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DISTRIBUTION OF HEAVY METALS AMONG THE COMPONENTS OF A NEW BIOFERTILIZER RECOMMENDED FOR SOIL REMEDY

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Lucrarea prezintă rezultatele cercetărilor privind evidențierea conținutului de metale grele din diferite tipuri de soluri din Dobrogea (psamosoluri şi soluri nisipoase, sărace în nutrienți), ape uzate epurate şi nămol rezidual utilizate ca materii prime în obținerea unui biosolid compozit cu rol de biofertilizator al acestor tipuri de solur. Luând în considerare valorile limită standard, conform legislației în vigoare, analiza conținutului de metale grele din probele de sol, nămol rezidual şi apă uzată epurată, a condus la concluzia că atât solurile analizate, cât şi cele două tipuri de materii prime nu prezintă depăşiri ale limitelor standard, iar noul biofertilizator, nu aduce un conținut suplimentar de metale grele prin bioacumulare şi nici riscul translocației acestora. Datorită prezenței bioionilor Na, K, Ca, Mg în raport molar optim, biofertilizatorul poate fi recomandat în agricultură ca nutrient pentru îmbunătățirea calității solurilor dobrogene.

The paper presents the results regarding the correlation among heavy metal contents in different samples of Dobrogea soils (psamosoils and sandy soils scanty in nutrients), treated waste water, sewage sludge with samples of a new biofertilizer that could be used for agriculture purposes. Taking into consideration the standard limits according to the legislation in force the analysis of the heavy metal content in soil samples, residual sludge and treated wastewater samples leads to the conclusion that the heavy metal level in the above mentioned raw materials and soils do not exceed standard limits and, therefore, the biofertilizer provides no supplementary heavy metal content by bioaccumulation, neither the translocation risk might take place. Due to the presence of Na, K, Ca and Mg as bioions present in optimal molar ratio, the new biofertilizer can be used as nutrient for the improvement of Dobrogea soils quality.

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1. Introduction

The opportunities for the improvement of agriculture production by using sewage sludge are rather limited by the heavy metal content in sewage sludge and, on the other hand, they should not cause hazardous effects on the soil quality.

These issues are covered by the Directive 86/278/CCE, which was transformed into OM 49/2004 for the approval of Technical Norms regarding the environmental protection and especially that of the soil, when the sludge is used in agriculture. This order was amended in October 2004 by the Order 334/2004 on environmental protection and especially that of the soil, when the sewage sludge is used. The Order 344/2004 revalues the agrochemical potential of sludge, prevents and reduces the harmful effects on soil, water, vegetation, animals and humans, so that it ensures their proper use. Moreover, the Order establishes [1 - 3]:

- the concentration levels of heavy metals such as: Cd, Cu, Ni, Pb, Zn, Hg in soil on which sewage sludge is applied;
- the maximum annual quantities of these heavy metals that can be inside the soil;
- the sewage sludge needs to be treated before being used in the natural environment.

The aim of our work is the evaluation of heavy metals content in different types of soils from Dobrogea, in sewage sludge and in wastewater involved in production of a new biofertilizer devoted to soil remedy [4 - 22].

2. Experimental

Several types of soils (psamosoils and sandy soils scanty in nutrients), sewage sludge and wastewater – primary sedimentation trap and secondary sedimentation trap samples, have been collected in the period 2009-2010 from Dobrogea area (Mamaia – Vama Veche) and wastewater used in a treatment plant from the same area [23].

There were also, a number of 6 biofertilizer samples with the different ratios of composition: vegetal marine biomass (between a minim value 20g until a maximum value 40g), zoobenthos (between 20g and 40g), sewage sludge (between 20g and 40g) and animal charcoal (10g).

Sample preparation

The soil, sewage sludge and biofertilizer as raw material were dried at 105°C, until constant mass. For each raw material, a number of 3 samples with different dried masses were analyzed.

A mixture of concentrated acids was used for mineralization: 5mL HNO_3 + 2mL HF + 2mL $HClO_4$. After the complete digestion, the content of the digestion vessels was decanted in 50 mL flasks to be analyzed.

For the metal content determination, measurements were performed by atomic absorption spectrometry in both Graphite Furnace (GF-AAS) and Flame (FL-AAS). The instrument used for the metal determination was ContrAA 700 from Analytik Jena, Germany, a high-resolution continuum source atomic absorption spectrometer. The instrument used for the Hg determination was DMA – 80, Milestone [24 - 27].

3. Results and discussion

The legal standard norms regarding the heavy metals limits in soil, sewage sludge for agriculture and wastewater are collected in table 1.

Table 1

Heavy metals limits in soil, sewage sludge and waste water [1,2]

Metal	Soils [mg/kg]		Sewage sludge [mg/kg]		Wastewater [mg/dm^3]
	Normal soil	Sensitive soil	Min	Max	
Al	*	*	0.0048	253370	5
Fe	*	*	2	24200	5
Mn	900	2000	6.3	340	1
Cd	1	5	1.96	3.8	0.2
Pb	20	250	0.12	413.56	0. 2
Cu	20	250	0.35	494.55	0.1
Cr	30	300	0.47	349	1
Ni	20	200	22.61	97.97	0.5
Zn	100	700	6.8	648.01	0.5
Co	15	100	*	*	1
Hg	0.1	4	*	*	0.05

* Values not reglemented yet

The results obtained for the ***soil*** samples indicate the following aspects:

- there are no values registered for the ions Cd, Co, Fe and Hg exceeding the standard values (Figure 1);
- for the Cr, Cu, Ni, Pb ions some exceeding values over normal admissible values were registered;
- The highest exceeding content in soils was registered for Zn content, by 20 times higher than the standard values.

Regarding the heavy metals content in ***sewage sludge*** samples, all the metal ions values are bellow the admitted limits, except for Zn and Mn ions, which are over the standard limits for all the samples.

The ***wastewater*** samples present all the heavy metal concentrations bellow the standard limits, with no other special comment.

Statistical analysis (Figure 1a) regarding variation interval of Al ions content in sewage sludge samples reveals that this is quite narrow compared to that registered for soil samples. Moreover, its values in sludge are within lower limits of variation than for soil samples. This suggests that the Al ions content will not lead to irreversible processes of soil degradation because of the compensate mechanisms of the Al effects which are active in these conditions.

A similar comparison of the heavy metal determinations and statistic analysis for soil samples and sewage sludge allow to conclude that the values and variation periods are similar for Cd, Hg, (Fig.1b), while for Co ion significant higher values are registered for sludge samples as compared to soil samples, the source for Co being certainly of anthropic origin (Fig. 1c).

Regarding the content in Cr, Cu, Ni and Pb ions one can notice higher values in sludge compared to soil samples (Fig.1e) the highest difference between variation periods being noticed for Cu, this indicating an intensive accumulation of copper in sludge. A similar behavior is observed for Fe content (Fig. 1d), while for Mn and Zn the content level and variation period are dominant in soil as compared to sludge (Fig. 1f).

The presence of Pb can be assessed to accidental fuel discharge and car washing laundry discharged in the wastewater network.

Regarding the 6 new biofertilizer samples, analysis on AAS were performed for determination of the level of bioions Na, K, Ca, Mg and heavy metals Al, Cr, Cd, Co, Cu, Fe, Hg, Mn, Ni and Pb.

The results obtained for the bioions and heavy metal content in the new biofertilizer samples are represented in figure 2 and can be interpreted as follows:

- the ratio between monovalent bio-ions Na^+ and K^+ is 3:1, while that between monovalent and divalent bio-ions (Ca^{2+}, Mg^{2+}) is in the favor of the first species (1.6:1), even though there is an extra Ca^{2+} content provided mainly from carbonates present in zoobentos shell mollusks;

- the highest concentrations of Na, K, Ca and Mg ions were found in biofertilizer sample 4;

- the Fe and Al content in biofertilizer is approximately 3 times higher than Zn and Cr content, and this high value for Al content identified in all six biofertilizer samples draw attention on the necessity to control carefully the evolution of this ion in biofertilizer fate;

- content of Cu, Pb ions is rather high in all six biofertilizer samples but with some exceeding values for Pb in biofertilizer samples 2, 3 and 6.

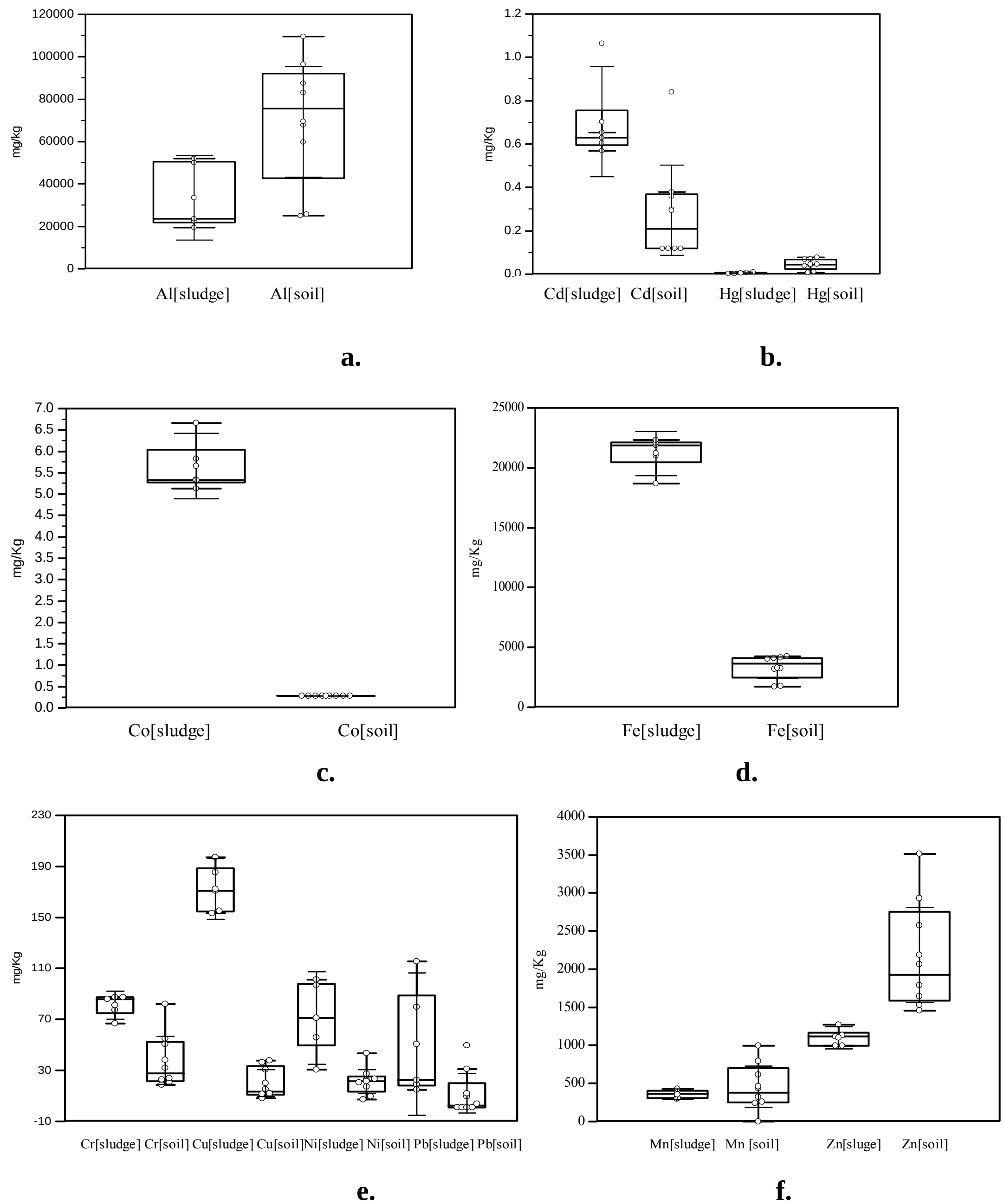

Fig. 1. Statistical analysis of the heavy metal content (mg/Kg) determined in soil and sewage sludge samples (Box-and-whisker means - error bars: 95% confidence interval for the mean): a) All; b) Cd and Hg; c) Co; d) Fe; e) Cr, Cu, Ni, Pb; f) Mn and Zn

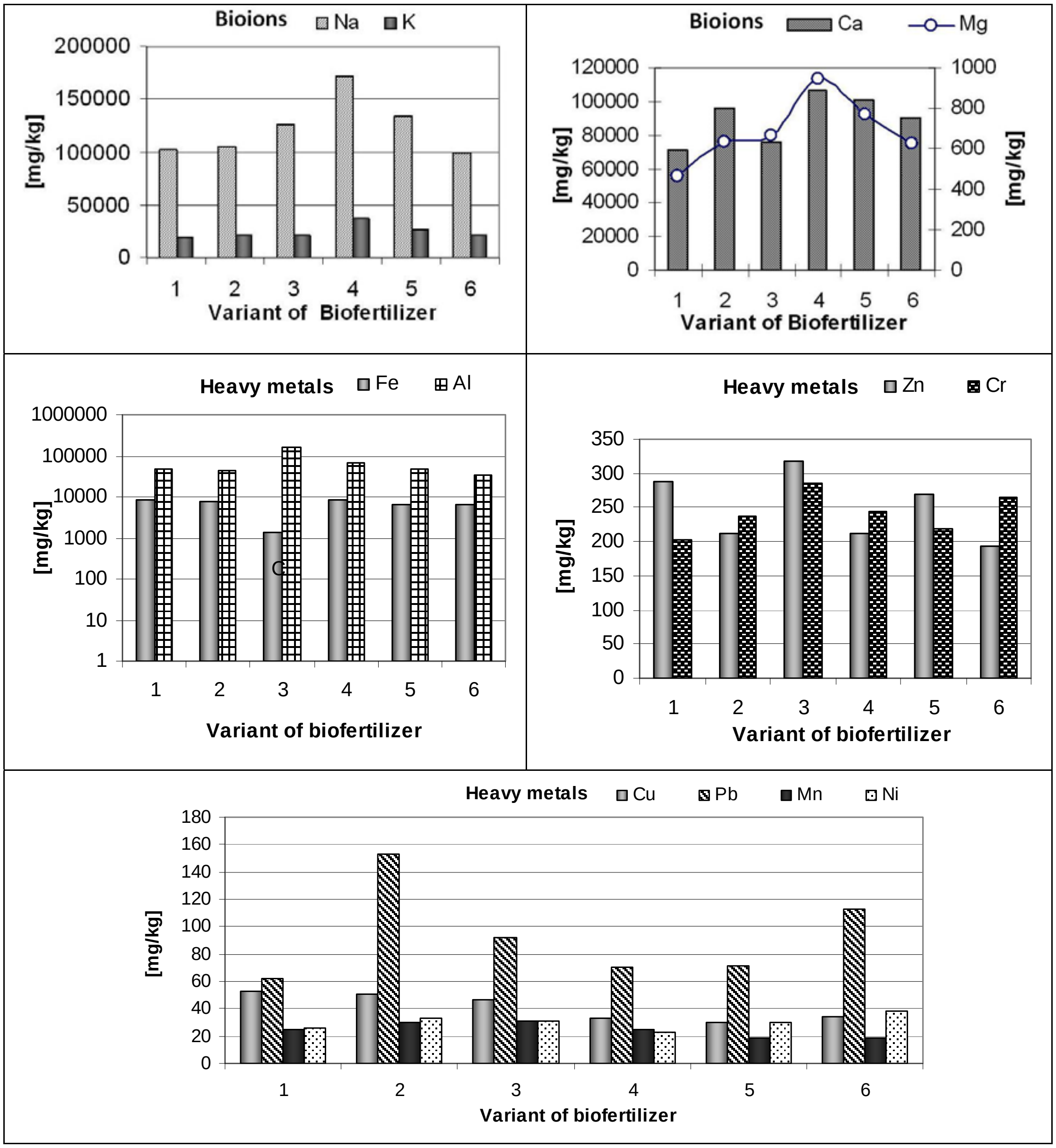

Fig. 2. The bioions and heavy metals content in the new biofertilizer samples

4. Conclusions

Analyses were performed for determination of the level of Al, Cr, Cd, Co, Cu, Fe, Hg, Mn, Ni and Pb from Dobrogea soil samples, sewage sludge, waste water and new biofertilizer samples, for agriculture improvement. The monovalent ions content was found higher than divalent ions content.

In addition with *p*H values which are neutral, the system carbonates-carbonates acid is capable to maintain the requested neutral reaction of the soil. There were not found significant supplementary heavy metal content in Dobrogea soil, sludge, waste water, biofertilizer;

It is recommended carefully attention especially for Al and Zn content in sludge samples, biofertilizer component, because of their high content in Dobrogea soils;

There will not be translocation risks regarding heavy metals for the crops which will grow on amended soils with this new biofertilizer;

The new biofertilizer could be successfully used for agriculture purposes.

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