

# The Use of Adsorbent Materials of Improving the Characteristics of Polluted Soils, Part 2 the Bioaccumulation of Metals in Plants Used in Phytoremediation Processes

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## Abstract

The study covers the advantages of phytoremediation processes of soils heavily polluted with total petroleum hydrocarbon (TPH) with the use of *Linum usitatissimum* (flax). To increase the potential development of technical crops on TPH soils polluted with  $74.12 \pm 3.5 \text{ g} \cdot \text{kg}^{-1}$  D.M., the contaminated soils were amended with fly ash; the ratio of polluted soil: fly ash 12:1 wt./wt. and fertilized with sewage sludge. The degree of accumulation of Fe in the stems was 21-33% higher than in the control sample and 6-27% in the seeds; the accumulation of Mn in the stems was 13.5-30% higher than in the control sample and 8-17% in the seeds; the accumulation of Cu in stems was 17-6% higher than in the control sample and for seeds 20-60%; the accumulation of Zn in stems was 13-27% higher than in the control sample with 49-63% in the seeds. In the harvested plant tissues from the studied variants the content of heavy metals Cd, Cr, Pb and Ni was less than the detection limit. Monitoring bioaccumulation of heavy metals in aerial plant tissue was needed to decide the sector where the biomass harvested from TPH polluted soil covered with vegetation.

**Keywords:** phytoremediation, total petroleum hydrocarbon

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## 1. Introduction

In soils contaminated with petroleum products there are formed soil conglomerates soaked with oil pellicles of non-polar character. Water does not adhere to these formations and air does not penetrate. Conglomerates are deficient in oxygen and inert in terms of microbial activity because: microbial consortia have ceased operations in these highly polluted environments, toxic [1-2]. Fly ash is a material with high agronomic

potential. Due to the high content of salts of Ca, Mg, of some metals that can act as micronutrients in plant development, in many cases ash can be successfully used as agricultural amendment, in order to determine the high productivity of crops. The limits of using fly ash as agricultural amendments can refer to: low capacity to retain water, the presence of micro elements in excess, the high capacity of correction and buffering the pH of the soil, etc. Mineralogical analysis shows that 70-90% of the fly ash particles consist of spheres based on amorphous aluminium silicates. The spheres may contain quartz and clays. Therefore, amorphous forms have much higher specific surface area than the crystalline ones and, as well, they have positive and negative surface

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charges which can bind electrostatically to chemical species in the soil solution. Amorphous forms are, therefore, effective adsorbents for various classes of reactive substances. Amorphous aluminium silicates can reactivate organic matter produced during the growth of plants in that certain space. They help C secretion and soil enrichment with organic matter and microbial population respectively. The fine texture of fly ash determines rapid loss of water. Mixing organic matter with fly ash can increase its structural stability and reduce water loss by its infiltration through the soil profile [3-4]. Furthermore the use of materials with the same water retention capacity as natural zeolites increase its structural stability and reduce water loss of destroyed soil. Application of fly ash on soils determines the increase of the extractable ions concentration by ion exchange. The degree of soil enrichment with pollutants depends on the added amount and on the adding rhythm. On the other hand, fly ash could be an essential admixture regarding the compaction of soils depleted of essential trace elements for plants, such as Mg, Ca, Zn, etc. It can be noted, however, in plants grown on fly ash dumps per se, or soils mixed with fly ash, a significant accumulation of metals. On the contrary, concentration of elements such as Cu, Cd, Pb may decrease considerably in plant tissue of the plants grown on these soils. These aspects are due to the nature of the ash, which causes precipitation of these metals as hydroxides [5-6].

The purpose of the studies was: 1. Identification of a tolerant plant species, to develop optimal layers for masking TPH polluted land, in the phytoremediation process. Moreover, the used species must not show properties of hyperaccumulation of toxic metals in the tissues; 2. Indication of possible uses of resulted biomass.

## 2. Materials and methods

The contaminated soil with TPH ( $74.12 \pm 3.50$  mg·kg<sup>-1</sup> D.M.) was amended with fly ash; the ratio of polluted soil was: fly ash 12:1 wt./wt. In the present study stabilized sewage sludge was used as fertilization agent. It contains, in addition to nutrients necessary for the growth of plants C, N, P, some toxic metals as *i.e.* Cu, Cr, Zn, Ni, Pb. The used biological sludge contains many species of bacteria recognize have the ability to

metabolize certain components of crude oil with non-polar and polar structures. As amendment, there was used fly ash from the ash deposit in the western part of the country, which in turn contains toxic metals as Cu, Cr, Zn, Ni, Pb. Increase of water retention capacity of the TPH polluted soil was achieved by using indigenous tuff from the Mirsid career, with 0.2-2.0 mm granulation. The cultivated plant was common flax (*Linum usitatissimum*). It belongs to the family *Linaceae* and appears as an herbaceous plant with a short or high branched stem, in which the technical length (the unbranched part) is the richest in fiber. Preparing experimental variants BI-1, BI-2, BI-3, BI-4 by soil fertilization in the absence/presence of fly ash and indigenous volcanic tuff amendments, were made as shown in Use of some adsorbent materials to improve the characteristics of polluted soils part 1.

The control version was the variant of arable soil cultivated with flax, M. Each experimental variant contains three replicas. Determination of ash and sewage sludge characteristics was performed according to receipts submitted by Mășu, 2012 [7]. Plant tissues were thoroughly washed with deionized water to remove any soil particles attached to plant surfaces. Plant sampling was done in agreement with the standardized methodology.

## 3. Results and discussion

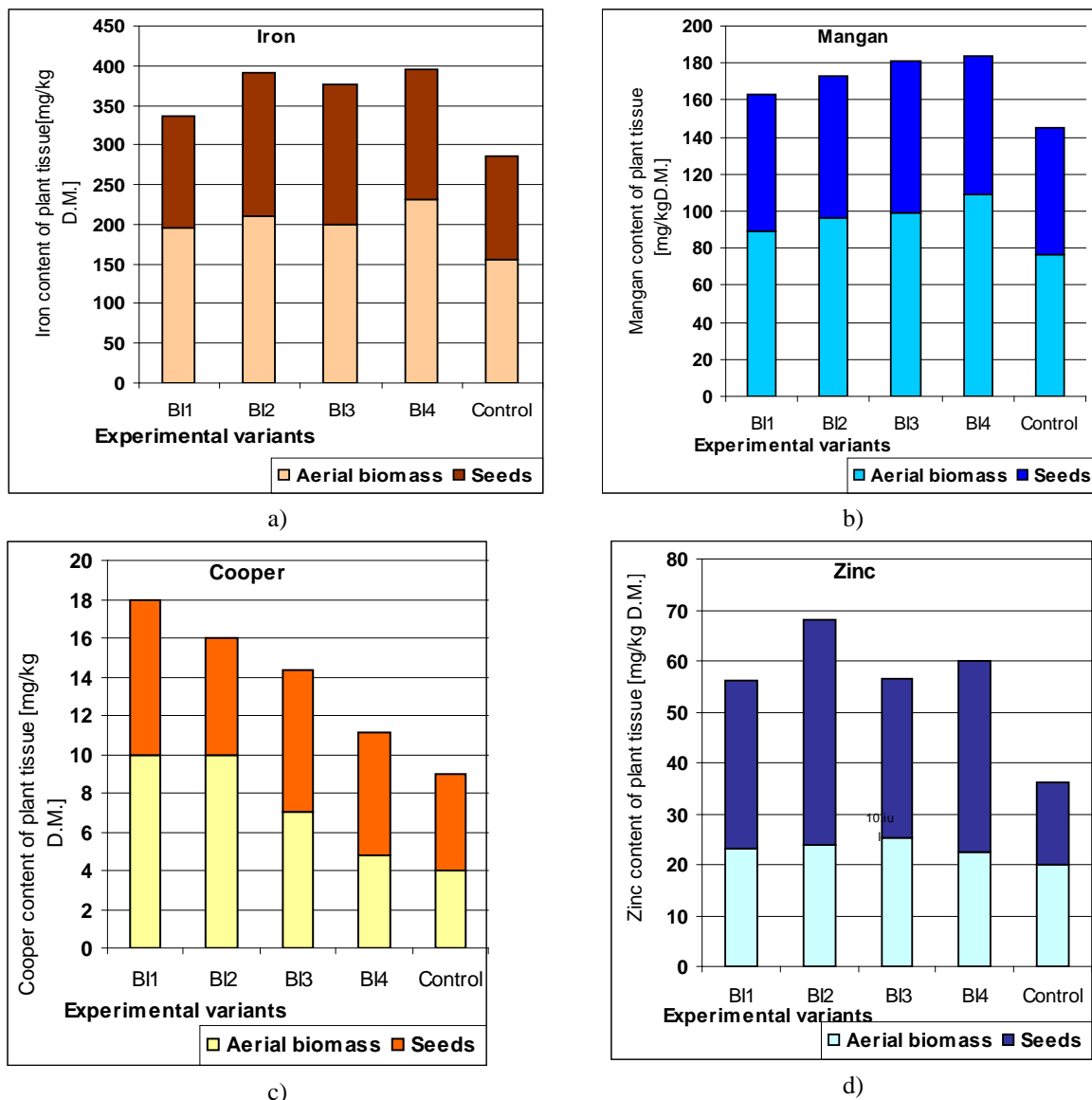
Table 1 presents the characteristics of the fertilizer agent and of the fly ash amendment.

In TPH polluted soil there are brought along with the fertilizer agent and the amendment used, different quantities of toxic metals such as Cu, Cr, Zn, Ni, Pb. In harvested plants, following the process of phytoremediation there were accumulated greater amounts of metals than in untreated soil samples from the M variant. The presence of ash on harvested crop soils causes increased bioaccumulation of metals in plants [8]. In Figure 1 there are presented the quantities of iron, manganese, copper, zinc metals bioaccumulated in strains (the technical part) and flax seeds grown on different experimental variants fertilized with sewage sludge and amended with ash or fly ash and indigenous volcanic tuff.

**Table 1.** Characteristics of the fertilizer agent and fly ash amendment

Organic matter[%]	Nutrients (%)		Metals content (mg·kg <sup>-1</sup> D.M.)						
	N	P	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Sewage sludge									
59.8	1.138	1.107	64.2	72.4	1830.6	150.0	68.6	19.6	124
Fly ash									
0.2-2.0*	< 0.05	< 0.02	79.5	79.5	2150.3	163.2	80.1	18.5	180

\* unburned coal, non-bioassimilable



**Figure 1.** Content of metals accumulated in flax stems and seeds grown in different experimental variants: a) Iron content, b) Manganese content, c) Copper content, d) Zinc content

It is seen from Figure 1a that for the studied variants, fertilized with sludge mixed with ash, Fe content accumulated strains increases with 21.0-33.2% and with 6.4-27.0% in seeds compared to the iron content determined in yields obtained on

the control variant. It is seen from Figure 1b that the studied variants fertilized with sludge mixed with ash in the absence/presence of tuff, there was reduced the Mn content accumulated in strains with up to 13.4-29.4% and 8.1-17.1% in seeds

compared to the manganese content in crop yields from the control version. The amount of copper accumulated in the aerial parts of the plant was 10 times lower than the amount of iron. It is seen from Figure 1c that the use of large amounts of sludge caused the highest accumulation of copper in the aerial part. Addition of volcanic tuff in the variant treated with fertilizer and fly ash has reduced bioaccumulation of copper content from the stalk with 31.4% and 13.6% reduction in seed v. metal content of harvested stalks from fertilized variant in the absence of tuff. The amount of zinc accumulated in plant stems and seeds were 13.0-21.2%, respectively 46.8-63.4% higher, vs. metal content of harvested stems from the control version. Yet, there can be seen from the figures that bioaccumulation of Cu was  $\leq 10 \text{ mg}\cdot\text{kg}^{-1}$  D.M. in both strains as well as in seeds, the amount of Zn was  $\leq 37.5 \text{ mg}\cdot\text{kg}^{-1}$  D.M., the amount of Mn was  $\leq 108.0 \text{ mg}\cdot\text{kg}^{-1}$  D.M., the amount of Fe was  $\leq 232.0 \text{ mg}\cdot\text{kg}^{-1}$  D.M. It is noted the fact that in seeds and stems, the amount of toxic metals Cd, Cr, Ni and Pb was below the limit of detection. In order to use the harvested parts of the plant, it is recommended careful monitoring of bioaccumulation of metals in both strains as well as in seeds, following the crops to be routed to the appropriate activities sectors in accordance with regulations.

#### 4. Conclusions

Plants of *Linum usitatissimum* used for phytoremediation of soils heavily polluted with petroleum products have not gained, in a complete cycle of vegetation, toxic metals Cd, Cr, Ni and Pb in topsoil fertilized with sewage sludge and amended with fly ash. In return, in the presence in topsoil of iron, manganese, copper and zinc metals brought by the fertilizer mixture consisting in fly ash and sewage sludge, plants showed a tendency to their bioaccumulation in both stems as well as in seeds. The amounts of Mn and Fe bioaccumulated in the harvested plants, from phytoremediation variants, were up to 29.4-33.2%

higher than the amounts bioaccumulated in plants grown on control soil, and the amounts of Cu and Zn were up to 60% and respectively 63.4% higher. To use the harvested stems and seeds of the plant used for phytoremediation, *Linum spp.*, it is recommended careful monitoring of bioaccumulation of metals. Crops must be routed to the appropriate activities sectors, in accordance with regulations on concentration of metals in the tissues.

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