

The Effect of Applied Organic Fertilizers on the Bioavailability of Heavy Metals in *Lolium Perenne*, Cultivated on Fly Ash Deposits

Smaranda Mășu¹, Neculai Dragomir²

¹ National R & D Institute for Industrial Ecology ECOIND, Branch of Timisoara, 300004 Timișoara, Piata Regina Maria, 1, Romania

² Banat's University of Agricultural Sciences and Veterinary Medicine, 300645, Timisoara, Calea Aradului no. 119, Romania

Abstract

The study aims to monitor the capacity of certain organic fertilizers (volcanic tuff and municipal sludge), applied as such and mixed with volcanic rocks with a high content in clinoptilolite, to determine the covering with vegetation of fly ash deposits resulted from the combustion of lignite in thermal plants. Both biosolids (20 t/ha) and volcanic rock with high clinoptilolite content (5 t/ha) determined the installation of a vegetative layer and diminished the soil metal bioavailability to the *Lolium perenne* plant biomass. When using the organic-zeolite mixture, a synergistic effect is recorded of the two components of the treatment agent and an increase of the biomass with 448%. Moreover, the resulted biomass shows the highest reductions of metal bioaccumulations, of 38-46% for Zn and Fe, of 62% for Cu and between 82-89% for Cr, Ni and Pb.

Keywords: bioaccumulation, fly ash, *Lolium perenne*, organic-zeolite fertilizer.

1. Introduction

The stabilization of solid residues, such as those of fly ash coming from thermal plants, resulted from the lignite combustion, can be done by covering them with a vegetative layer formed of plant species resistant to the high content of heavy metals.

Generally, the toxic action of heavy metals, where such fly ash deposits are lacking organic matter, affects the growth and development of plants by reducing the bioavailability of nutrients and replacing them with heavy metals [1-4].

Introducing certain organic and inorganic materials in the structure of these deposited fly ashes would create a suitable environment for

plant development, as very important primary biological links from which the entire food chain forming in the new ecosystem type will benefit.

The researches showed that applying organic fertilizers, such as municipal sludge, significantly change the physical, chemical and biological properties of the upper layers of the fly ash deposits. These alterations determine the increase of the water retention capacity, microbial activity improvement and the maintaining of a suitable pH. Concurrently, the organic matter from the applied biosolids complexes heavy metals in forms less available to plants. Also, organic matter increase from such deposits and the vegetative layer diminish or stop the deflation, erosion, and severe drying of the upper layer phenomena. Under such conditions, ash deposits can seize significant quantities of organic carbon from the influence zone [5].

Studies performed by Herwijnen et al. 2007 showed that by applying municipal sludge to a

* Corresponding author: Smaranda Mășu,
Tel/Fax 0049(0)256220359 email
smarandamasu@yahoo.com

Lolium perenne culture, cultivated on a soil polluted with heavy metals, metal accumulation in plants was reduced by 80%. When using the green waste compost, heavy metal accumulation in plants was only of 48% [6 - 8].

2. Materials and methods

Researches were done “in situ”, on fly ash deposits coming from coal combustion a thermal plant.

The experiment comprised 6 variants, with parcel surface of 3m², placed according to the randomized block method, in three repetitions. The experimental variants comprised the following treatments, with organic fertilizers: Fly ash, control sample (C), Fly ash + Biosolids (C - B), Fly ash + Tuff (C - T₁), Fly ash + Pillared tuff (C - T₂), Fly ash+ Biosolids + Tuff (C - B - T₁), Fly ash + Biosolids + Pillared tuff (C - B - T₂).

Tuff is an indigenous volcanic rock with zeolite content (approx. 70% clinoptilolite), with a 0.2-2 mm coarseness. The pillared volcanic tuff (called tuff-Aln) was prepared in the (ECOIND) laboratories [7]. This is dispersed as 80% DM aqueous suspension. The volcanic tuff (simple or pillared) quantity was applied in a 5 t/ha dose.

Biosolids, formed from the anaerobic fermented municipal sludge, had when applied a humidity of 89.2%, an organic matter content of 26.4%, 0.83% total nitrogen, 0.75% phosphorous and a 6.2 pH. Metal content is presented in Table 1.

Biosolids quantity was distributed on the fly ash parcel with specific devices and incorporated along with the other inorganic materials (pillared indigenous tuff, in a 20 t/ha dose.

Bioavailability alteration of metals (Cr, Cu, Fe, Ni, Pb, and Zn) from the fly ash was evaluated by cultivating *Lolium perenne* species - TM-81 variety, and by a test based on the accumulation of these metals in the aerial part of plants.

Soil samples analysis was done to determine the total iron, zinc, copper, chromium, nickel and lead concentrations according to the analysis method: the heavy metals were extracted from the soil samples by heating with Aqua Regia for 2hrs, at reflux. After interrupting the heat, the system was left in stand-by for 16 hrs. Then the samples were diluted in a flask with distilled water to exactly 50 ml. Plant tissues were thoroughly washed with distilled water to remove any soil particles attached to plant surfaces. The tissues were dried (105°C) to a constant weight. Plant samples with precise weight are then brought to 550°C; to the residual materials 5ml of concentrated hydrochloric acid are added, samples are maintained 30 minutes on the dry sand bath. After filtering those in a paper filter with small porosity, were taken to a calibrated flask with hydrochloric acid 1:1 solution. Plant and soil extracts analysis was done using a spectrophotometer, Varian Spectra AAS.

Table 1. Heavy metal content from the anaerobic fermented municipal sludge (biosolids).

	Metal content mg/kg DM							
	Fe	Mn	Cu	Cd	Cr _{tot}	Zn	Ni	Pb
Biosolids	2353.7	314.9	425.9	209.3	134.7	351.0	14.7	175.2

Table 2. Metal concentration from the experimental variants of treated and untreated fly ash, cultivated with *L. perenne*.

No.	Experimental variant	Heavy metal content from top soil Mg/kg DM					
		Cr	Cu	Fe	Ni	Pb	Zn
1	C(control sample)	85.8	63.8	4636.4	50.1	12.9	65.8
2	C-T1	85.3	62.6	4604.5	53.6	13.1	69.1
3	C-T2	84.4	61.6	4622.7	49.6	12.7	72.0
4	C-B	85.6	65.9	4711.9	49.3	14.1	82.6
5	C-B-T1	84.0	66.1	4636.4	48.0	12.9	83.3
6	C-B-T2	84.6	67.1	4731.8	50.1	13.7	84.5
	Average	84.9	64.5	4657.2	50.1	13.2	72.6

The detection limit of the device is 0.001 mg/l. Studies of quantitative ratios between

plants species from a phytocenosis allows finishing of ecological research onto any biocenosis. From a

practical point of view it is searched the biomass production, the rate of this process productivity and its contribution to the ecosystem stability and biodiversity. To achieve this, the following indices were studied: abundance and supremacy, density, frequency, constancy and vitality. The abundance is given by the number of plants from the species growing in a phytocenosis. The abundance is an expression of plants density and vitality, but also of favorable environmental conditions.

Supremacy expresses the degree of soil covered with plants, resulted due to aerial parts projection on soil. Because the abundance is in direct relation with supremacy, a supremacy-abundance index was proposed by Braun-Blanquet, taking into consideration the following Cover – Abundance Scale[8].

Table 2 shows the concentration of metals from the upper layer of the treated and untreated fly ash, used for the experimental variant.

3. Results and discussion

Covering degree of *Lolium perenne* at harvesting on 15.06.2010, according to the Braun-Blanquet scale is presented below:

Fly ash – covering degree of 20%, Level 2, ranged between 5-25%; Fly ash -Tuff – covering degree of 50%, Level 3, ranged between 25-50%; Fly ash -Biosolids-Tuff – covering degree of 55%, Level 4, ranged between 50-75%; Fly ash -pillared tuff, Fly ash –biosolids; Fly ash -biosolids-pillared tuff – covering degree 60%, Level 4, ranged between 50-75%.

Simple volcanic rock addition to the fly ash experimental variant as well as to the biosolids fertilized fly ash determined the doubling of plant density according to the Braun-Blanquet scale classification. Biomass quantity increase on these experimental variants is of 145-166%

compared to the quantity of biomass harvested from the experimental variant fly ash, as concluded from Table 3. Plants from the volcanic rock treated variants are more vigorous compared to those grown on fly ash experimental variant(control sample). Moreover, from Table 4 we conclude that plants grown on these two experimental variants show a higher DM content (17.15-19.3%) vs. those grown on the C variant(control sample) (15.43%).

In the case of the experimental variants whose upper ash layer is treated with C-B fertilizer, with pillared volcanic tuff as such, C-T₂, or mixture of organic fertilizer and pillared tuff, plant density triples according to the Braun-Blanquet scale vs. the density of plants grown on experimental variant C(control sample) biomass quantity increases by 226-290% when the organic fertilizer and modified volcanic rock are separately added. When the fly ash is treated with the organic-zeolite mixture, a synergistic effect of the two components of the treatment agent and biomass quantity increase by 448% is recorded.

In Figure 1 is shown to reduce the amount of metals bioaccumulated in the aerial part of plants harvested from treated upper layer of fly ash vs. biomass harvested untreated experimental variant, control sample

The highest accumulation of metals in the plant tissues is for the culture from the experimental variant C, control sample.

Inorganic material addition of pillared and unmodified tuff determines the reduction of Cr, Cu and Fe content, and for the other metals their influence is insignificant.

Organic fertilizer addition determines for some metals the reduction of bioaccumulation in the plant tissues (Cr, Ni, Fe and Pb), but for others it determined an augmentation of the bioaccumulation (Cu and Zn).

Table 3. Phytomass quantity of *Lolium perenne* harvested from the experimental variants % biomass increase vs. C- control sample

No.	Experimental variant control sample	Biomass quantity Kg/ha	% Biomass increase vs.C-control sample
1	C ()	805	-
2	C-T1	1169	145
3	C-T2	2340	290
4	C-B	1823	226
5	C-B-T1	1337	166
6	C-B-T2	3607	448

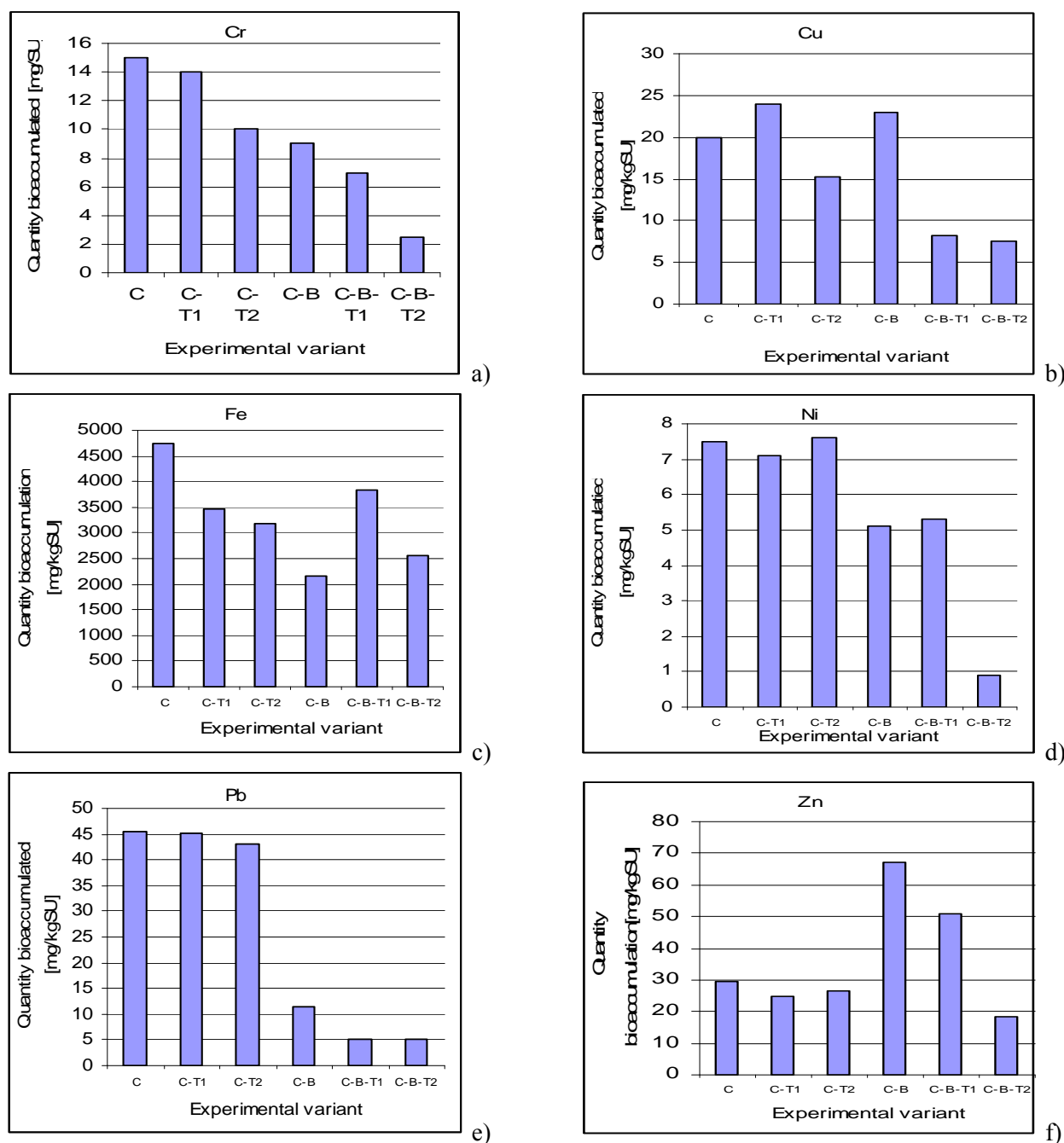


Figure 1. Metal quantity bioaccumulated in the *Lolium perenne* plant tissue vs. the treatment applied to the upper layer of ash.

When using the treatment with organic-zeolite fertilizers a general synergistic effect of metal reduction from *Lolium perenne* plant tissues is recorded. The use of organic-zeolite fertilizer formed of biosolids and pillared volcanic rock shows the highest reductions of bioaccumulation of metals from plant tissues, of 38-46% for Zn and Fe, of 62% for Cu and between 82-89% for Cr, Ni and Pb.

4. Conclusions

Volcanic rock addition, as such, both to the fly ash experimental variant and fly ash fertilized with biosolids variant determined the doubling of plant density according to the Braun-Blanquet scale classification. Biomass quantity increase is of 145-166% compared to the biomass quantity harvested from the fly ash experimental variant. Also, the

treatment determined a reduction of Cr, Cu and Fe content.

The treatment of the upper fly ash layer with biosolids, with pillared volcanic tuff as such or with organic fertilizer mixture and pillared tuff determined the increase of plant density by three times according to the Braun-Blanquet scale vs. control sample. Biomass quantity increases by 226-290% when the organic fertilizer and pillared volcanic tuff are separately added. When using the organic-zeolite fertilizer a synergistic effect of the two components of the treatment agent and biomass quantity increase by 448% is recorded. Moreover, the resulted biomass shows the highest reductions of metal bioaccumulation of 38-46% for Zn and Fe, by 62% for Cu and between 82-89% for Cr, Ni and Pb.

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