	0.17 23.61	0.08 11.11	2.13	0.00	100.0
32	CaP^2Fe^2 3.4g+22g+4g	0.88	0.32 36.36	0.21 23.86	0.11 12.50	1.92	0.00	100.0
33	Ca^2PFe^2 6.8g+11g+4g	0.72	0.25 34.72	0.21 29.17	0.04 5.56	5.25	0.00	100.0
34	$Ca^2P^2Fe^2$ 6.8g+22g+4g	0.89	0.34 38.20	0.30 33.71	0.04 4.49	7.50	0.00	100.0
43	CaPZ 3.4g+11g+5g	0.85	0.33 38.82	0.25 29.41	0.08 9.41	3.12	0.21 84.00	0.04 16.00
44	CaP^2Z 3.4g+22g+5g	0.94	0.39 41.49	0.26 27.66	0.13 13.83	2.00	0.10 38.46	0.16 61.54
45	Ca^2PZ 6.8g+11g+5g	0.78	0.32 41.02	0.20 25.64	0.12 15.38	1.67	0.00	100.0
46	Ca^2P^2Z 6.8g+22g+5g	0.99	0.36 36.36	0.23 23.23	0.13 13.13	1.77	0.00	100.0

Table 4. Content and composition of organic matter, after 12 months composting. Designated: a - % of soil sample, b - % of total C, c - % of humic acids total content (h), f – fulvic acids; P - peat; C - coal powder; Fe - Fe hydroxide

№	Treatments and amounts of amendments, g/kg soil	$C_{Tot.}$ %	Organic C, (%) Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			C_h/C_f	C- in humic acids fractions, (%)	
			total	H	F		“free” and R_2O_3 complexed	Ca comlexed
7	$P^{0,5}$ 5.5g	1.14	0.47[a] 41.23[b]	0.28 24.56	0.19 16.67	1.47	0.14 50.00[c]	0.14 50.0
8	P 11g	1.26	0.45 35.71	0.26 20.63	0.19 15.07	1.37	0.22 84.62	0.04 15.38
9	$P^{1,5}$ 16g	1.01	0.38 37.62	0.20 19.80	0.18 17.82	1.11	0.17 85.00	0.03 15.0
10	P^2 22g	1.24	0.44 35.48	0.24 19.35	0.20 16.13	1.20	0.17 70.83	0.07 29.17
15	PFe^1 11g+1g	1.28	0.35 27.34	0.26 20.31	0.09 7.03	2.89	0.13 50.00	0.13 50.0
16	P^2Fe^1 22g+1g	1.41	0.56 39.72	0.27 19.15	0.29 20.57	0.93	100.00	0.0
17	PFe^2 11g+4g	1.16	0.45 38.79	0.24 20.69	0.21 18.10	1.14	100.00	0.00
18	P^2Fe^2 22g+4g	1.41	0.56 39.72	0.29 20.57	0.27 19.15	1.07	0.20 68.97	0.09 31.03
19	CaP 3.4g+11g	0.93	0.32 34.41	0.22 23.66	0.10 10.75	2.20	0.00	100.0
20	Ca^2P 6.8g+11g	1.05	0.38 36.19	0.20 19.05	0.18 17.14	1.11	0.00	100.0
21	CaP^2 3.4g+22g	1.31	0.46 35.11	0.26 19.84	0.20 15.27	1.30	0.16 61.54	0.10 38.46
22	Ca^2P^2 6.8g+22g	1.12	0.41 36.61	0.26 23.21	0.15 13.39	1.73	0.00	100.0
27	$CaPFe^1$ 3.4g+11g+1g	1.22	0.53 43.44	0.31 25.41	0.22 18.03	1.42	0.20 64.52	0.11 35.48
28	CaP^2Fe^1 3.4g+22g+1g	1.47	0.42 28.57	0.24 16.33	0.18 12.24	1.33	0.22 91.67	0.02 8.33
29	Ca^2PFe^1 6.8g+11g+1g	1.24	0.29 23.39	0.29 23.39	0.00	-	0.00	100.0
30	$Ca^2P^2Fe^1$ 6.8g+22g+1g	1.57	0.59 37.58	0.24 15.29	0.35 22.29	0.69	0.17 70.83	0.07 29.17

Table 4. cd.

№	Treatments and amounts of amendments, g/kg soil	$C_{Tot.}$ %	Organic C, (%)			C_h/C_f	C- in humic acids fractions, (%)	
31	$CaPFe^2$ 3.4g+11g+4g	1.60	0.58 36.25	0.27 16.87	0.31 19.38	0.87	0.17 62.96	0.10 37.04
32	CaP^2Fe^2 3.4g+22g+4g	1.45	0.61 42.07	0.38 26.21	0.23 15.86	1.65	0.00	100.0
33	Ca^2PFe^2 6.8g+11g+4g	1.39	0.40 28.78	0.25 17.99	0.15 10.79	1.67	0.10 40.00	0.15 60.00
34	$Ca^2P^2Fe^2$ 6.8g+22g+4g	1.53	0.42 27.45	0.34 22.22	0.08 5.23	4.25	0.00	100.0
43	CaPZ 3.4g+11g+5g	1.28	0.38 29.69	0.20 15.62	0.18 14.06	1.11	0.17 85.00	0.03 15.0
44	CaP^2Z 3.4g+22g+5g	1.23	0.46 37.40	0.27 21.95	0.19 15.45	1.42	0.00	100.0
45	Ca^2PZ 6.8g+11g+5g	1.00	0.33 33.00	0.17 17.00	0.16 16.00	1.06	0.00	100.0
46	Ca^2P^2Z 6.8g+22g+5g	1.38	0.40 28.98	0.40 28.98	0.00	-	0.22 55.00	0.18 45.0

It is observed that soil treated with organo-mineral mixture of peat and CaO does not lead to changes in total C content after 45 days of composting.

The type of humus is changed from humic-fulvic to humic in all studied treatments except treatment № 21 (CaP^2), as in this case is observed presence of “free” and R_2O_3 bounded humic acids. Lime material, as component of the organo-mineral composite, positively influences maturity of humic acids (lower values of the ratio E_4/E_6). In the other studied treatments humic acids are bounded to Ca and Mg ions which is a precondition for favourable soil physical properties (Table 3). After 12 mounts composting in treatment № 21 (CaP^2) is observed increasing of organic C content. The type of humus is fulvic- humic or humic (in treatment № 19 - CaP). In all studied treatments, except for № 21 CaP^2, humic acids are 100 % bonded with Ca and Mg ions (Table 4).

The result of soil treating with organo-mineral mixture containing 25% Fe/100g waste material and peat, after 45 days composting is manifested as considerable increasing of total carbon that is approximately twice higher in comparison to the treatments where peat alone is applied to soil. The favourable effect on soil organic matter is observed in treatment with the lowest amounts of ferrous and peat (Fe^1P^1), that is the best in respect to the degree of humic acids condensation. In the higher doses (Fe^2P^2) - influence is negative. Humic acids are represented as “free” and bounded to the mobile R_2O_3 forms in the treatments with higher dose ferrous. As a result of increasing the absolute values (from 0.05 to 0.26) is enhancing of their mobility (Table 3). The most favourable treatment in respect to humus state is those one with the low dose Ca - № 27, while for treatments with the high dose - № 33, respectively.

After 45 days of organo-mineral composting the combined treatment with $Fe(OH)_3$, CaO and peat (№ 27 - 34) has the most expressive effect on the humus type that in all treatments is turned from humic- fulvic to humic. Humic acids are 100 % bounded in Ca complexes in all treatments (45 days of composting), except treatment № 28 (CaP^2Fe^1). In respect to the humus state the best treatments with low and high dose are № 27($CaPFe^1$) and № 34 ($Ca^2P^2Fe^2$), respectively (Table 3). After 12 mounts of composting organic C content increases in all treatments. The most favourable treatment after applying the low dose of Ca is № 32 (CaP^2Fe^2), while for high dose - treatment № 34 ($Ca^2P^2Fe^2$) (Table 4).

Organo-mineral mixture containing zeolite (Z), CaO (Ca) and peat (P) has a positive effect on humus state that turned humus type from humic- fulvic to humic. In all studied treatments content of “free” and R_2O_3 bonded humic acids increases four times (for low dose Ca) and twice (for high dose Ca) compare to the control ones. In the rest two treatments humic acids are 100 % bonded with Ca & Mg) ions. It is established that the amounts of extractable organic matter increase in all studied treatments. Addition of zeolite to organo-mineral mixture - lime and peat (№ 43 - 46) advances the process of humic acids formation.

Conclusions

After 45 days of composting with increased doses of CaO is proved the favourable effect on soil organic matter composition. The humus type is changed from humic-fulvic to humic ones. It is observed decreasing ($Ca^{0.5}$) or absence (Ca, $Ca^{1.5}$ and Ca^2) of ‘free’ and R_2O_3 complexed humic acids after 12 months of composting.

It is observed favourable effect on both, humus type (Ca^2C) and the maturity of humic acids (CaO alone).

It is proved the positive effect on the composition of soil organic matter after 45 days of composting with organo mineral mixture: $Fe(OH)_3$, CaO and coal powder. The type of humus is changed from humic- fulvic to humic ones.

It is established both, stabilizing the soil organic matter - humic acids are 100 % bonded with Ca, and a tendency of slightly increasing of total carbon in the treatments with organo-mineral composites zeolite (Z), CaO (Ca) and coal powder (C).

After 45 days of composting, more favourable effect on humus status is established for a composite: lime compounds, peat and ferrous hydroxide. After 12 months of composting it is found: increasing of total carbon (twice); humic acids; and decreasing of fulvic acids - precondition for favourable soil physical and physical – chemical properties. Observed increasing of “free” and R_2O_3 complexed humic acids, as a result of peat transformation is due to probably less amount of lime material in the treatments of low dose of lime material.

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ALFALFA GROWTH AND HEAVY METAL UPTAKE AFTER ADDITION OF LIME, PEAT AND FERRIFEROUS MATERIAL TO ACID SOIL

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Abstract

The results from a greenhouse experiment on the effect of organo-mineral liming amendments consisted of peat, ferric hydroxide and calcium oxide on plant biomass after growing in strongly acid heavy metal contaminated soil (Dystric Fluvisols) are presented. The amount of lime material in ameliorating mixtures was calculated basing on total (hydrolytic) acidity of the soil.

The investigated organio-mineral mixture increased the effectiveness of soil remediation. The similarly good effectiveness of combination of Ca and ferric hydroxide at two tested lime doses was noted. Increasing of the doses did not affect the yield.

Because of high specific surface and reactivity, the amorphic and micro-crystalline, oxides of Fe adsorbed copper and zinc at pH 4 despite the iso-electric point is around pH 8. One of the reason of positive role of ferric hydroxide is the hypothesis that at low pH different chelatic compounds blocked the inter package spaces and decreased the mobility of various forms of heavy metals located there.

The measurement of heavy metal contamination in upper parts of alfalfa showed that most of the received production is at risk sanitary limits and application as forage must be controlled.

Introduction

Heavy metal contamination of soil is a serious problem for surviving of ecosystems. The main negative effects are related to plant uptake of elements with a risk of toxicity at lowered soil pH. To prevent negative changes a number of different amelioration measures is applied.

The melioration effect of the traditionally applied liming was defined as a possibility for complete hydroxide deposition of heavy metal contaminant and decreasing of a contact ion exchange between the their hydroxyl forms and the plant roots. This can result in applied the high amount of lime materials, which was unfavorable but overliming, was negative reflected on plant growth.

For improvement of liming neutralization effect at heavy metal polluted acid soil was suggested an ameliorative scheme of treated with organo-mineral compounds (Raytchev et al., 2001; 2001a; 2002). This scheme considered as way of organization between heavy metals, applied materials and soil colloids as their responsiveness to the changes in the environment. A presence of humus containing materials in the total mixture created buffer system in respect of reactionary medium pH, which is allow a relative excess applying of lime material in soil.

In present work was show the results of organo-mineral compounds tested effect on alfalfa production and Cu uptake by green biomass after growing in strongly acid heavy metal contaminated soil. The amount of lime material in ameliorating compounds was calculated base on total (hydrolytic) acidity of the soil.

The intensity of natural degradation processes taking place of the soils in Zlatitsa-Pirdop region, it refers main damage of acid-alkaline balance and heavy metal polluted was a major argument at choice of that object for researching in this work. Another important reason was the big difficulties, connected with stability of detoxic by liming in soils of affected ecosystem.

Material and method

The investigation has been carried out in conditions of green house pot experiments in pots of 1.5 kg with strongly polluted alluvial-delluvial soil - Dystric Fluvisols (Radengond, 1996; Radengond and Dimitrov, 1996;1996a;1996b) was taken from superficial horizon (0-20) close by Union Miniere Pirdop Copper in the region of Pirdop-Zlatitsa. The mechanical composition of soil was determined as loamy-sand. In clay fraction (13%) absented minerals with expanding lattice but dominated illite (55%), chlorite and caolinite. In the soil was established strongly contaminated, particularly copper compounds (Cu 845mg/kg), as and another amphoteric elements (Zn -87mg/kg; Cd- <1mg/kg; Co -18 mg/kg; Ni -28 mg/kg and Cr -87 mg/kg), which amounts in soil do not exceed their background content. According the active acidic and buffer systems, reactive-ability of soil characterized with moderate to weakly colloidity (Ganev, 1990). The reaction was strongly acid (pH 4.0) and was observed toxic for plants exchange (exch.Al=3.7cmol/kg) and hydrolytic acidity (exch.$H_{8,2}$=11.2cmol/kg). Organic C was 0.80%. The sum of permanent and variable electronegative charge, which was determined the amount of exchange absorbing cations to $pH_{8,2}$ was CEC=22.8 cmol/kg.

As organic components of ameliorative compounds were tested coal powder (anthracite waste from Svoge mine; pH 7.74 and ash content 15-20%) and peat (from Venec region-pH 7.6 and 15-20% ash content), containing humus matter with the lower condensation degree from these of anthracite coal. Organic manure was carried in preliminary with pH = 6.5, containing N – 5.0%; P_2O_5 – 2.8%; K_2O – 3.4%; CaO – 4.9%; MgO – 0.7%; SiO_2 – 3.2%; H_2O – 8.0%; ash – 28.0%. It applied aim at activating colloid state on part of the heavy metal cations and facilitated their interaction with components of ameliorative compounds.

As absorbing addition to organo-mineral mixture was included and ferriferous adsorbent, containing 55% $Fe(OH)_3$ (25 g Fe/100 g). The reason for this was possibility for it co- precipitated of opposite charge hydroxyl forms of polyvalent cations. The acidic character of copper precipitates supposed presence of copper sulfide, which at this condition could to form micelle with negative charge. The each other to them coagulation with positive charge colloids of ferrous hydroxide was a special case of an electrolytic coagulation.

The applied peat amount (OM and OM^2) was calculated from formula 1 and 2 (Raytchev et al., 2002):

$$[OM]^1 \text{ (g/100g)} = (50\text{x } \Sigma \text{ exch.Al})/\%HA \qquad (1)$$

$$[OM]^2 \text{ (g/100g)} = (25\text{x } \Sigma \text{ exch.Al})/\%HA \qquad (2)$$

where:

%HA- is organic composition of humus containing material, g/100g. its amount is determined ash content of the material %HA = 100 - % ash;

exch.Al- is the exchange soil acidity, cmol/kg;

50 - is the coefficient expressing the optimal amount of humic acids (g), necessary to bind of 1 cmol Al^{3+} by the anionic part of the complex heteropolar calcium salts.

25- is the coefficient expressing the optimal amount of humic acids (g), necessary to bind of 1 cmol Al^{3+} in the organo-mineral absorbing complexes.

The receiving volume with formula 1 was $[OM]^1$ = 2,2g /100g and formula 2 - $[OM]^2$ = 1.1g/100g (or for peat- P^1 and P^2). Because of the high pH volume (pH>7.5) was not provided for applying the additional amount of lime components for neutralized of free acidic groups.

In all variants were added 0.5 g manure /100g soil, which lead to increased of humus content in pot with HS^{man}=0.21% (42% humus in manure). For neutralized of manure acidic group was necessary additional amount CaO that is why it humus content was including in the formula for evaluating of the lime norm ($LM_{H8.2}$). It is necessary considering the acidification because of waiting mineralization of manure at the liming. In this case, the lime norm evaluated of formula:

$LM_{H8.2}$ (g/100g) = n_{LM}x[exch.$H_{8.2}$ + 0.8x(%HS+HS^{manure}) xK],

where

n_{LM-} (n_{LM} =100/N) is the amount (g) of the lime material with neutralized capacity N (cmol/kg), corresponding to 1 cmol; n_{LM} = 0.03 kg/cmol;

%HS – organic C in the soil;

HS^{manure}- organic C in the manure;

K = exch.Al/[exch.Al + Σ(exch.Ca + exch.Mg)].

The variants of carrying out alfalfa pot experiment and the amounts of applied ameliorating materials were show on scheme 1.

After 75 days composting of tested materials at moisture 70% of the field capacity in 2-kg soil per pot (three replications) 50 alfalfa seeds were sow. After each swath was account dry weight of upper alfalfa production and heavy metal content in the accumulated biomass by atom absorption.

The transfer factor (TF) calculated according to formula:

TF = C_{plant} / C_{soil},

where

C_{plant} –total metal content in plant, mg/kg dry weight

C_{soil} –total metal content in soil, mg/kg

An average yield volume of all variants for all cuts in the collected alfalfa by cuts was calculated. Statistical programs for determined sum of forming biomass [$\Sigma^{4swates}$(biomass)(g/pot)].In the all calculates the amount soil in pot (1.5 kg) was accounted.

For determined of heavy metal uptake with upper biomass was done calculating of metal content (mg/kg dry weight), multiplied by receiving average yield from variants for each cut (mg/pot).

Scheme 1. Variants of green- house experiment

№	Variants
К	Non- treated soil – 2 kg / pot
1	Background = BC + 5 g granule farmyard manure / kg soil
2	$Ca^{0.5}$ – BC + 2.3 g CaO / kg soil
3	Ca – BC + 3.4 g CaO / kg soil
11	$CaFe^{1}$ – BC + [3.4 g CaO + 1 g Fe] / kg soil
13	$CaFe^{2}$ – BC + [3.4 g CaO + 4 g Fe] / kg soil
19	CaP – BC + [3.4 g CaO + 11.0 g peat / kg soil
21	CaP^{2} – BC + [3.4 g CaO + 22.0 g peat] / kg soil
27	$CaPFe^{1}$ – BC + [3.4 g CaO + 11.0 g peat + 1 g Fe] / kg soil
28	$CaP^{2}Fe^{1}$ – BC + [3.4 g CaO + 22.0 g peat + 1 g Fe] / kg soil
31	$CaPFe^{2}$ – BC + [3.4 g CaO + 11.0 g peat + 4 g Fe] / kg soil
32	$CaP^{2}Fe^{2}$ - фон + [3.4 g CaO + 22.0 g peat + 4 g Fe] / kg soil
5	Ca^{2} – BC + 6.8 g CaO / kg soil
12	$Ca^{2}Fe^{1}$ - BC + [6.8 g CaO + 1 g Fe] / kg soil
14	$Ca^{2}Fe^{2}$ – BCн + [6.8 g CaO + 4 g Fe] / kg soil
20	$Ca^{2}P$ – BC + [6.8 g CaO + 11.0 g peat] / kg soil
22	$Ca^{2}P^{2}$ – BC + [6.8 g CaO + 22.0 g peat] / kg soil
29	$Ca^{2}PFe^{1}$ – BC + [6.8 g CaO + 11.0 g peat + 1 g Fe] / kg soil
30	$Ca^{2}P^{2}Fe^{1}$ – BC + [6.8 g CaO + 22.0 g peat + 1 g Fe] / kg soil
33	$Ca^{2}PFe^{2}$ - BC + [6.8 g CaO + 11.0 g peat + 4 g Fe] / kg soil
34	$Ca^{2}P^{2}Fe^{2}$ – BC + [6.8 g CaO + 22.0 g peat + 4 g Fe] / kg soil

Results and discuss

At low dose Ca (control variant: Ca)

A.1. By swathes

In all variants the date for alfalfa yield from I swathe were comparative homogenous except of variant: CaP^2 and CaPFe, which production increasing in accordance 27.3%(GD 0.1%) and 13.8% (GD 1%) comparison with control (пpand Ca). In variants CaFe (25.6%) and CaP (15.2%) the strongest decreased Cu content was established. In all the rest variants is observe weakly increment Cu and Zn (Table 1).

The results from second swath showed up a better positive effect of the ferrous additional to organo-mineral mixture. The yield was increased twice more with compare of control (GD 0.1%). A weak tendency to increasing of Zn uptake by biomass obtained. Essentially, in variant $CaFe^2$ the increment (40%) of Cu content was found out.

In the third swath a significant difference in yield (around 50%, GD 1%) at the variants with ferrous additional to organo-mineral compound was established. Commonly, ferrous additional lead to considerable Zn increases in plant.

The date of the forth swath was quite homogeneous as the yield as the uptake content of Cu and Zn. The variants with ferrous additional again was made exceptions in respect of Zn output.

A.2. A totality (as a sum of four swathes).

In all variants with Fe additional to organo-mineral compound and a variant with lime material with double-added dose of peat alfalfa production increasing was more of 30 % (GD 0.1%) Copper content in biomass was varied narrow limits except of variant Ca Fe^1 (the increasing is 30%). The applied only peat or low dose of Fe lead to Cu content decreasing with 15% compared of control (Figure 1).

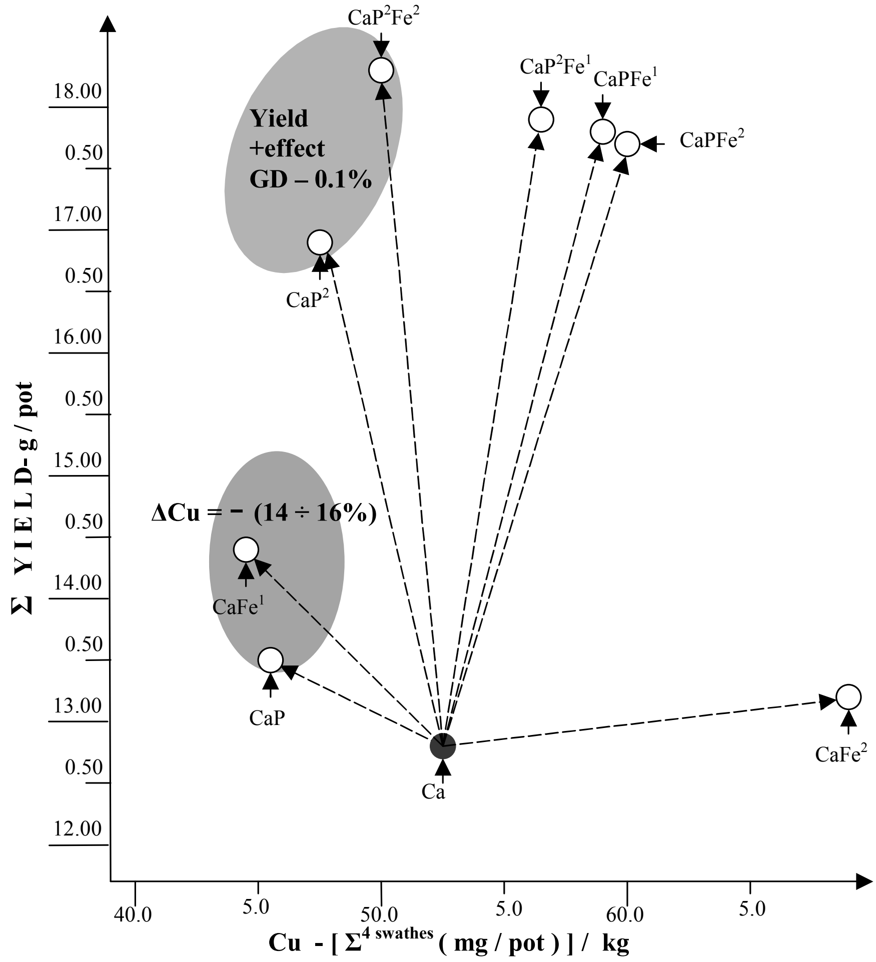

Figure 1. Cu output after acid soil amelioration with mixtures with low dose of Ca, peat and Fe

Table 1. Alfalfa yield and Cu content (ppm) in variants with Ca, peat and Fe^{+2}→ before sowing; ←^{3} after experiment

№	Variants	pH ^{2}→	I swath		II swath		III swath		IV swath		pH ←^{3}	$\Sigma^{4swathes}$, mg/pot	
			Y	Cu	Y	Cu	Y	Cu	Y	Cu		Y	Cu
3	Ca	6.9	3.49	62.5	1.85	76.0	3.93	46.5	3.48	37.5	7.3	12.74	0.67
11	CaFe^1	6.9	3.67	46.5	2.80	60.0	4.11	48.0	3.86	28.0	7.0	14.44	0.64
13	CaFe^2	6.9	2.87	71.5	2.55	107	4.32	64.0	3.53	45.0	6.9	13.26	0.91
19	CaP	7.1	3.35	53.0	1.87	62.5	4.16	46.0	4.13	30.0	7.2	13.52	0.61
21	CaP^2	7.2	4.44	61.0	2.87	57.0	4.78	46.0	4.84	30.5	7.3	16.90	0.80
27	CaPFe^1	7.0	3.97	76.5	4.20	72.0	5.64	49.5	4.00	40.5	7.0	17.80	1.05
28	CaP^{2}Fe^1	7.0	3.75	69.5	3.97	84.0	6.15	45.5	4.13	34.5	7.0	17.99	1.02
31	CaPFe^2	7.0	3.47	67.5	4.57	88.5	5.84	43.5	3.86	43.5	6.9	17.75	1.06
32	CaP^{2}Fe^2	7.1	3.43	73.5	4.21	65.0	6.16	37.0	4.51	38.5	7.0	18.22	0.92
GD – 5%			0.48		1.13		0.99		0.85			1.93	
1%			0.66		1.56		1.36		1.17			2.66	
0.1%			0.91		2.14		1.87		1.61			3.66	
5	Ca^2	7.5	2.93	55.5	1.89	150	3.38	51.0	2.98	30.0	7.7	11.16	0.75
12	Ca^{2}Fe^1	7.2	3.44	52.0	2.59	75.5	4.50	54.0	3.81	41.0	7.0	14.34	0.77
14	Ca^{2}Fe^2	7.1	3.44	54.5	2.66	94.0	3.56	61.0	4.34	43.5	7.0	14.00	0.84
20	Ca^{2}P	7.3	3.64	59.0	2.36	53.5	4.49	39.0	4.37	15.5	7.5	14.87	0.58
22	Ca^{2}P^2	7.3	4.16	63.0	3.04	72.0	4.25	51.5	4.86	35.5	7.5	16.31	0.87
29	Ca^{2}PFe^1	7.0	4.09	70.0	3.95	96.0	5.50	36.5	4.09	42.0	7.3	17.64	1.04
30	Ca^{2}P^{2}Fe^1	7.2	3.78	65.0	4.86	93.5	5.89	39.5	4.14	41.5	7.3	18.68	1.12
33	Ca^{2}PFe^2	7.0	3.62	49.0	4.50	54.5	5.88	32.0	4.35	39.5	7.1	18.35	0.79
34	Ca^{2}P^{2}Fe^2	7.4	3.76	57.0	4.36	67.5	6.29	46.0	4.41	38.0	7.4	18.81	0.92
GD – 5%			0.56		0.95		0.77		0.72			1.67	
1%			0.77		1.31		1.06		0.99			2.30	
0.1%			1.05		1.79		1.45		1.37			3.16	

Distribution of variants according to all biomass production (as a sum of four swaths) is:

↗ $\le CaFe^2 \le CaP \le CaFe^1$ – 1^{-st} group

Ca

↘ $< CaP^2 \le CaPFe^2 \le CaPFe^1 \le CaP^2Fe^1 \le CaP^2Fe^2$ – 2^{nd} group (GD 0.1%)

At the double dose peat (P^2) or the combination of P^1 and P^2 with Fe^1 and Fe^2 found strongly increasing of the yield. The added of Fe was the more effectiveness compared of peat applied.

The five variants of optimal group (2^{nd} group) with ameliorating mixture, containing combinations of the low dose Ca, the two doses peat and the two doses Fe, were expressed a good effectiveness on the biomass compared to control.

The differences in cation exchange capacity (CEC) volumes are minimal but at variants with pH<7 was presented significantly a weakly acidic exchange hydrogen (H_A= exch.$H_{8.2}$-exch.Al). The exchange acidity fully neutralized.

According to the establishing changes in retraced parameters, the variant $CaPFe^2$ accepted as optimal.

At high dose Ca^2 (control variant: Ca^2)

B.1. By swathes

At first swath, the yield of alfalfa in all studied variants surpassed the control variant (Table 2). In the variants only lime material and Fe additional the production increasing (17%) was much weakly. The concentration of Cu was varied around control volume and decreasing of Zn uptake showed about times reduction.

The results from second swat showed a good difference among the containing Fe organo-mineral mixtures and the yield was from 1.5 to two times increasing. The amount of Cu uptake was the lower compared to control (at variant Ca^2P is about three time reduction). A similar tendency observed for Zn, but it was not a good expressing and was broken at variants with low Fe dose (Ca^2PFe^1 and $Ca^2P^2Fe^1$).

Table 2. Effectiveness of ameliorative mixtures with low dose of Ca GD 0.1%)

№	Variant	pH (H_2O)	Physic-chemical parameters*		LN **	Y ***	Cu	Zn
			CEC	exch.$H_{8.2}$			[Σ(mg/pot)]/kg	
2	$Ca^{0.5}$	6.8	21.8	2.0	0.23	11.0	59.0	75.0
3	Ca	7.3	22.0	0.8	0.34	12.7	52.6	52.6
21	CaP^2	7.3	22.1		0.34	16.9	47.3	53.2
27	$CaPFe^1$	7.0	22.0	2.5	0.34	17.8	59.0	63.0
31	$CaPFe^2$	6.9	21.9	2.2	0.34	17.7	59.7	82.2
28	CaP^2Fe^1	7.0	22.0	2.8	0.34	18.0	56.7	66.1
32	CaP^2Fe^2	7.0	22.3	2.0	0.34	18.2	50.5	71.9

In third swat, increasing of biomass statistically proved difference established in all variants except of -Ca^2Fe^2. The concentration of Cu was increased at the

combining of lime material with peat and Fe, while the mixture lime material and Fe increasing Cu uptake by biomass. The concentration of Zn was not differed in variants and control, but it was sufficiently the lower of second swat results (except of variant Ca^2P^2).

The results from fourth swath are more homogeneous in respect of three retraced indexes. The increasing of green production was more of 30% in all variants. The lowest concentration of Cu was obtained at variant Ca^2P (about 2 time reduction of the control).

B.2. A totality (as a sum of four swathes).

In all variants, the significant increasing of biomass observed (more than 23%). The maximal yield found in variants with Fe added in organo-mineral compounds (Figure 2). The lowest value of Cu the biomass is in variant Ca^2P-decreasing with 40%. This reduction for Zn was strongly in all variants.

The variants could group in following scheme according to biomass production (as a sum of four swathes):

$$Ca^2 \begin{cases} \nearrow < Ca^2Fe^2 \leq Ca^2Fe^1 \text{ (GD 1\%)} \\ \searrow < Ca^2P \leq Ca^2P^2 \leq Ca^2PFe^1 \leq Ca^2PFe^2 \leq Ca^2P^2Fe^1 \leq Ca^2P^2Fe^2 - \text{(GD 0.1\%)} \end{cases}$$

The six variants of optimal group (2nd group) with ameliorating mixture, containing the high dose Ca, combined to the two doses peat and the two doses Fe, were expressed a good effectiveness on the biomass compared to control. The concentration of Cu in plant production was about 47.3-59.7mg/kg per pot (Table 3).

Table 3. Effectiveness of ameliorative mixtures with high dose of CaO (GD 1% и 0.1%)

№	Variants	pH (H_2O)	Physico-chemical parameters*			LN **	Y ***	Cu	Zn
			CEC	exch.$H_{8.2}$	exch.Al			[Σ(mg/pot)]/kg	
2	$Ca^{0.5}$	6.8	21.8	2.0		0.23	11.0	59.0	75.0
5	Ca^2	7.7	22.3			0.68	11.2	64.6	100.0
20	Ca^2P	7.5	21.9			0.68	14.9	39.0	53.2
22	Ca^2P^2	7.5	22.8			0.68	16.3	53.3	69.2
29	Ca^2PFe^1	7.3	22.4	1.6		0.68	17.6	59.0	73.7
33	Ca^2PFe^2	7.1	22.2	1.6		0.68	18.4	43.0	51.8
30	$Ca^2P^2Fe^1$	7.3	22.2	1.5		0.68	18.7	60.0	69.6
34	$Ca^2P^2Fe^2$	7.4	22.5			0.68	18.8	48.9	57.4

Where:
*-cation exchange capacity (CEC), hydrolitical acidity (exch.$H_{8.2}$) and exchange acidity (exch.Al), cmol/kg;
**-Lime norm: CaO, g/100g;
***-yield – g/pot from 4swathes;
$Ca^{0.5}$- Lime norm, calculated according to Ganev (1987; 1990);
[Σ(mg/pot)]/kg – uptake of Cu or Zn - mg/kg per pot from 4 swathes.

The combination of high dose Ca^2 with peat was more effectiveness from only Fe added to lime material. At the same time, mixture of peat and Fe was more favorable compared of variants without Fe additional.

Variants **Ca^2PFe^1**	Yield = 17.6g/pot	Cu = 59.0(mg/pot)/kg	Zn = 73.7(mg/pot)/kg
Variants **$Ca^2P^2Fe^1$**	Yield = 18.7g/ pot	Cu = 60.0(mg/ pot)/kg	Zn= 69.6(mg/ pot)/kg
Variants **Ca^2PFe^2**	Yield = 18.4g/ pot	Cu = 43.0(mg/ pot)/kg	Zn= 51.8(mg/ pot)/kg
Variants **$Ca^2P^2Fe^2$**	Yield = 18.8/ pot	Cu = 48.9(mg/ pot)/kg	Zn= 57.4(mg/ pot)/kg

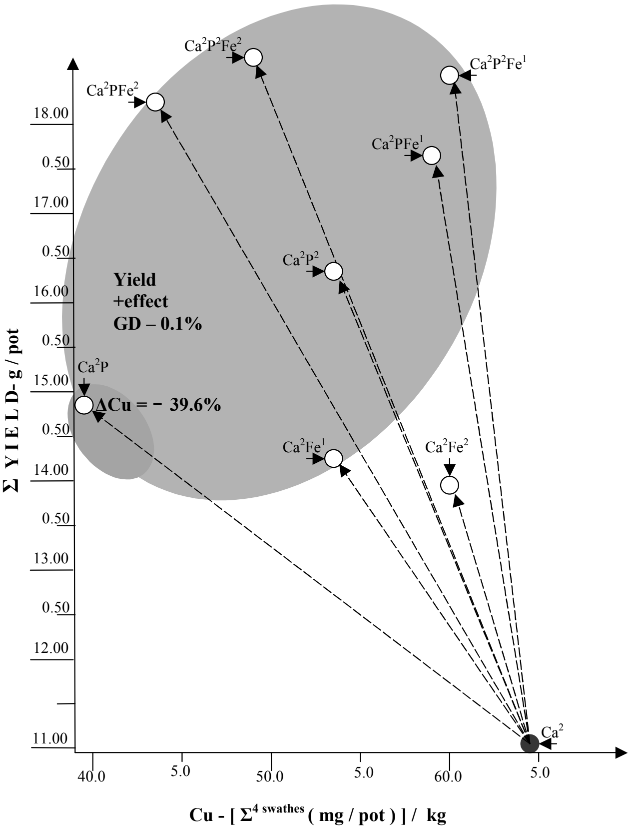

Figure 2. Cu output after acid soil amelioration with mixtures with high dose of Ca, peat and Fe

The differences in cation exchange capacity (CEC) volumes are minimal but at variants with pH<7 was presented significantly a weakly acidic exchange hydrogen H_A (H_A= exch.$H_{8.2}$-exch.Al). The exchange acidity fully neutralized.

According to the establishing changes in retraced parameters for the optimal variants were accepted $Ca^2P^2Fe^2$ and Ca^2PFe^1 (Table 3).

Among the three the most effective variants of the two experiments with ameliorate compounds of calcium and peat (at the low and high doses Ca) the differences in the alfalfa production and Cu output by biomass were not big (Table 4).

Table 4. Effectiveness of ameliorative mixtures of CaO, peat and Fe, characterized as optimal (GD 1% и 0.1%)

№	Variant	pH	Physico-chemical parameters *			LN	Yield	Cu	Zn
		(H_2O)	CEC	exch.$H_{8.2}$	exch.Al	**	***	[Σ(mg/pot)]/kg	
2	$Ca^{0.5}$	6.8	21.8	2.0		0.23	11.0	59.0	75.0
3	Ca	7.3	22.0	0.8		0.34	12.7	52.6	52.6
5	Ca^2	7.7	22.3			0.68	11.2	64.6	100.0
32	CaP^2Fe^2	7.0	22.3	2.0		0.34	18.2	50.5	71.9
29	Ca^2PFe^1	7.3	22.4	1.6		0.68	17.6	59.0	73.7
34	$Ca^2P^2Fe^2$	7.4	22.5			0.68	18.8	48.9	57.4

Where:
*-cation exchange capacity (CEC), hydrolitical acidity (exch.$H_{8.2}$) and exchange acidity (exch.Al), cmol/kg;
**-Lime norm: CaO, g/100g;
***-yield – g/pot from 4swathes;
$Ca^{0.5}$- Lime norm, calculated according to Ganev (1987; 1990);
[Σ(mg/pot)]/kg – uptake of Cu or Zn - mg/kg per pot from 4 swathes.

The coefficients of biologic absorption of copper (transfer factor)

The transfer factor as a function of metal content in soil trace out hyperbolic curved, that mean it can apply for a low concentration of chemistry elements in soil. Probably this is due to a fact that at higher concentrations of heavy metals in soil the deviations from the linear dependency of these coefficients as a function of their concentration could be significant.

A comparative analyze of results from swathes shown that transfer factor of Cu was within in the normal limits (0.1-1). The observing differences related to long vegetation period and possibility for summing of four swathes. It could explain as difference intensity of growth as necessary of regular watering (summer season, 4th swathe). The coefficients of biologic absorption calculated for the sum of the four swathes are in the range of the normal concentration (0.04-0.08) but a direct dependency between the concentration of Cu in the soil and its transfer in the plants. Hence, only the transfer factor can not be used as an indicator for the sanitary condition of the production obtained.

Conclusion

The investigated organic- mineral mixture increased the effectiveness of remediation. The similar good effectiveness of combination of Ca and ferric hydroxide at two tested lime doses means that this combined application is main factor in positive changes. Increasing of the doses did not affect the yield.

Because of the high specific surface and reactivity the amorphyc and micro-cristaline, oxides of Fe adsorbed copper and zinc at pH 4 despite the iso-electric point is at pH 8. One of the reason of positive role of ferric hydroxide is the hypothesis that at low pH different helatic compounds blocked the inter package spaces and decreased the mobility of located there forms of heavy metals.

The assessment of heavy metal contamination of upper part of alfalfa showed that more of received production is at risk sanitary limits and application as forage must be controls.

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ALFALFA YIELD AND COPPER UPTAKE AFTER TREATMENT OF HEAVY METALS POLLUTED SOIL WITH LIME, COAL POWDER AND FERRIC OXIDE

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Abstract

In the recent study results of testing an influence of organo-mineral meliorative mixtures on the produced alfalfa green biomass and the copper uptake which is cultivated on an acid soil highly polluted with heavy metals have been presented (Dystric Fluvisol). Combinations of CaO, coal dust and additive of ferric oxide materials have been used. The quantity of the lime material included in ameliorative mixtures has been calculated according to hydrolytic acidity of the chosen soil.

A positive impact of the investigated quantities of lime material and coal present in the mixture and other additives (iron hydroxide and farmyard manure) for ignition and catalysis of colloid processes and better ameliorative effectiveness has been established.

At the same time the buffer action of the organic components with high aromatic rate introduced in coal dust justifies the intake of higher lime quantities in acid soil strongly polluted with copper. Probably this impact is a consequence of large amount of OH-groups involved in the neutralization and hydrogen ions liberation from activated phenolic hydroxide groups.

The coefficients of biological absorption calculated as the sum of the four swathes (cuts) are in the range of the normal concentration and a direct dependence between the concentration of Cu in the soil and its transfer to the plants was noted. Probably this is due to a fact that at higher concentrations of heavy metals in soil the deviations from the linear dependence of the uptake as a function of heavy metal concentration could be significant.

Hence only the transfer factor can not be used as an indicator for the sanitary condition of the production obtained.

Introduction

Utilization of some natural materials as additives for improvement of soil-chemical and productive properties of the soil in many cases solves rather rational part of arising problems in the ecosystem. Many of them are lime materials, incinerated ash and basic slag and additives enriched with iron, phosphate meliorants like hydroapatites and dissolved phosphates (Nikolov et al., 1999; Pierzynski and Schwab, 1993; Shende et al., 1994). Brown coal or a mixture from carbonate sediment and anthracite coal dust are used for improvement of the humus condition and as a detoxicant for heavy metals in polluted soils and their very good effectiveness is proved too (Arsova, 1998; Raytchev, 1996; Arsova and Raytchev, 2000).

In this study the results from testing of the impact of organo-mineral meliorative mixtures on the obtained alfalfa green biomass and the copper taking out that is cultivated on the strongly polluted wit5h heavy metals acid soil. The combinations of CaO, coal dust and an additive of iron containing materials are used. The quantity of the lime material included in the composition of the meliorative mixtures has been estimated on the basis of their hydrolytic acidity of the chosen soil.

Materials and methods

The investigation has been carried out in conditions of green house pot experiments in pots of 1.5 kg with strongly polluted alluvial-delluvial soil - Dystric Fluvisols (Radengond, 1996; Radengond and Dimitrov, 1996a; 1996b; 1996c), taken from its surface horizon (0-20 cm) nearby copper factory "Umicore" , Pirdop. The presence of some other elements (Zn – 87 mg/kg; Cd - < 1 mg/kg; Co – 18 mg/kg; Ni – 28 mg/kg and Cr – 87 mg/kg) has been established which quantities in soil do not exceed their background content. In illite fraction (13%) of this clay sand, loamy sand soil hydromica (55%), chlorites and kaolinite are dominated. This reflects on the values of their phisico-chemical characteristics: strongly acid reaction ($pH_{H2O} = 4.0$); toxically for plants exchange (exch.Al = 3.7 cmol/kg) and hydrolytic acidity ($exhc.H_{8.2} = 11.2$ cmol/kg); the sum of permanent and variation electronegative charges CEC = 22.8 cmol/kg; the quantity of permanent electronegative charges $CEC_{SA} = 15.5$ cmol/kg; the quantity of variation electronegative charges $CEC_A = 7.3$ cmol/kg (Ganev, 1990); low content of organic C (0.80%).

In the tested meliorative mixture are included: coal dust (anthracite waste from coal-mine "Svoge" – pH = 7.74 and ash content 15%) that contain humus substances with high condensation rate; iron containing adsorbent which contain 55% $Fe(OH)_3$ or 25 g Fe/100 g; CaO with neutralizing ability n_{LM} = 0.03 kg/cmol. Organic manure with pH = 6.5, containing: N – 5.0%; P_2O_5 – 2.8%; K_2O – 3.4%; CaO – 4.9%; MgO – 0.7%; SiO_2 – 3.2%; H_2O – 8.0%; ash – 28.0% is preliminary included .

The quantity of the introduced coal dust (OM and OM^2) is estimated by formulae 1 and 2 (Raytchev et al., 2002):

$[OM]^1$ (g/100g) = (50x Σexch.Al)/%HA (1)

$[OM]^2$ (g/100g) = (25x Σexch.Al)/%HA (2)

where

%HA – Organic compound of humus containing substance, g/100g. Its quantity has been determined by ash content of the substance: %HA = 100 - % ash;

Σ exch.Al – Exchange acidity, cmol/kg.

50 –coefficient describing the optimal necessary quantity humus acids in kg associating 1cmol Al^{3+} in anion part of the complex heteropolar salts with calcium;

25 –coefficient describing the optimal necessary quantity humus acids in kg associating 1cmol Al^{3+} in organo-mineral adsorption complexes.

Lime norm is determined according to equation:

$LM_{H8.2}$ (g/100g) = n_{LM}x[exch.$H_{8.2}$ + 0.8x(%HS+HS^{manure}) xK],

where

n_{LM} – neutralizing ability of the lime material, kg/cmol. For CaO that is applied in the experiment carried out n_{LM} = 0.03 kg/cmol;

%HS – organic C in soil

HS^{manure} – organic C in farmyard manure;

K = exch.Al/[exch. Al+ Σ(exch. Ca + exch.Mg)].

The determined quantities of the tested materials are:

C^1 = 1.1g/100g; C^2 = 2.2g/100g;

$CM^{CaO} \rightarrow Ca$ = 0.34g/kg; $2CM^{CaO} \rightarrow Ca^2$ = 0.68g/kg.

OM^{manure} = 0.5g/100g;

Fe^1 = 0.1g/100g; Fe^2 = 0.4g/100g.

Variations of the carried out green house experiment with alfalfa and the quantities introduced ameliorative materials are shown on diagram 1.

Scheme 1. Variants of green- house experiment

№	Variant
C	Non- treated soil – 2 kg / pot
1	Background - BC + 5 g granule farmyard manure / kg soil
2	$Ca^{0.5}$ – BC + 2.3 g CaO / kg soil
3	Ca – BC + 3.4 g CaO / kg soil
11	$CaFe^{1}$ – BC+ [3.4 g CaO + 1 g Fe] / kg soil
13	$CaFe^{2}$ – BC + [3.4 g CaO + 4 g Fe] / kg soil
23	CaC – BC + [3.4 g CaO + 11.0 g coal] / kg soil
25	CaC^{2} – BC + [3.4 g CaO + 22.0 g coal] / kg soil
35	$CaCFe^{1}$ – BC + [3.4 g CaO + 11.0 g coal + 1 g Fe] / kg soil
36	$CaC^{2}Fe^{1}$ – BC + [3.4 g CaO + 22.0 g coal + 1 g Fe] / kg soil
39	$CaCFe^{2}$ – BC + [3.4 g CaO + 11.0 g coal + 4 g Fe] / kg soil
40	$CaC^{2}Fe^{2}$ - BC + [3.4 g CaO + 22.0 g coal + 4 g Fe] / kg soil
5	Ca^{2} – BC + 6.8 g CaO / kg soil
12	$Ca^{2}Fe^{1}$ - BC + [6.8 g CaO + 1 g Fe] / kg soil
14	$Ca^{2}Fe^{2}$ – BC + [6.8 g CaO + 4 g Fe] / kg soil
24	$Ca^{2}C$ – BC + [6.8 g CaO + 11.0 g coal] / kg soil
26	$Ca^{2}C^{2}$ – BC + [6.8 g CaO + 22.0 g coal] / kg soil
37	$Ca^{2}CFe^{1}$ – BC + [6.8 g CaO + 11.0 g coal+ 1 g Fe] / kg soil
38	$Ca^{2}C^{2}Fe^{1}$ – BC + [6.8 g CaO + 22.0 g coal + 1 g Fe] / kg soil
41	$Ca^{2}CFe^{2}$ - BC + [6.8 g CaO + 11.0 g coal + 4 g Fe] / kg soil
42	$Ca^{2}C^{2}Fe^{2}$ – BC + [6.8 g CaO + 22.0 g coal + 4 g Fe] / kg soil

After 75-day composting of the tested materials at 70% of water capacity in 2 kg of soil 50 alfalfa seeds in each pot are sown. Four swathes are done in blossom phase. After each swath the mass of plant green part and concentration of heavy metals in the accumulated biomass by atom absorption has been reported.

The coefficient of biological absorption (transfer factor – TF) is calculated by equation:

$$\mathbf{TF} = C_{plant} / C_{soil}$$

where:

C_{plant} – Total metal content in a plant, mg/kg dry mass;

C_{soil} –Total metal content in soil, mg/kg dry soil.

Results

At low dose Ca (control variant Ca)

A.1. By swathes

The yield of alfalfa at the first swath is similar for all variant excluded the variant CaCFe^{2} – the increasing is 24.9% (at LSD 1%) compared with the control variant (Table 1). High decreasing of Cu in plant biomass was found at variants CaC (43.2%) and CaFe^{1} (25.6%). In opposite side is variant CaCFe^{1} with Cu increasing of 23 % in upper part.

Table.1. Yield (Y- g DW/pot) and concentration of Cu (mg/kg) in alfalfa plants in variants with Ca, Coal and Fe

№	Variant	pH* $^{2}\rightarrow$	I swath		II swath		III swath		IV swath		pH $\leftarrow^{3}$	$\Sigma^{4swathes}$, mg/pot	
			Y	Cu	Y	Cu	Y	Cu	Y	Cu		Y	ΣCu
3	Ca	6.9	3.4	62.5	1.8	76.0	3.9	46.5	3.4	37.5	7.3	12.7	0.6
11	CaFe^{1}	6.9	3.6	46.5	2.8	60.0	4.1	48.0	3.8	28.0	7.0	14.4	0.6
13	CaFe^{2}	6.9	2.8	71.5	2.5	107.0	4.3	64.0	3.5	45.0	6.9	13.2	0.9
23	CaC	7.0	3.1	35.5	2.2	44.5	3.8	37.0	3.6	34.0	7.1	12.9	0.4
25	CaC^{2}	7.1	3.9	63.0	3.5	46.5	5.0	38.5	3.6	34.0	7.2	16.1	0.7
35	CaCFe^{1}	7.0	2.9	81.0	2.3	184	4.2	57.5	2.8	50.5	6.9	12.4	1.0
36	CaC^{2}Fe^{1}	7.0	3.6	63.5	2.9	146	4.3	43.5	3.6	46.5	6.9	14.6	0.9
39	CaCFe^{2}	7.1	4.3	51.0	3.8	59.0	5.4	39.5	4.1	43.2	7.2	17.8	0.8
40	CaC^{2}Fe^{2}	7.3	3.8	53.5	3.1	70.5	5.3	47.5	3.6	42.5	7.3	15.9	0.8
GD – 5%			0.5		0.6		1.1		0.7			1.6	
1%			0.7		0.9		1.5		1.0			2.2	
0.1%			1.0		1.2		2.1		1.4			3.0	
5	Ca^{2}	7.5	2.9	55.5	1.8	150.0	3.3	51.0	2.9	30.0	7.7	11.0	0.7
12	Ca^{2}Fe^{1}	7.2	3.4	52.0	2.5	75.5	4.5	54.0	3.8	41.0	7.0	14.3	0.7
14	Ca^{2}Fe^{2}	7.1	3.4	54.5	2.6	94.0	3.5	61.0	4.3	43.5	7.0	14.0	0.8
24	Ca^{2}C	7.3	3.4	70.5	4.1	59.0	5.0	35.0	4.1	33.5	7.2	16.7	0.5
26	Ca^{2}C^{2}	7.4	3.9	60.0	3.3	41.5	4.5	30.5	3.7	29.0	7.5	15.5	0.6
37	Ca^{2}CFe^{1}	7.2	3.6	44.0	3.5	78.0	4.7	36.0	4.3	41.5	7.2	16.3	0.7
38	Ca^{2}C^{2}Fe^{1}	7.2	3.8	47.5	2.5	64.5	5.3	36.0	4.1	32.5	7.3	17.2	0.7
41	Ca^{2}CFe^{2}	7.4	3.8	45.0	3.6	60.0	6.0	32.0	4.4	37.5	7.5	18.0	0.7
42	Ca^{2}C^{2}Fe^{2}	7.4	3.9	55.0	3.0	72.0	5.6	31.5	4.0	42.5	7.5	16.7	0.7
GD – 5%			0.5		1.5		0.7		0.7			1.4	
1%			0.7		2.1		1.0		1.0			2.0	
0.1%			1.0		2.9		1.3		1.3			2.7	

The tendency of Zn concentration in plant biomass is slightly increasing in variants compared with the control excluding variants with double dose Fe- $CaCFe^2$ and CaC^2Fe^2.

At the second swath the differences are higher and at all variants (without CaC) we shown positive significant difference compared with the control. In variant CaC we established the highest decreasing of copper (41%). In some of variants- $CaFe^2$, CaC^2Fe^1 and $CaCFe^1$ we found extremely increasing of Cu (from 40% to 136%). In the same variants the concentration of Zn increased from 39 to 79%.

At third swath the significant difference in yield was shown in variants with double-added dose of Fe. High decreasing of Cu content was shown in variants without Fe (19-20%). The quantity of Zn output is not different from the control variants (exceptions are variant $CaFe^2$- increasing with 38%, variant CaC^2- increasing with 27% and $CaCFe^1$- with 23%)

The fourth swath is quite homogenous as the yield as the output concentrations of Cu and Zn.

A.2. A totality (as a sum of four swathes)

Some of variants $CaCFe^2$, CaC^2Fe^2 and CaC^2 showed high increasing of yield (more than 25%) and low concentrations of Cu in upper biomass was detected (Figure 1). In variant $CaFe^1$ the increasing of yield is 13 % and the copper is lower than the control again. In variant CaC^2Fe^1 concentration of Cu in biomass increased to 30%. At low dose coal - variant CaC the yield was low but Cu in biomass decreases with 30%.

Summarizing the combination of low dose Ca and low dose Fe increases the yield with 13 %, decreases the concentration of Cu in biomass with 16%, while double dose Fe leads to negative effects on parameters.

Combination of low dose Ca with low dose coal does not increase yield but decreases the concentration of copper uptake (29%). Adding of Fe to low dose coal has negative effect. Increasing of Fe in the mixture conducted to significant increasing of the yield (39% compared with the control and all variants without Fe) and the concentration of Cu in biomass decreases with 10 %. Double increasing of organic matter leads to 26% more yield and decreasing of Cu is 13%. Addition of low dose Fe in this combination expresses negative changes. The same is situation with applying of higher dose Fe.

Distribution of variants according to all biomass production is:

Ca

$\leq CaCFe^1 \leq CaC \leq CaFe^2 \leq CaFe^2$ – 1st group

$< CaC^2Fe^1$ – 2nd group(GD 5%)

$< CaC^2Fe^2 \leq CaC^2 \leq CaCFe^2$– 3rd group (GD 0.1%)

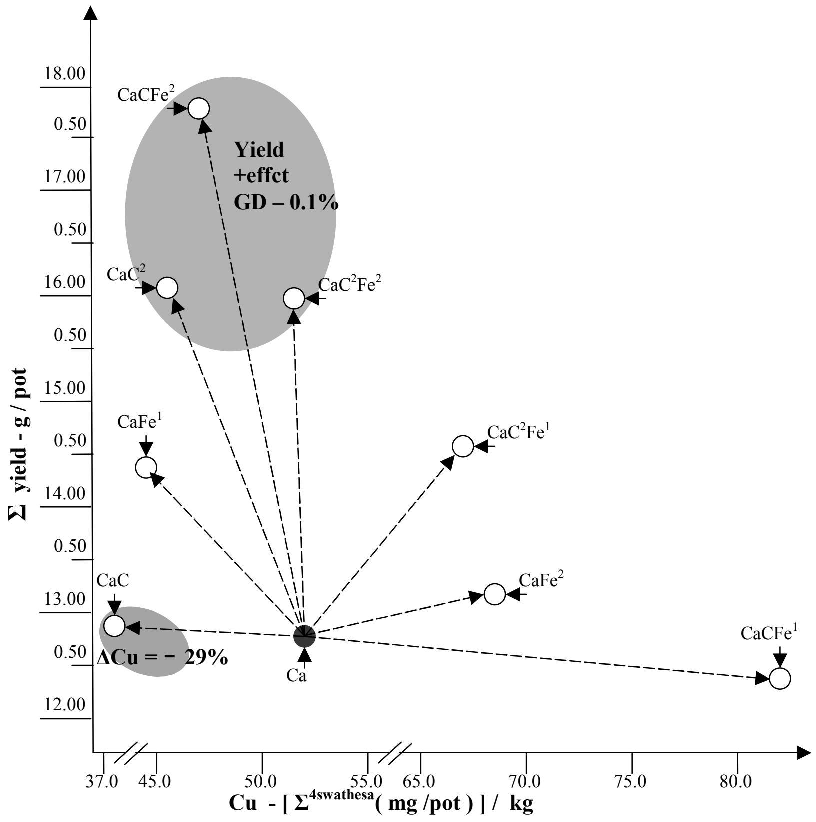

Figure 1. Output of Cu after amelioration with mixtures with low dose Ca

Among these three groups the most effective are variants in the third. Combination of Ca with coal leads to slowly increasing of biomass and low concentration of Cu in plant material. The variants in the third group express good effectiveness on the biomass quantity compared with the control and concentration of Cu in plant biomass about 45-51 mg/kg per pot (Table 2).

Table 2. Effectiveness of ameliorative mixtures with low dose of Ca (GD 0.1%)

№	Variant	pH	Physic-chemical parameters			LM	yeild	Cu	Zn
		(H_2O)	CEC	exch.$H_{8.2}$	exch.Al	**	***	[Σ(mg/pot)]/kg	
2	$Ca^{0.5}$	6.8	21.8	2.0		0.23	11.0	59.0	75.0
3	Ca	7.3	22.0	0.8		0.34	12.7	52.6	52.6
25	CaC^2	7.2	21.8			0.34	16.1	45.3	59.0
39	$CaCFe^2$	7.2	21.4			0.34	17.8	47.2	52.7
40	CaC^2Fe^2	7.3	22.0			0.34	16.0	51.3	58.9

The differences in $T_{8.2}$ are minimal and total acidity is fully neutralized.

The optimal variant is CaC^2 (Table 3).

High dose Ca^2 (control Ca^2)

Table 3. Effectiveness of ameliorative mixtures with high dose of CaO (GD 1% and 0.1%)

№	Variant	pH	Physico-chemical parameters*			LM	yeild	Cu	Zn
		(H_2O)	CEC	exch.$H_{8.2}$	exch.Al	**	***	[Σ(mg/pot)]/kg	
2	$Ca^{0.5}$	6.8	21.8	2.0		0.23	11.0	59.0	75.0
5	Ca^2	7.7	22.3			0.68	11.2	64.6	100.0
37	Ca^2CFe^1	7.2	22.0			0.68	16.3	47.8	49.1
24	Ca^2C	7.2	22.2			0.68	16.7	34.7	56.2
42	$Ca^2C^2Fe^2$	7.5	22.3			0.68	16.8	46.0	49.6
38	$Ca^2C^2Fe^1$	7.3	21.9			0.68	17.2	43.5	49.9
41	Ca^2CFe^2	7.5	22.2			0.68	18.0	42.2	48.3

Where:

*-cation exchange capacity (CEC), hydrolitical acidity (exch.$H_{8.2}$) and exchange acidity (exch.Al), cmol/kg;

**-Lime norm: CaO, g/100g;

***-yield – g/pot from 4swathes;

$Ca^{0.5}$- Lime norm, calculated according to Ganev (1987; 1990);

[Σ(mg/pot)]/kg – uptake of Cu or Zn - mg/kg per pot from 4 swathes.

B.1. By swathes

The yield of alfalfa in all studied variants surpassed the control variant (Table 1). The concentration of Cu is decreased (about 20 %) in variants Ca^2CFe^1 and Ca^2CFe^2 while the most negative is result in variant Ca^2C- increasing with 27%. The differences in Zn uptake between variants and control are very big and showed about 4 time reduction.

During the second swath the tendency is in increasing of biomass but statistically proved is only in variants with low coal doses.

The situation was similar in third swath where the combining of lime material with coal leads to decreasing of Cu concentration in plants material, while the mixture lime material + Fe did not affect copper uptake. The concentration of Zn in higher than in second swath and is not differed in variants and control.

The results from fourth swath are more homogeny.

B.2. A totality (as a sum of four swathes)

The significant increasing of biomass was shown in all variants. The maximal yield we found in variant Ca^2CFe^2 . The lowest value of Cu the biomass is in variant Ca^2C.

The variants could be grouped in following scheme according to biomass production

$$\mathrm{Ca^2} < \mathrm{Ca^2Fe^2} \le \mathrm{Ca^2Fe^1}\ (\mathrm{GD} \begin{array}{ll} \nearrow & \le \mathrm{Ca^2C^2} \\ \rightarrow & < \mathrm{Ca^2CFe^1} \le \mathrm{Ca^2C} \le \mathrm{Ca^2C^2Fe^2} - (\mathrm{GD}\ 1\%) \\ \searrow & < \mathrm{Ca^2C^2Fe^1} \le \mathrm{Ca^2CFe^2} - (\mathrm{GD}\ 0.1\%) \end{array}$$

Optimal variants are Ca^2C, Ca^2CFe^1 and $Ca^2C^2Fe^2$ (Table 4).

The coefficient of transfer of Cu for all variants varies from 0.04 to 0.05 (Table 5).

Conclusion

The changes in colloidal processes and ameliorative effectiveness by application of amendments (lime material, coal powder) and additives (ferric oxide and farmyard manure) were investigated. The optimal variants contained high dose Ca^2 combined with two doses coal and two doses Fe expressed increasing of alfalfa biomass compared to the control variant. The combination of low dose Ca and low dose Fe increases the yield (13%) and reduces the copper concentration in biomass with 16%. Addition of Fe showed negative effect on studied parameters. The combination of Ca and coal powder leads to slow increasing of biomass and copper uptake.

Our results confirm amelioration of heavy polluted acid soils with high doses of lime material and coal powder respectively organic compounds with well expresses level of aromatization.

The calculated coefficients of biological uptake (transfer factor) of Cu are in the normal limits. This parameter is not very indicative for green house experiments because of high concentration of pollutant in soil and stress conditions which plant have to surpass.

Table 4. Effectiveness of ameliorative mixtures of CaO, $Fe(OH)_3$ and coal powder, characterized as optimal (GD 1% и 0.1%)

№	Variant	pH (H_2O)	Physico-chemical parameters*			LN **	yield ***	Cu	Zn
			CEC	exch.$H_{8.2}$	exch.Al			[Σ(mg/pot)]/kg	
2	$Ca^{0.5}$	6.8	21.8	2.0		0.23	11.0	59.0	75.0
3	Ca	7.3	22.0	0.8		0.34	12.7	52.6	52.6
5	Ca^2	7.7	22.3			0.68	11.2	64.6	100.0
25	CaC^2	7.2	21.8			0.34	16.1	45.3	59.0
37	Ca^2CFe^1	7.2	22.0			0.68	16.3	47.8	49.1
24	Ca^2C	7.2	22.2			0.68	16.7	34.7	56.2
42	$Ca^2C^2Fe^2$	7.5	22.3			0.68	16.8	46.0	49.6

Where:
*-cation exchange capacity (CEC), hydrolitical acidity (exch.$H_{8.2}$) and exchange acidity (exch.Al), cmol/kg;
**-Lime norm: CaO, g/100g;
***-yield – g/pot from 4swathes;
$Ca^{0.5}$- Lime norm, calculated according to Ganev (1987; 1990);
[Σ(mg/pot)]/kg – uptake of Cu or Zn - mg/kg per pot from 4 swathes.

Table 5. Transfer coefficient of Cu- distribution

№	Variant	1st swath	2nd swath	3rd swath	4th swath	$\Sigma^{4swathes}$
3	Ca	0.055	0.071	0.057	0.024	0.06
5	Ca^2	0.066	0.178	0.060	0.036	0.08
11	$CaFe^1$	0.073	0.090	0.055	0.044	0.05
12	Ca^2Fe^1	0.062	0.089	0.064	0.048	0.06
13	$CaFe^2$	0.085	0.127	0.076	0.053	0.08
14	Ca^2Fe^2	0.064	0.111	0.072	0.051	0.07
23	CaC	0.042	0.053	0.044	0.040	0.04
24	Ca^2C	0.009	0.070	0.041	0.040	0.04
25	CaC^2	0.075	0.055	0.046	0.040	0.05
26	Ca^2C^2	0.071	0.049	0.036	0.034	0.05
35	$CaCFe^1$	0.096	0.218	0.068	0.060	0.097
36	CaC^2Fe^1	0.075	0.173	0.051	0.055	0.08
37	Ca^2CFe^1	0.052	0.092	0.043	0.049	0.057
38	$Ca^2C^2Fe^1$	0.056	0.076	0.043	0.038	0.05
39	$CaCFe^2$	0.060	0.070	0.047	0.051	0.056
40	CaC^2Fe^2	0.063	0.083	0.056	0.050	0.06
41	Ca^2CFe^2	0.053	0.071	0.038	0.044	0.05
42	$Ca^2C^2Fe^2$	0.065	0.085	0.037	0.050	0.05

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THEORETICAL ANALYSIS OF pH-BUFFERING REACTIONS OF HUMIC COMPOUNDS DURING MELIORATION OF ACID SOILS POLLUTED WITH HEAVY METALS

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Abstract

The present analysis of buffering function of humus substances on the reaction of media under organo-mineral liming of polluted with heavy metals acid soil aims to propose a theoretical base for solving problems, connected with determination and assignment of meliorated norms.

The presentation is based on the reported results about the purpose of chelating of ionic forms of amphoteric elements and the formation of complex heteropolar salts via connection of free acid groups of humus acids with Ca^{2+} of the liming materials. The main buffering component are phenolic –OH groups, which can compensate in a definite limits their relative excess preventing the effect of over liming.

The base hypotheses is build on the assumption of formation of *t* bond between molecular conformation of macromolecules of humic acids and the activity of H^+ of phenolic –OH groups. It is illustrated with the proposed mechanisms for the intramolecular rearrangement between both valence and coordination bonds connected with the central atom groups in the anionic part of the complex heteropolar salt.

The buffering function of humic acids on pH of the reactive media is shown in the limits of the same “coordination capacity” of –COOH and phenolic –OH groups in their molecules. Its depletion is a precondition for the formation of the clay-humus adsorbent complexes with the participation of the polyvalent cations. The decreased ability for ionic exchange between soil adsorbent and root system destroys the nutrient balance and has a negative effect on the quantity of the biomass in this condition.

INTRODUCTION

The behavior of the polyvalent cations in the soil is defined trough buffering capacity of soil adsorbent. In the process of ameliorative treatments, except their hydroxide precipitation, other chemical forms are involved (Gongminet al., 1991; Madrid et al., 1991; Duquette and Hendershot, 1990; Cavallaro and McBride, 1984; Harsch and Doner, 1985; Chen et al., 1990; Ganev, 1990; Chouldjian, 1978; Taga et al., 1991; Waller and Pickering, 1990; Alloway and Ayres, 1994; Cambier, 1994; Orlov, 1985; Atanassova, 1993).

They are a consequence of their complex bonding with the soil organic substances, their precipitation on the fresh formed gels, octahedral coordination in the aluminosilicates and admixed occlusion.

The precise definition of the ameliorative norms for the immobilization of heavy metals in acid soils, is one of the main problems of liming. The shortage of strong bases creates a risk for incomplete hydroxide precipitation and overliming reflects negatively on the balance of the plant nutrient regime.

It is established experimentally, that including of humus components to ameliorative mixture shows some buffering influence on pH values of the treated soils. The bonding of the humus acids (HA) free functional groups with Ca^{2+} of the liming materials and the chelate ionic forms of heavy metals facilitates the formation of complex heteropolar salts. The ability for intra-molecular rearrangement between valent and coordination bonded in both ionic or molecule's forms associations in the range of their corresponding "coordination capacity" is a precondition for some buffering influence on pH values of the reactive media.

THEORETICAL ANALYSIS

The present study aims to propose general principles concerning formation a buffer system of soil adsorbent and its responsiveness to components of organo-mineral liming mixture, applied for amelioration o9f heavy metals polluted acid soil. Probable mechanisms of its impact on pH of the reaction media are illustrated with some examples schemes.

Basic hypothesis

Possible explanation for the buffering effect of ameliorative mixture of humus substances and liming materials on pH of the meliorated acid soils even after application of relative excess of liming component is the following assumption: Bond between molecular conformation of macromolecules of humic acids and the activity of H^+ of phenolic –OH groups.

A reason for such ability is their colloid character, which is defined from their concentration and pH of the media (Schnitzer, 1991). These are macromolecules with pH-dependant charge, which pH ~ 4 is negative, but its value is insignificant (Arora et al., 1979).

The most important in steric features of this high molecular formations is connected with the flexibility of their chains, which reduces with the increasing of both, amount of the polar groups and size of the steric net. This property is very important, because it allows formation of “clatrat” compounds, during which molecules bonded mechanically, thanks to the steric configuration.

After suitable treatment of the soil is possible to activate interactions between negative charged colloids of the clay minerals and humus substances on one hand and positive charged ions or hydroxides forms of the amphoteric elements on the other. The flexibility and the high activity of the organic fragments facilitates formation of stable adsorptive solvent layers on the surface of the mineral colloids, forming “sandwich” charged structure of organo-mineral nucleus (SA^-) of soil adsorbent. It is known that the positive charged hydrosols of polyvalent cations generate zones of coagulation, which makes easier their interaction with clay negative charges and acid groups of humus substances (Friedrichsberg, 1984; Kokotov et al., 1986; Raytchev, 1996).

The special character of the negative charged zone of SA^- is function of the function groups' state of humus acids. With the increasing of pH is also increased and dissociation of -COOH-groups and the value of their negative charges enhanced. Their molecules conformation, from spiral or spherical at low pH, goes through an extended chain (Arora et al., 1979; Schnitzer, 1991; Tarchitzky et al., 1993). In the open spaces are shown some specific adsorptive centers and their closeness with phenolic -OH groups facilitates their activation.

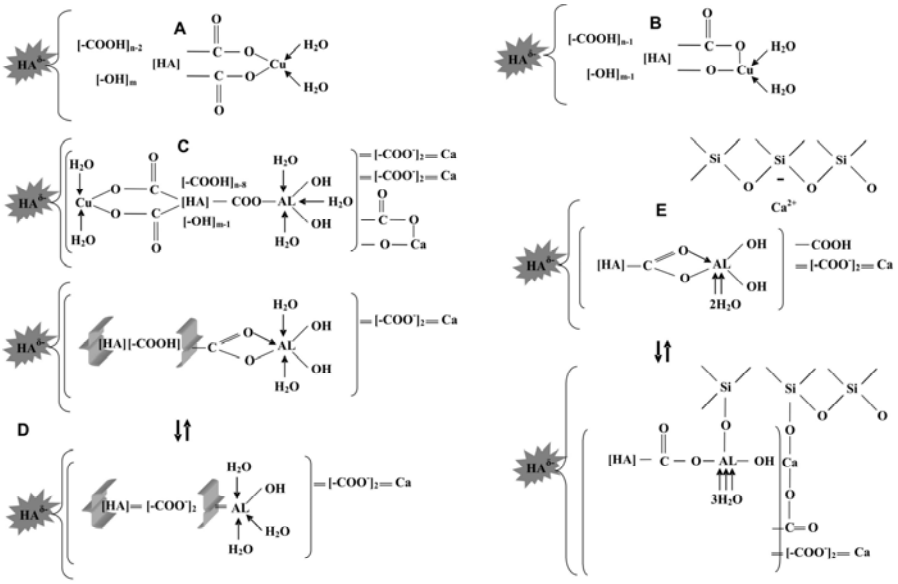

Figure 1. Formation of buffering system of soil adsorbent in organo-mineral liming of acid soils. Bonding of polyvalent cations in chelat complexes (A, B) and heteropolar salts (C), intra molecular rearrangement in their adsorptive layer (D) and formation of clay-humus complexes (E)

Mechanisms

The application of humus materials in the soil increases the concentration of acid groups and makes easier bonding of polyvalent ions in chelating complexes (Fig.1-A). The main role in a chelate formation plays, the origin of the humus materials, so the pH of the media. At pH values phenolic hydroxyls groups are included in this reactions (Orlov, 1985) (Fig.1-B).

In the beginning of the neutralization Al, replaced from strongly acid positions and partly Ca^{+2} of liming materials, carboxylic groups of HA which are dissociated at low pH participate in this reaction. The absence of changes in pH after application Ca in excess is an indication for probable dissociation of inactive to those moment acid groups. Released H^+ ions compensate the alkalization and buffer the system in the limit of some optimal pH value (Fig.1-C).

Ions of Al can take different positions in the anionic part of the humus complexes: to replace H+ from -COOH group and to coordinate with oxygen of =CO group. The replaced protons after intra molecular rearrangement migrate comparatively easy in the iintra adsorbent layer. After their reaction with -OH groups of Al(OH) they form H_2O molecules, which are coordination around Al to reach their coordinating number 6 (Fig. 1 – D).

The excess of acid groups moves the equilibrium to both, bonding H^+ ion of hydroxyl cations and coordination of water molecules to the central cation of the complex compound. After getting beyond of a definite concentration of acid groups over attitude concerning the ability of central cation for coordination, it can be expected acidification of the media.

At higher concentrations of humus acids, in the respect to the applied liming material, the potential excess of acid groups helps the formation of "bridge" bond between HA and clay minerals via polyvalent cations. Including Ca in similar structures blocks its participation in exchange reactions with H^+ on plant ion exchanger (Fig. 1 – E).

The truth of these mechanisms is proved with experimental facts on the influence of different ratios between components of organo-mineral liming mixture in the reactions of the media and yield of plant biomass (Arsova and Raytchev, 2000; 2001; Raytchev et al., 1999; 2000; 2001; 2001a; 2002; Raytchev and Arsova, 1998).

COCLUSION

The buffering action of humus acids on pH of the reaction media is associated trough intra molecular rearrangement in the anionic part of the complex heteropolar salt between valence and coordination bonded with central nucleus groups.

According to the shown mechanisms

- Buffering action of humus acids on pH in the limits of corresponding "coordinate" capacity depends on the simultaneous presence of both, -COOH and phenols -OH groups.
- The increased amount of phenolic -OH groups in the molecules of the high-humified compounds increases the buffering ability and can compensate the relative excess from liming materials in definite limits, preventing the effect of overliming.

- The shortage of calcium ions excluded participation of these groups in complex heteropolar salts formation and this defines the dynamic character of their participation in similar compounds.
- The ability of taking out some of the hydrogen cations towards -OH groups and their bonding in neutral water molecules, incline to coordinate towards the central cation of the complex compound, compensate the excess of acid groups.
- The depletion of the ability for intra molecular rearrangement in the anionic part of the molecule is a precondition of formation of clay-humus adsorptive complexes using cation bridges with the participation of polyvalent cations. Consequence of this is the reduced ability for ion exchange capacity between soil adsorbent and root system.

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