ECOLOGICAL PHYTOSTABILIZATION OF FLY ASH DUMPS WITH *Salix spp*. CROP

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Abstract

In this study, we followed a strategy for vegetation fly ash dumps. For this purpose *Salix spp.* was used. This plant was chosen deliberately in order to form, in time, a stable and health ecosystem. The resulting biomass can be used as a renewable energy source. The experiment was performed in situ, in a delimited compartment, from a power plant fly ash dump. *Salix spp*. cultures were monitored for 18 months on soils fertilized with 25 t/ha sewage sludge anaerobically stabilized. From experimental studies, it was found that the species *Salix. spp*. developed similar to a culture performed on unpolluted land. In the *Salix. spp*. burning strains ash, it was found no accumulation of Pb and Cd. Burning *Salix spp.* ash included Cr, Ni and Cubetween 10 - 30 mg/kg dried matter; Mn and Fe between 178- 313 mg/kg dried matter. Thus, by using species *Salix spp.* for phytostabilization, fly ash dumps can be made ecological, restoration of ecosystems and landscape and obtaining alternative energy.

Keywords*: alternative energy sources, ecological phytostabilization, Fly ash, Salix spp.*

1. Introduction

Fly ash and slag management issue is very topical nationally and internationally as the largest share of thermal stations is occupied by the solid fuel (combustion of fossil coal). Coal combustion results in 10 -30% by-products, mainly ashes. In recent years there have been research to use fly ash in several areas: in addition to the cementing, stabilize materials as the basis for roads, land consolidations, recovery of land as agricultural soil amendment. In developed countries some amount of fly ash produced annually is re-used, but it is still a big difference between the amount produced and used [1,2].
In Romania the situation is even more unfavourable in terms of valorisation of fly ash and slag products.
The most common fly ash and slag management consists of final disposal on land. Currently, in Romania there are 108 deposits of ash and slag occupying approx. 2,800 ha [3]. This method of ash disposal leads to the degradation of large areas of land and is one of the major environmental problems facing both developed countries and our country.
Fly ash and slag deposits contain millions of tons of inert inorganic material, lacking nutrients that can ensure the initiation and maintenance of topsoil, leading to the degradation of natural biotope. The absence of vegetation cover on deposits of ash and slag increases their instability to the impact of weather conditions (precipitation, wind, temperature differences) [4] leading to environmental pollution in the vicinity of the dump. As such, the restoration of soil in areas where there are deposits of ash and slag became a requirement of the communities in the area [5, 6].
The effort to cover deposits of fly ash and slag with plants and/or shrubs resistant to hostile environment is common with authorities and owners of such dumps and aims to restore the

landscape of the area on the one hand and limiting dispersal pollutants on the other hand [7, 8, 9, 10].
In this context it is proposed to phytostabilize the ash and slag deposits by using energy crops (*Salix spp.)* and energy valorisation of the obtained crop. The use of energy crops is in line with the Directive 2009/28 / EC on promoting the use of renewable energy.
Since the harvest *Salix spp*. is considered an important source of renewable energy, this study aims at assessing the accumulation of metals (Fe, Mn, Cu, Cr, Ni, Pb, Cd and Zn) in willow crop. The quantities of metals accumulated in crop willow are found in the resulted ash from combustion.

2. Materials and Methods

As part of the experimental study, two in situ experimental plots were set up, in a compartment of an fly ash and slag landfill that was temporarily closed. The experimental plots were fertilized with stabilized sludge resulted from a municipal wastewater treatment plant in the presence solid prebiotic preparation (seaweed extract), *(group SA and sa)* and absence of a solid prebiotic preparation (seaweed extract), *(group S and s).* The energy crop that was cultivated was *Salix spp*., Inger variety.

Determination of metals (Cd, Cu, Cr, Ni, Pb, Zn, Mn and Fe) from the ashes of *Salix spp*. was done according SRISO 11047-99. The method used atomic absorption spectrophotometry in order to determine metals from ash extracts in aqua regia prepared in compliance with ISO 11466-99. An atomic absorption spectrophotometer type Avanta was used.

Determination of uptake coefficient for metals from soil by *Salix spp.*
The uptake coefficient (an indicator introduced by US EPA) is the ratio between the amount of metal accumulated in the harvest of *Salix spp* grown on experimental plots (deposits of slag and ash containing metals), Q_P, and the amount of metal within the same plant species grown on control plots (energy plants nursery),Q_M, ($UC = Q_P / Q_M$)

3. Results and Discussion

Experimental studies and research conducted aimed at the following:
- Determining the capacity of accumulation of metal (Fe ,Mn, Cu, Cr, Ni, Pb , Cd and Zn) in *Salix spp*. crop;
- Determination of metals taking over from the soil by *Salix spp* grown on ash and slag storage vs. the ground control (nursery)
- Quantitative determination of metals in the ash resulted from burning crop *Salix spp*. coming from the deposit of ash and slag and burning *Quercus cerris*

A. The metal accumulation capacity (Fe ,Mn, Cu, Cr, Ni, Pb , Cd and Zn) in crop *Salix spp.*

Figure 1 shows the amounts of metals determined in ash obtained by burning crop *Salix spp.* since the 1st year of vegetation (Culture I) and the 2nd year of vegetation (Culture II , after 18 months of initiating culture of *Salix spp*.)
Samples analysed in experimental studies and presented in this paper represent the average of three samples.

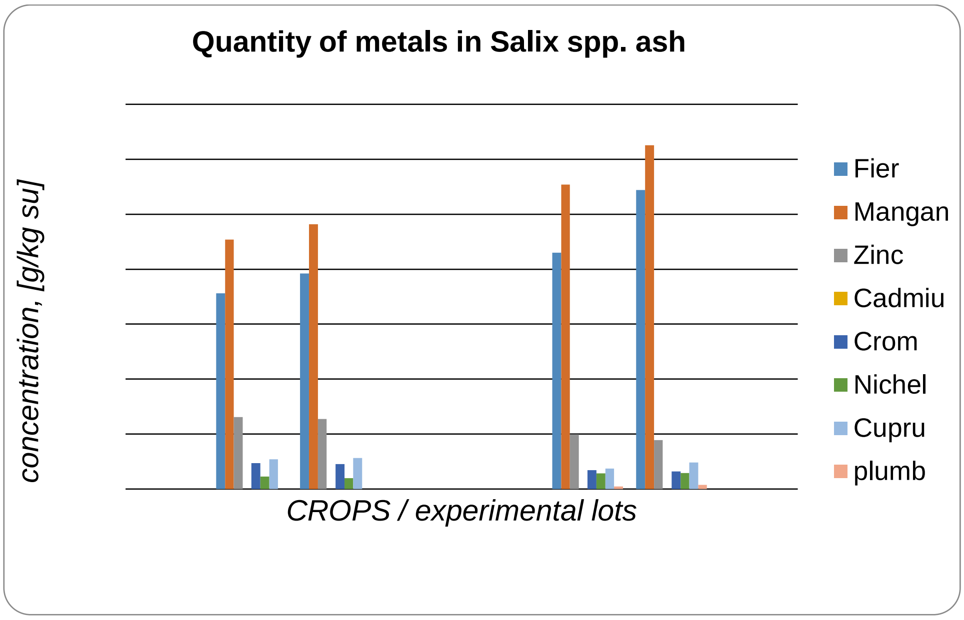

Figure1. Comparative analysis of metal concentration in the ash obtained by burning the *Salix spp*. crop during 2 years of vegetation.

By analysing the obtained results, the harvest *Salix spp* after the first year of vegetation shows a metal storage capacity similar to that determined after the 2nd year of vegetation.
Concentrations of metals in wood ash *Salix spp*. are similar for the two experimental versions of the same crop.
In both crops most abundant metal found in the ashes of *Salix spp*. are Mn and Fe, the concentrations ranging between 178 and 313 mg/kg dm. Accumulated Mn concentration is higher than that of Fe.
Ash contains small amounts of Cr, Ni and Cu concentrations ranging between 10 and 30 mg / kg dm, the smallest amount is recorded in the case of Ni, about 10 mg / kg dm.
Salix spp crop does not accumulate Pb and Cd. Concentrations are very low or even below the detection limit.
The prebiotic solid preparation has no influence on bioaccumulation of metals in crop *Salix spp.*

B. Determination of uptake coefficient of *Salix spp* from the deposit of ash and slag vs. the controls

This parameter can highlight the affinity of *Salix spp*. in case the topsoil shows a high concentration of metals. The taking over coefficient (UC) express the degree of accumulation of metals in *Salix spp.* crop grown on land polluted vs. the degree of accumulation of a control crop (culture *Salix spp*. from an energy plant nursery).
Coefficients of metal taking over are shown in Table 1 for Fe, Mn, Cr, Cu, Cd, Ni, Pb and Zn in *Salix spp*. crop (S-UC1, UC2 and UC3-S-S). The coefficients show-the amount of metal taken from the harvest of *Salix spp* in the 2nd year of vegetation in the upper deposit of ash and slag (experimental groups) fertilized with sludge stabilized, 25 t/ha, and the amounts of heavy metals within controls for the same type of culture and development phenophase. Analyses were conducted on the three control samples of *Salix spp*. from three different control lands.

Table1. Metal uptake coefficients in the harvest of *Salix spp.* from the ash and slag landfill fertilized with stabilized sludge

Metals	***UC-S***		
	UC1-S	***UC2-S***	***UC3-S***
Iron	1.7	1.9	2.2
Manganese	1.6	2.1	2.5
Zinc	1.5	1.7	1.6
Cadmium	-*	-*	-*
Chrome	1.3	1.0	1.4
Nickel	1.2	0.8	1.1
Copper	1.7	1.5	1.4
Lead	-*	-*	-*

** - metals undetected in the harvest of Salix spp.*

From the comparative analysis of the uptake coefficients of heavy metals in *Salix spp*. crop of the surface layer of the deposit of ash and slag calculated against the amount of metals accumulated in crops *Salix spp*. from the 3 control soils (table 1), the following findings can be highlighted:
- In all three cases analysed UC values are higher than unit, which means that willow crop accumulates amounts of metals greater than those grown on control soils.
- UC values for Mn, Fe and Zn are higher than 1.5; 2.5 was registered for Mn, which highlights that *Salix spp*. works as a bioaccumulation of Mn, Fe and Zn.
- For Cr, Ni and Cu, UC values are less than 1.5 suggesting that the 2 crops of *Salix spp*. from the deposit of ash and slag and nursery accumulate similar amounts of these metals. This confirms that *Salix spp*. shows less capacity to bio-accumulate Cr, Ni and Cu.
- Pb and Cd were not detected in crop *Salix spp*. harvested from the experimental crops or nursery crops.

C. Quantitative determination of metals in the ash from the burning mass of *Salix spp.* crop coming from the deposit of ash and slag and burning *Quercus cerris*

Figures 2 and 3 show the comparative amount of metals in the ash from burning crop *Salix spp* coming from the experimental groups *vs*. ash resulting from the combustion of burning *Quercus cerris*
It results that the ash from the combustion of *Quercus cerris* contains much higher amounts of Fe and Mn compared with ash obtained from burning crop *Salix spp*. from the experimental groups. Wood crop *Quercus cerris* acts as a bio-accumulator for Fe and Mn like *Salix spp*. However, the concentrations determined in the ashes of *Quercus cerris* are 30-40 times higher for Fe and 6 to 10 times higher in the case of Mn.
Zn accumulated amount is more than 2.7 times in the case of *Salix spp*. ash vs *Quercus cerris* ash.
The quantities of Ni and Cu found in the ashes of *Salix spp*. are similar to those found in the *Quercus cerris* ash.

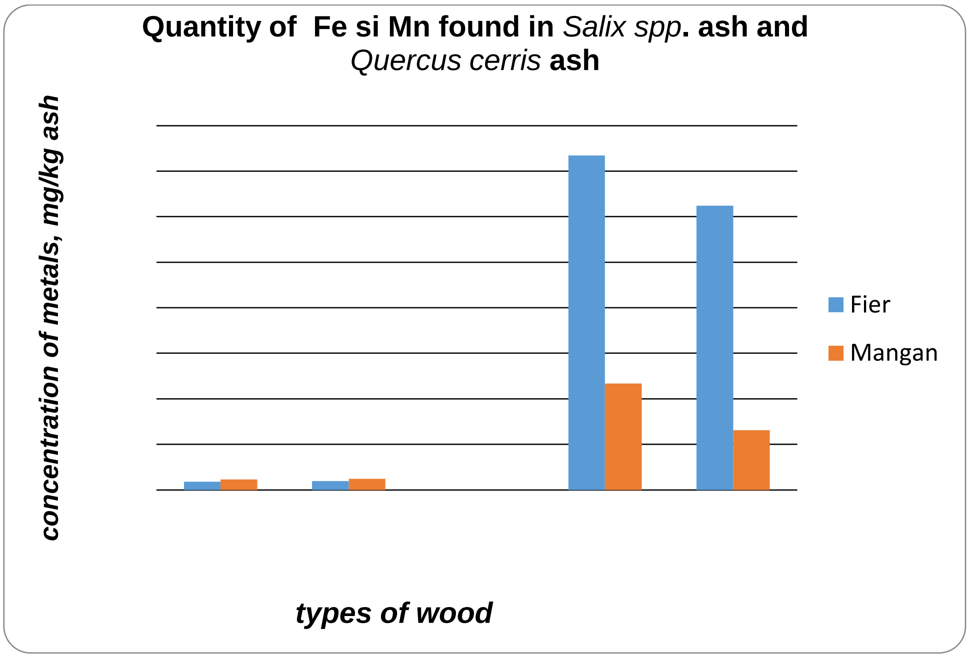

Figure 2. Quantity of Fe and Mn in *Salix spp*. ash (grown on the ash and slag landfill) vs. Quercus cerris ash

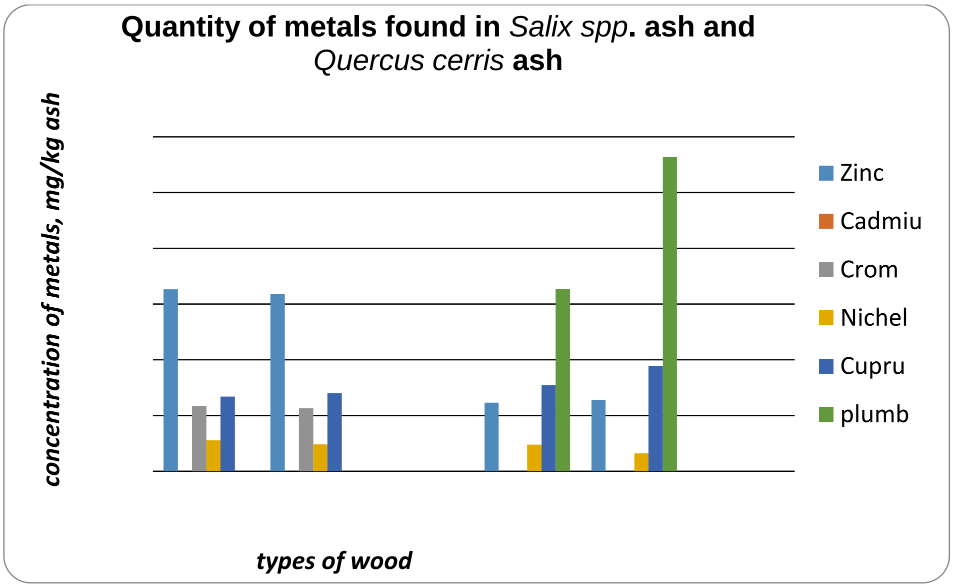

Figure 3. Quantity of Zn, Cd, Cr, Ni, Cu, Pb from *Salix spp* ash (grown on the ash and slag landfill) vs. *Quercus cerris* ash

Both *Salix spp* ash and *Quercus cerris* ash contains no cadmium concentrations, the detected concentrations was below the detection limit.
Salix spp. ash does not accumulate Cd and Pb, and the *Quercus cerris* ash does not accumulate Cd and Cr.

4. Conclusions

Experimental studies were carried out over a period of 18 months from the initiation of cultures *Salix spp*. (2 years of vegetation), in situ, in an ash and slag landfill temporarily closed.

Salix spp. harvest accumulate Mn, Fe, Zn, Cu, Ni showing a degree of greater accumulation of Mn (between 227 and 313 mg/kg ash), Fe (between 178-272 mg/kg ash) and Zn (between 45-65 mg/kg ash).
The addition of prebiotic (solid algae extract) does not influence the storage capacity of metals in crop *Salix spp*.
Uptake coefficient values are higher than unit, which means that *Salix spp*. crop grown on the ash and slag landfill accumulates amounts of metals greater than those grown on control soils (in the nursery). This is explained by the fact that *Salix spp*. behaves like a bio-accumulator for Fe, Mn, Zn Cu, Cd and does not accumulate Ni and Cr even on land that shows higher concentrations of these metals.
After 2 years of vegetation, *Salix spp*. crop coming from the ash and slag landfill accumulates double of the amount of Fe and Mn, with 60% more Zn, 36% more and 20% more Cr as compared to *Salix spp*. harvest from a nursery over a similar vegetation period.
By comparing the concentrations of metals in the ash coming from *Salix spp*. ash and slag landfill with those of MAPPM Order 756/1997, one can notice that these values are around the common figures for soil.
Also concentrations of metals from the ashes of *Salix spp*. are below the admitted values within Order 344/708/2004followed up by MMGA 27/2007 approving the technical norms for environmental protection, and in particular of the soil when sludge from sewage treatment plants is used in agriculture.
Salix spp. crop initiated and developed on a deposit of fly ash and slag can be energetically used taking into account the metal content existing in the ash.

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