Eco-Technological Solutions for the Remediation of Polluted Soil and Heavy Metal Recovery

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Additional information is available at the end of the chapter

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1. Introduction

Increasing industrial activities and the lack of appropriate measures to counteract its effects are causing a progressive pollution of air, water and soil with heavy metal emissions. Studies have shown that after the downturn of the industrial activity of metallurgical plant, as is in case of the industrial platform of Targoviste (Romania), heavy metals do not persist in air or water, but tend to concentrate especially in soil and sediment. The heavy metal concentration exceeding the threshold in soil can be considered as risk for human health and remediation technics should be applied to decrease the metal content in soil. The classical methods of soil remediation are expensive and some of them involve the removal of huge volume of soil. An alternative of such methods are the bioremediation methods which involve only eco-friendly materials and procedures, lead to metal recovery with minimal impact on the environment and are cost-effective.

Phytoremediation is a process which uses green plants to remediate the soil polluted with heavy metals or other contaminants. The use of different species of plants in the bioremediation process of polluted soils is an adequate option, with minimal influence over the environment, without destroying the soil, which also provides the opportunity to recover the heavy metals. Phytoremediation is a cheaper method, by 50-80% compared to other methods of bioremediation [1]. The disadvantage of this method is that it can be a much more slowly process of remediation, requiring several seasons of plant growth. The contaminants may reduce the growth of plants and the resulted biomass, enriched with heavy metals, is potentially harmful in the food chain.

Through the application of phytoremediation on heavy metals polluted soils, the resulting plant biomass will have a high content of toxic metals [2]. This biomass is considered waste and requires controlled and responsible disposal because of the risk of toxicity for environment, and transfer into the food chain. With the decomposition of plant biomass, metals can be washed by rain and transported back into the soil. In order that the phytoremediation process to result in effective outcomes and the level of heavy metals from the environment to decrease, not only to move those metals from one area to another, the remediation of polluted soils should end with quantitative recovery of metals [3]. The recovery of heavy metals has the advantage of increasing the economic value of the phytoremediation process by transforming this method in a financial self-supporting approach of environmental remediation.

There have been numerous studies on the phytoremediation process, having examined the species of plants that have greatest ability to accumulate heavy metals, factors affecting results of phytoremediation and the areas to be covered with plants for remediation purpose, but studies on treatment, storage or use of resulting biomass are insufficient. Some studies presented the possibilities of heavy metal recovery from different waste, even from agricultural waste. The present research aims to put in one sentence the phytoremediation process and the recovery of heavy metals from the phytoremediation by-products.

The research focused on identifying methods of heavy metal recovery from ash, resulted from the incineration of biomass. The phytoremediation process needs to end up with the heavy metal recovery to obtain (a) de-polluted soil, (b) ash with low content of heavy metals, that can be used as fertilizer in agriculture and (c) amounts of heavy metals that can be recovered in the industry to obtain an economic advantage by financially self-supporting of the phytoremediation process. Because of the lack of researches in this domain, this research was conducted based on the results of those studies that aim to recover metals from different kind of waste (from agriculture, sewage sludge, or woods).

2. Heavy metals in soil

Heavy metals are harmful for the human health, because they tend to accumulate in the living organisms. This bioaccumulation is caused by the high rate of absorption comparing to the rate of metabolism or excretion of the harmful compounds. The emissions from the metallurgical plants are transported by air masses up to 10 km from the pollution source and are deposited on the ground leading to an increase of heavy metal concentration in the upper layer of soil.

In soil, the soluble metals go into the soil solution and can be absorbed or immobilized by plants or can be leached to the deeper layer of soil and to the ground water (Figure 1). Some metals are chemical or physical adsorbed to soil particles. The fate of metals in soil depends on the depth of soil layer, on the erosion processes and on the pH. The heavy metals adsorbed to the soil particles from the upper layer can be subject to the erosion processes and transported by surface waters or by wind. The metals absorbed to deeper soil particles can be subject to microbiological and chemical degradation, can be stabilized by the plant root, or can cross from stable to available forms according with pH. The biological activity influences the speed

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and rate of pollutants degradation and the clay-humus complex represents an efficient buffer in neuter or alkaline soil reaction [4].

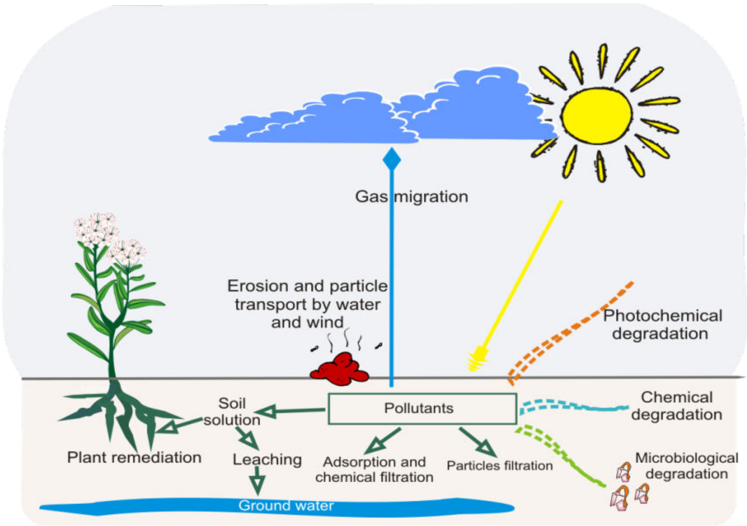

Figure 1. The fate of pollutants in soil [2]

The availability of metallic compounds in soil for plants depends on the soil texture, organic matter content of soil, cation exchange capacity, calcium carbonate equivalent and pH. Soil organic substances play an extremely important role because they can delay both the accumulation and transfer of metals and their movement into the soil. Metal toxicity in soil can be increased or reduced by the organic substances. Soil pH directly influences the availability of metals as soil acidity determines the metal solubility and its ability to move in the soil solution. Concerning the content of phosphorus in soil there are areas where uptake of metals is accelerated or rather diminished due to the presence of high doses of P_2O_5. In addition, the physiology of the plant species influences accumulation of metals. For example, in the case of cadmium uptake by grain was noted either a competition or a synergism in case of high concentrations of lead in the soil [5].

For soil protection, the limits for various pollutants have been established only under certain conditions and soil parameters. It was not taken into account the fact that on light soils, low-carbon, there is a strong influence of acid rainfall leading to a strong mobilization and uptake into plants of toxic heavy metals. This does not happen on heavier soils rich in limestone.

The solubility of zinc in soil was studied by Herms and Brummer [6], who demonstrated the extent to which this element is dissolved by increasing acidity of the soil and became available to plants absorption. In a low-zinc soil, a pH value of 5 could lead to a lasting effect of uptake large amounts of zinc, with all the negative consequences that result. Zinc equilibrium in the soil solution is realized at the level of 1200 mg/kg soil and a pH of 7, at level of 100 mg/kg soil and pH of 6 and at a level of only 40 mg/kg at a pH of 5. These levels of equilibrium make the low-zinc soil to release in the soil solution dangerous amounts of this element.

3. Phytoremediation process

Phytoremediation is defined as the process which uses green plants for the relief, transfer, stabilization or degradation of pollutants from soil, sediments, surface waters and groundwater.

In order to be used in phytoremediation, the selected plant species must be tolerant for the pollutant to be extracted, to quickly develop high biomass, to accumulate metals in harvestable parts, to have a well-developed root system and have a high bioaccumulation factor. This factor must be 20 or more for the phytoremediation to reduce the contamination of soil by 50% over a period of 10 crops [7]. The level of metal bioaccumulation and recovery is directly proportional to the quantity of biomass.

Plants that accumulate high levels of metals are known as hyperaccumulators and can accumulate 50-100 times more metal than a normal plant. There are about 400 hyperaccumulator species and the level of concentration is 10000 mg/kg for Zn and Mn, 1000 mg/kg for Cu, Co, Ni and As, and 100 mg/kg for Cd [8].

Thlaspi caerulescens species is the most studied and known as a hyperaccumulator plant with tolerance capacity for high concentrations of heavy metals in soil (e.g. Cu, Zn, Ni, Cd). Other tolerant species for heavy metals is *Berkheya coddii*, which was studied in South Africa, on ultramafic soils enriched with Ni [9]. The authors found, in leaves, values of Ni concentration about 18000 mg/kg, exceeding several times the metal content in soil (1300 mg/kg) without presenting symptoms of toxicity.

Uptake by the root is the most important way to get trace elements in plants, but have been observed absorption and adsorption processes of metals at level of other tissues. Metal uptake in plants is influenced by the species-specific ability, pedological factors, of which the most important are pH, Eh, fluid regime, clay content, cation exchange capacity, nutrient balance and concentration of other heavy metals. Also, the weather demonstrated some indirect effects on metals absorption rate in plants, mainly due to the influence on the amount of water in the environment [10]. In general, a high-temperature environment positively influences the absorption of micro-nutrients by plants [11].

A disadvantage of phytoremediation is that many hyperaccumulator plants produce a small quantity of biomass. For example, *Thlaspi caerulescens* produces only 2-5 tons/ha, but are plants that produce a larger quantity of biomass 9 t/ha for *Alyssum bertolonii*, or even 22 t/ha for *Berkhya coddii* [12].

Hyperaccumulation involves the absorption, transport and translocation of metals in tissues, where can be stored large amounts of these elements. One of the most studied mechanisms for the metal isolation use metallothionein-derived peptides and phytochelatins. Metal binds to

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organic sulfite in cysteine, which form the majority of metallothionein-derived peptides. It has been shown that metallothioneins and phytochelatins are stimulated by exposure to metals [13].

Phytoremediation of heavy metal polluted soils involves the following processes (Figure 2):

a. Phytoextraction represents the process which uses plants for the absorption, translocation and accumulation of pollutants from soil, to root systems and shoots. Herbaceous plants are suitable for phytoextraction because they grow quickly, forming a large amount of biomass and can remediate different types of soils. Four species of grass, *Vetiveria zizoniodes*, *Paspalum notatum*, *Pennisetum glaucum, Stenotaphrum secundatum* were used to decontaminate open mines. The first species is the most effective one, and the addition of fertilizers is not necessary.

b. Phytodegradation represents the process that uses plants for degradation of organic compounds. The organic compounds are degraded by plants or isolated in vacuoles for later degradation. In general, organic compounds can be degraded on several levels: partial conversion to less toxic compounds, partial degradation and subsequent isolation and complete degradation.

c. Phytovolatilization represents the process of absorption of pollutants by plants and volatilization into the atmosphere by the foliar system. Some plants are able to convert the metal ions in the more volatile forms by the phytovolatilization, which may reduce the toxicity and can translocate the metals to the stomata. Poplar can volatilize trichlorethylene, eucalyptus can volatilize methyltertiarybutylether, selenium can be transformed into Indian mustard and methyl mercury associated with plant roots can be converted from Hg^{2+} to volatile Hg.

d. Phytostabilization represents the process that use the plants which showed immobilization capacity for some metals or capacity for create binding condition for metals which will be adsorbed to soil particles and will be less available. These plants can also transform some toxic molecules in less toxic forms (e.g. Cr^{6+} to Cr^{3+}). To stabilize heavy metals in soil have to be used plants with low capacity of accumulation to reduce the dispersion of metals by grazing or by plant death. Among the remediation techniques of mining areas, phytostabilization is a method with good results in prevention of acid mine discharges and metal stabilization [14].

Heavy metals behave differently and have a different mobility depending on plant species. Therefore, Pb, Cr and Cu tend to be stabilized and retained in the root, Cd, Ni and Zn are more easily translocated to aerial tissues, and Cd is transported even to the harvestable tissues of plants [15].

For Pb there are some plant species, such as *Brassica juncea*, *Vetiveria zizinioides*, *Cardaminopsis halleri*, *Cynodon dactylon* and *Sorghum halepense* presenting hyperaccumulative capacity. To improve the ability of plants to accumulate heavy metals, the polluted soil can be amended with chelates that increase the metal bioavailability. This method has disadvantages of the high risk of metals to be more easily leached to the groundwater, in addition to the higher cost of remediation.

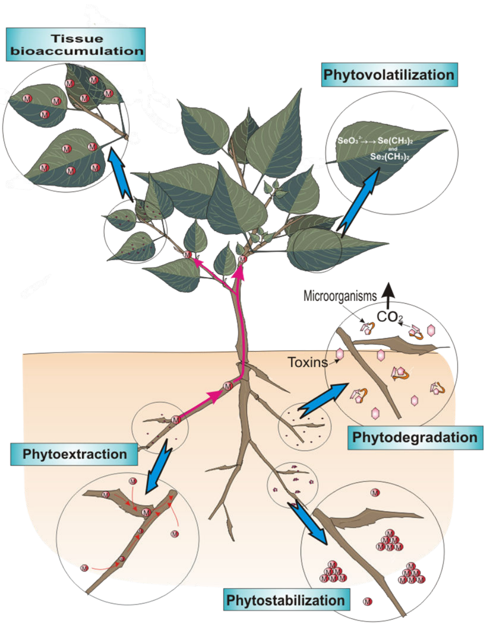

Figure 2. Phytoremediation of heavy metals polluted soil [2]

Among the plants that can be used in phytoremediation of mine tailings, studies have focused on *Eriophorum angustifolium*, a plant resistant to substrates with a wide range of pH from 10.9 to 2.7. Other species of plants that can be grown in a low pH environment are *Carex rostrata*, *Eriophorum scheuchzeri*, *Phragmites australis*, *Typha angustifolia*, *Typha latifolia*, which grows to a pH value of 2.1, 4.4, 2.1, 3.0 and 2.5 respectively [14].

The studies made since 1977 by the American biologist Dr. Robert Brooks [16], have shown that metals can be extracted from plants (e.g. Ni, Zn, Pb and Au), but the facility of this process depends on the density and solubility of the elements. From the first experiments was obtained 0.01 g of Ni from few kilograms of plant biomass and, more recently, 10 g of Au were obtained from a two hectares of rape culture, established in the vicinity of abandoned mines in California.

4. Methods for heavy metal recovery

So far there have been numerous studies on the phytoremediation process, having examined the species of plants that have a greater ability to accumulate heavy metals, factors affecting the results of phytoremediation and areas that should be remediated with plants. In terms of treatment, storage or heavy metal recovery from the biomass resulted from the phytoremediation process the reference studies are scant.

Delplanque et al. [17] conducted a study on the behavior of metals during the combustion of leaves and shoots of *Salix* (grown for phytoremediation), describing the type of ash obtained from the use of biomass as an energy source and the level of heavy metal concentration. At the end of their study, the authors concluded that the combustion of biomass obtained from phytoremediation reduces the waste volume, but ash cannot be used as fertilizer in agriculture due to high levels of heavy metals.

The international researches in the last decade deal with developing several techniques and methods of incineration and recovery of heavy metals from industrial waste [18,19], garbage [20] and vegetable waste resulting from agriculture [21,22,23]. Unlike industrial waste and garbage, the biomass obtained from the phytoremediation process has a higher content of organic matter and low ash content, only 5% of the dry matter [24]. Compared with agricultural waste, collected from the fields containing heavy metals within normal levels, biomass resulting from phytoremediation process contains much higher concentrations of heavy metals. Considering these aspects and morphological differences between the species used in phytoremediation, heavy metal recovery methods must be adapted for each type of biomass used (grass species, tree species), according to the concentration and metal mixture.

4.1. Thermal treatment

During the thermal treatment (incineration or pyrolysis), the organic matter from biomass is destroyed and metals remain in ash as oxides [25] which can be recovered by hydrometallurgical processes [22,23,26] and bio-hydrometallurgical processes [27], ion exchange [28,29,30,31,32], flotation [19,33], magnetic field [34,35] or electrolysis [3,18,21] and bio-electrochemical procedures [36].

Due to the high content of oxygen, plant biomass can be easily incinerated, requiring only small volume of air during the combustion. In addition, relatively low sulfur content of the biomass is an advantage because there are no harmful gases released in the atmosphere during the combustion [20]. A negative aspect of incineration at very high temperatures (over 600 °C) is the fact that some heavy metals, including those with the greatest risk of toxicity, are volatile: Pb, Zn, Cd, Se [37]. Volatilization of metals can be exploited as an advantage in the recovery of metals, because these elements condense in the cooler areas of the incineration oven and are adsorbed on fine particles of ash retained in the cyclone or on filters [37,38]. The metal recovery is more efficient due to higher metal concentrations by mass of ash [20,37]. The mechanism which determines the behavior of metals during incineration process is characterized by three aspects: (a) evaporation in the combustion areas and condensation of metals in the lower temperature zones of the furnace, (b) physical adsorption on specific surface area of ash particles, and (c) chemo-absorption [38]. The surface area of ash particle is determined primarily by unburned carbon and assessed by electron microscopy (SEM) and is a determining factor for the adsorption of volatilized metals [18,38].

To minimize the risk of volatile metals reaching the atmosphere, the incineration plant shall be fitted with ash particle filtering and retrieval (filters and cyclone). Mercury, selenium and arsenic are metals with the highest percentage of vaporization into incineration system.

Mercury is highly volatile and can be delivered almost entirely as vapor in the form of HgO and $HgCl_2$. Oxidized form of mercury is easily collected from air pollution control system [37].

Keller et al. [3] demonstrated by their study that, better results of the thermal treatment of the biomass are obtained by pyrolysis, under reducing conditions, compared to incineration. The researchers aimed only the recovery of volatile metals (especially copper and zinc), from shoots of Salix use in phytoremediation. These statements are subject to the heavy metal content of ash, which have to lie under the maximum permissible level if they are used as amendment.

4.2. Hydrometallurgical processes

Extraction of heavy metals by ash leaching is a complex chemical process which offers the possibility of obtaining quantitative precipitated metal. The solutions used for leaching of ash must be environmentally friendly, efficient, cheap and with a high capacity for regeneration.

In the leaching process, the extraction of heavy metals is subject to such factors as the solubility and availability of the metal. The solubility can be influenced by pH, the chemical form of inorganic species, organic matter, and the reducing properties. Most metals from waste indicated a higher solubility in acid solutions [39]. Singer et al. [40] tested the extraction of aluminum with citric acid at different temperatures and the results showed that the extraction of metal was considerably influenced by the concentration of the acid used and by temperature. Based on this study, Machado et al. [23] have studied the recovery of Ni and Zn in a multi-component solution by precipitation in the form of alkali metal hydroxide. As a result of the experiment the researchers obtained a recovery rate of over 99% and a purity of 92% for Ni and 99.4% for Zn. The main factor which influences the precipitation of metals from NaOH solution was the pH, which defined the precipitation of Ni at pH 14 and the precipitation of Zn at pH 10. Recovery of Cd, Cu and Pb by leaching with $NaHCO_3$ was investigated by Lezcano et al. [22] who obtained different amounts of metal in relation to pH.

To increase the solubility of metals from ores, Hoque & Philip [27] proposed the introduction of a microbial population, to convert insoluble metal sulfides into soluble metal sulfates. For example, for the extraction of copper from copper sulfide, it was oxidized by microorganisms to copper sulfate. The metal ions have been concentrated in the aqueous phase and the solid residues were removed [27]. A similar technology is used for the conversion of solid metal in water soluble form, in the presence of microorganisms. The technology is called biooxidation and is used for the microbiological oxidation of metal-containing minerals to be extracted.

Bio-hydrometallurgical processes are used in copper metallurgy in the presence of the bacterium *Thiobacillus ferooxidans*, carrying bivalent iron to trivalent iron oxidation [41]:

$$CuFeS_2 + 4\ O_2 \rightarrow CuSO_4 + FeSO_4$$

$$FeSO_4 + H_2SO_4 + \frac{1}{2}\ O_2 + \text{bacteria} \rightarrow Fe_2(SO_4)_3 + H_2O$$

$$2\ Fe_2(SO_4)_3 + CuFeS_2 + 3\ O_2 + 2\ H_2O \rightarrow CuSO_4 + 5\ FeSO_4 + H_2O$$

The reaction takes place in aqueous solution, and the last two reactions are cyclic ensuring the continuous development of the leaching process of the chalcopyrite, while copper passes in

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the solution as sulfate. Another type of bacteria is used to oxidize the sulfur (*Thiobacillus sulfooxidans*). The solutions obtained by leaching, after purification and concentration, can be processed to extract metal ions which we are interested in.

4.3. Electrochemical processes

Electrochemical processes for the extraction of heavy metals have the advantage of selective recovery of metals, depending on the metals reduction potential of the metal to be extracted, but in order to obtain a high purity for every metal, tests must be performed to optimize the factors which influence the metal deposition on the electrode (pH and the electrolyte concentration, the temperature of the electrolytic bath and the metal species). The metal extraction by electrolysis is common use in the metallurgy of zinc, copper, nickel, etc.

Each metal has a specific ion discharge potential, which corresponds to the minimum potential at which an ion electrode begins to discharge continuously and visible (substance discharge). When a substance has more ions, they are discharged successively as they achieve the potential of each download. On this basis is realized the separation and selectively deposition of a number of metal ions from the same solution, if their discharge potentials are differing by at least 0.2 V, otherwise they are deposited at the same time. The ions can be electro-gravimetric separated with a determination error of less than 0.1%.

Fukuta et al. [42] have obtained the selective recovery of Cu, Ni and Zn with sodium sulfide, but in 2011, Machado et al. [43] conclude that, because of the difference in deposition potential of only 0.25 V, the separate recovery of Ni and Zn by electrolysis may be compromised, with the risk of co-deposition of the two metals. For this reason, the research was continued and the electrolyte was used to test the removal of the two metals by precipitation. Ni extraction by electrochemical processes was tested also by Lee [18]. The subject solution of this experiment was a spent electro-less nickel plating solution, the electrode used as the anode was made of platinum, and the cathode was made of stainless steel. Just as in the previous studies, pH played a key role in the extraction of Ni, and, at the end of the process, the metal was obtained in the form of nickel hydroxide and nickel fine particles.

The study conducted by Kirkelund et al. [21] to remove the Cd from the residual plant material by electrochemical methods is based on the principle of electro-migration of ions in solution, in an electric field. The researchers used membranes for the anions and cations exchange to optimize the process. Optimization of results for metal extraction was pursued also by Modin et al. [36] who applied a bio-electrochemical process for recovering Cu, Pb, Cd and Zn in dilute solutions. The anode was inoculated with micro-organisms from the sewage sludge and in the anode chamber a nutrient solution was circulated. The advantage of this method is the less energy consumption for the metal discharge and the selectivity of metal extraction [44].

5. Material and method

The present study was conducted on seven perennial grass species from *Juncaceae* and *Poaceae* family, to find the best solutions for the phytoremediation of soils in the vicinity of metallurgical plant of Targoviste (Figure 3). The aim of research was to evaluate the capacity of these plants species to accumulate heavy metals which were found in high concentrations (above the normal range in agricultural soils) on the studied site. The best accumulative species, *Lolium perenne* was used in an experiment of heavy metal extraction from plant biomass to test the efficiency of metal recovery methods in case of phytoremediation procedure.

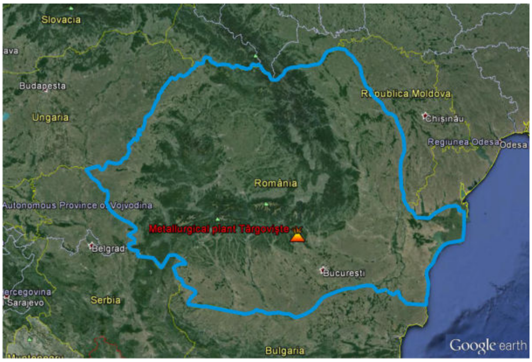

Figure 3. Studied area in the vicinity of metallurgical plant of Targoviste

5.1. Research course

Sampling points of plants and soil were chosen so that the results to reflect a snapshot of the impact of metallurgical activities in this area by particles emissions. Sampling was done at distances between 500 and 1000 meters from the source of pollution, from three different points, chosen according to triangle method. The results of metal concentration represent the average of these three samples. The depth of sampling was chosen according with the depth to which the roots of plant culture normally develop. Was formed a mean sample from the column of soil between 0 – 20 cm depth.

Plants were harvested in two seasons, summer and autumn 2008. Was harvested the entire plant, including the root system. For each plant sample, the soil underneath was collected, down to the horizon where the plant developed its root system. The soil was used to establish the bioaccumulation factor of each plant species by comparing the metal concentration in plants with the metal concentration in soil.

The harvested plants were wild growing species which already were adapted to high pollution level of the soil. They were perennial grasses, which usually are used as forage for animals: *Lolium perenne, Festuca pratensis, Stipa capillata, Agrostis alba, Cynodon dactylon, Agrostis tenuis* and *Luzula campestris*.

The plants and soil samples were processed in the laboratory for elemental analysis by ICP-AES (see section 5.2). After harvesting, the fresh plants sample were cleaned with deionized water to remove the soil particles, dried at 60 °C for few hours, ground to a fine powder and analyzed to establish the metal concentrations. The soil samples were dried at 40 °C for 24 hours, ground to a fine powder, sieved at 250 μm (according to SR ISO 11464).

Based on the results of bioaccumulation for studied plant species, *Lolium perenne* was chosen for the subsequent experiment for heavy metal recovery. In the vicinity of metallurgical plant, a 10x10 m experimental plot was cultured with this species. During the growing period no amendments were added. After one growing season, the plants were mowed and used for the experiment of heavy metal extraction by hydrometallurgical and electrochemical processes.

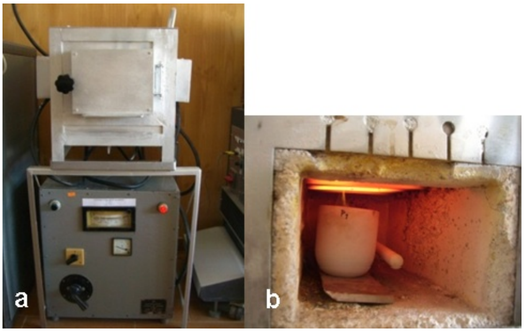

Figure 4. Plant biomass incineration: (a) heat treatment oven with forced rod, (b) incineration process

First the plants were dried for few hours, at 105 °C to remove the water and to decrease the biomass volume [45]. After drying stage, the plants were incinerated in alumina crucibles using a heat treatment oven with forced rod (Figure 4), nominal voltage of 220 V, nominal amperage of 30 A, and maximum temperature 1300 °C. The incineration was conducted at temperature between 400 °C and 600 °C in two stages. The first stage was the heating up to 500 °C for 30 minutes, followed by a 90 minutes of burning at temperature of 500 - 600 °C. Weighing was made for the raw biomass, for the biomass after drying and after incineration to establish the percentage of dry matter and percentage of ash.

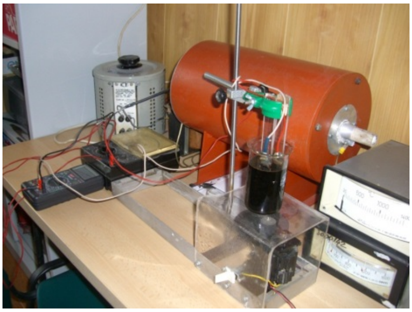

Figure 5. Electrolyses cell

Leaching of ash was made by mixing 10 g of ash with 200 ml of nitric acid (HNO_3), concentrated to 65%. The mixture was heated to boiling point for 60 minutes and then cooled down to room temperature. After complete cooling, in the mixture were added, on ice, 200 ml of concentrated sulfuric acid (H_2SO_4). After half an hour of rest, the mixture was filtered.

For the extraction of heavy metals, an electrolytic cell was designed (Figure 5), with stainless steel electrodes and 200 ml of the filtrate obtained from the leaching of the ash as electrolyte. The electrolysis was carried out for 90 minutes with an electric intensity of 1.5 A, and a voltage of 11.4 V. The microscopic and gravimetric methods were used to assess the metal deposition on electrodes.

5.2. Analytical methods

Determination of heavy metal concentration, in both plants and soil underneath, was done by Inductively Coupled Plasma - Atomic Emission Spectrometry method (ICP-AES). For analyze, the samples were mineralized in Berghof microwave digester, plants by mixture with 10 ml of nitric acid concentrated 65% and 2 ml of hydrogen peroxide, and soil in mixture 1:1 with nitric acid (according with Berghof method). The advantage of this method is the multielemental detection, which give the possibility, in one shot, to read a wide range of elements [46]. For this research, analyzes were conducted with Liberty 110 spectrometer of Varian brand. The minimal detection limits of device range according to the analyzed element and is 0.4 mg/kg for Zn, Mn and Cu; 0.5 mg/kg for Cr and Co; 0.6 mg/kg for Sn, Ni and Pb. The concentrations values for analyzed metals were expressed in milligrams of metal per kilogram of dry soil or plants (mg/kg).

The soil pH was determined with a portable pH-meter, WTW 3110 SET 2, with precision of 0.01 units. For pH analyzes, 5 g of each soil sample were mixed with 50 ml KCl 0.1N, F 1000, Tt 0.0056 g/ml and homogenized for 15 minutes with a magnetic stirrer.

The deposition on electrodes was evaluated by microscopy and quantitative assessed by Energy Dispersive X-Ray Fluorescence method (EDXRF) [47], using a PW4025 – MiniPal – Panalytical type EDXRF Spectrometer. The XRF determinations were conducted in Helium atmosphere, excited for 300 s, without any filter, at 16 kV voltage. The current intensity was automatically adjusted by the use of a 3.6 μm Mylar tissue [48]. The surface of electrodes was evaluated for heavy metal concentration before and after electrolysis.

5.3. Data analysis

The bioaccumulation factor (BF) for studied plants was calculated as the ratio between metal concentration in plants and metal concentration in soil:

$$BF = \frac{C_{plant}}{C_{soil}} \tag{1}$$

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where: C_{plant} represents the metal concentration in plants and C_{soil} represents the metal concentration in soil.

To calculate the percentage of metal concentration by drying, the metal content of dry matter was reported to the element content of the fresh biomass and to calculate the percentage of metal concentration by incineration, the metal content of ash was reported to the element content of the dry matter.

Percentage of metal extraction into solution (%) was calculated as ration between the metal content of 400 ml solution (filtered leachate) and the metal content of 10 g of ash:

$$\text{Percentage of metal extraction into solution}(\%) = \frac{\text{solution concentration} * 400/1000}{\text{ash concentration} * 10/1000} \quad (2)$$

The quantity of metal recovered by electrolysis was calculated according with the mass of metal deposition on cathode (0.7 mg), percentage of ash from the fresh biomass (5.1%) and the mass of fresh plants that can be harvested from one hectare (40 t):

$$\text{Recoverd metal}(\mu g/5\,g\,\text{ash}) = \frac{\text{metal concentration in cathode deposit}(mg/kg)}{1000} * 0.7 \quad (3)$$

From 40 t of fresh biomass of *Lolium perenne* that can be harvested from one hectare, with a percentage of ash of 5.1%, can be obtained 2.04 t of ash.

$$\text{Recoverd metal}(\text{g per ha}) = \frac{\text{recoverd metal}(mg/5\,g\,\text{ash})}{5} * 2.04 \quad (4)$$

6. Results

6.1. Heavy metal concentration in soil

The soil samples consisted in the upper layer of soil, 0 – 20 cm, where the most of the roots can be found. The content of soil in macronutrients was about 13 g/kg for Ca, 3 g/kg for Mg, and 1 g/kg for P and K. The soil reaction had the value of 7.30±0.42. Heavy metal concentration in soil (Table 1) was compared to the normal values of agricultural soils and alert thresholds for industrial soils according with the Romanian regulations [49]. The average content of Cu, Sn and Pb in soil exceeded the alert threshold for agricultural soils, 100, 35, 50 mg/kg respectively, but in some sampling points the concentrations exceeded even the alert threshold for industrial soils, 250, 100, 250 mg/kg. For Zn, the mean concentration in soil was in normal limit for agricultural soil (300 mg/kg), but in some sampling points exceeded the alert threshold of 700 mg/kg. The Co concentration in soil had low values with a uniform distribution between the sampling points. None of the samples showed values of Co concentration higher than 30 mg/kg, the alert threshold for agricultural soils. The mean value of Ni concentration did not exceed the alert threshold for agricultural soils (75 mg/kg), but the concentration was varying in a wide range from one sampling point to another and some results showed values of concentration close to the alert threshold for industrial soil (200mg/kg). The mean concentration of Mn in studied sample of soil was higher than alert threshold for agricultural soil (1500 mg/kg), and some of results showed values of Mn concentration that exceeded the alert threshold for industrial soils (2000 mg/kg). The mean concentration of Cr was just under the alert threshold for agricultural soils (100 mg/kg), but some sampling points showed values for Cr concentration higher than the alert threshold for industrial soils (300 mg/kg).

Metal	Soil concentration (mg/kg)		Metal	Soil concentration (mg/kg)	
	Mean ±SD	Range		Mean ±SD	Range
Cu	152.4±177.7	21.9-600.4	**Co**	15.9±4.3	7.1-23.54
Zn	194.3±231.7	42.6-870.3	**Ni**	53.4±48.6	11.9-185.4
Sn	65.7±30.7	24.6-125.41	**Mn**	1545.7±334.07	1159.9-2348.76
Pb	65.2±87.2	<LD-294.3	**Cr**	98.0±112.0	12.9-315.6

<LD – below limit of detection

Table 1. Heavy metal concentration in soil underneath plants (mg/kg dry matter)

The wide variability of metal concentration in soil was according with the orientation and the distance against the pollution source. Some heavy metals showed a uniformity in metal distribution (e.g. Co and Sn), which is probably because of the geological origin of these metals, more than from the pollution source.

6.2. Heavy metal bioaccumulation in plants

Perennial grasses develop a large plant biomass in a relatively short time and are known as heavy metal tolerant biosystems, accumulating high levels of these elements. Also, perennial grasses have a high content of dry matter: *Lolium perenne* 36%, *Festuca pratensis* 33%, *Stipa capillata* 43%, *Agrostis alba* 42%, *Cynodon dactylon* 40%, *Luzula campestris* 50% and *Agrostis tenuis* 46%, compared to other species such as *Papaver rhoeas*, *Cirsium arvense* or *Artemisia vulgaris* which have only 12 – 36 % dry matter.

According to the perennial grasses tolerance for heavy metals and because of environmental and weather conditions favorable to their development, analyzed plant species have adapted to the toxic heavy metal concentration in soil and accumulated these elements to high levels [50]. In addition to these aspects, the concentration of metals in plants was influenced by plant age, topography and synergistic and antagonistic effects of the elements found in soil.

The heavy metal concentration in perennial grasses was widely different between the species for all studied metals (Table 2). Copper concentration range between 1.76 and 113.83 mg/kg, with the highest value for *F. pratensis*. In the same species was found the highest value for the tin concentration, 379 mg/kg, while the lower value of tin concentration was for *L. campestris*, 8 mg/kg. Zinc concentration range for studied species between 62 – 922 mg/kg, and lead concentration varies between not detectable level of concentration in most of studied species and 201 mg/kg. The maximum values of zinc and lead concentration were found for *L. perenne* species, 922 mg/kg and 201 mg/kg respectively.

The cobalt concentration was below limit of detection for three of studied species. The highest values of this element concentration were found for species *S. capillata* and *A. tenuis*. The accumulation of Co was influenced by the metal concentration in soil and by the soil moisture which lead to the leaching of some cobalt compound and increasing of cobalt availability for plants. The mean values of Ni concentration in studied species of plants varied widely from one species to another even inside of the same genus. The lowest value of Ni concentration was 3.88 mg/kg for *A. tenuis* and the highest was for *A. alba*, 60.23 mg/kg. The range of Mn concentration was between 165.9 mg/kg and 703.92, with the highest values of concentration for *L. perenne* species. The mean concentration of Cr in studied plants ranged between 10.04 mg/kg for *L. campestris* and 191.99 mg/kg for *S. capillata.*

Species	Cu	Zn	Sn	Pb
L. perenne	61.95±15.7	921.67±136.2	217.83±40.1	201.23±14.9
F. pratensis	113.83±22.8	130.62±48.2	379.23±103.2	<LD
S. capillata	10.04±3.9	88.22±2.8	265.25±17.4	<LD
A. alba	31.83±5.5	85.34±7.12	250.04±74.2	5.21±3.2
A. tenuis	0.99±0.6	72.33±3.8	235.94±12.1	2.72±0.1
C. dactylon	25.11±2.4	62.09±2.0	186.13±31.4	<LD
L. campestris	1.76±0.4	71.69±2.9	8.38±0.9	7.38±0.5
Species	**Co**	**Ni**	**Mn**	**Cr**
L. perenne	<LD	12.55±4.6	703.92±156.2	114.19±35.4
F. pratensis	<LD	33.58±11.6	341.90±41.5	173.99±28.6
S. capillata	4.49±0.4	27.72±2.5	342.13±16.6	191.99±12.8
A. alba	3.20±2.0	60.23±20.5	362.07±79.2	56.75±15.1
A. tenuis	4.60±0.2	3.88±0.4	269.39±16.5	21.96±2.53
C. dactylon	2.61±1.1	28.60±10.6	296.33±48.7	28.95±3.9
L. campestris	<LD	17.18±1.41	165.90±0.8	10.04±1.4

<LD – below limit of detection

Table 2. Mean concentration of heavy metals in perennial grasses (mg/kg dry matter)

For phytoremediation process to be effective it is better to use those biosystems species adapted to the climatic and soil conditions of the area to be de-polluted. For this reason, the species used in the studies were chosen from those plants that normally grow in the industrial area of the city of Targoviste, perennial grass which are effective to mowing and rebuild their vegetative mass. In addition, the losses caused by death of leaves are greatly reduced.

The bioaccumulation capacity of plants was estimated as the ratio of metal content in soil and the metal concentration in plant. This ratio is called bioaccumulation factor (BF) [7] and we evaluated as weak accumulators the species which have a BF value between 0.8 - 1.2, as good accumulators the species with a value of BF between 1.5 - 5.0 and hyperacumulators those species with higher BF than 5.0 (Table 3).

Absorption and accumulation of metals in perennial grasses was influenced by both species and the soil underneath, pH, moisture and metal content in soil. The bioaccumulation of the studied metals was differently influenced by pH of soil and metal content.

Even *F. pratensis* and *L. perenne* showed the highest values of Cu, Zn, Sn concentration, they did not show the highest accumulation capacity for those metals. The best accumulator for Cu, Zn and Sn were the plants of *C. dactylon* species which showed BF values of 1.12, 1.37 and 6.06 respectively for Cu, Zn and Sn. Lead was very well accumulated by *L. campestris* which showed a very high level of metal bioaccumulation, 12.3. Tin was the metal with best bioaccumulation in perennial grasses.

Metal	BF	Accumulation gradient	Metal	BF	Accumulation gradient
Cu	0.88±0.2	*A. alba* – weak	**Pb**	1.04±0.1	*L. perenne* – weak
	1.12±0.1	*C. dactylon* – weak		4.54±0.2	*A. tenuis* – good
Zn	0.92±0.1	*L. campestris* – weak		12.3±0.9	*L. campestris* – hyper
	0.98±0.1	*A. tenuis* – weak	**Co**	<0.8	Not accumulative
	1.00±0.1	*A. alba* – weak	**Ni**	1.26±0.05	*L. campestris* – good
	1.31±0.3	*L. perenne* – good		1.27±0.42	*C. dactylon* – good
	1.37±0.1	*C. dactylon* – good		1.63±0.63	*A. alba* – good
Sn	2.43±0.1	*S. capillata* – good	**Mn**	<0.8	Not accumulative
	3.00±0.8	*A. alba* – good	**Cr**	0.83±0.08	*F. pratensis* – weak
	4.10±0.8	*F. pratensis* – good		1.16±0.23	*C. dactylon* – weak
	4.11±0.6	*L. perenne* – good		1.51±0.11	*A. tenuis* – good
	5.85±0.1	*A. tenuis* – hyper		2.11±0.10	*S. capillata* – good
	6.06±0.3	*C. dactylon* – hyper		2.68±0.75	*A. alba* – good

Table 3. Bioaccumulation factor (BF) of heavy metals in plant species – metal accumulation capacity of plants (not accumulative, weak accumulative, good accumulative or hyper accumulative)

None of the studied species of perennial plants showed accumulative capacities for either Co or Mn. This was probably because of the exclusion mechanism of these plants for the two elements. For Ni, three of studied species showed accumulative capacity: *L. campestris*, *C. dactylon* and *A. alba*, while for Mn five studied species showed accumulative capacity. For the phytoremediation of soils polluted with Ni and Cr, the best species to use is *A. alba*, because it showed the highest values of BF, 1.63 and 2.68 respectively.

6.3. Heavy metal extraction from plant biomass

Following the phytoremediation of soil polluted with heavy metals, a crop of 400 kg of plants was obtained which contain heavy metals, but the concentrations of these elements in the biomass is very low for the use of these plants for heavy metal extraction process. In order to concentrate the metal, plants were subjected to a drying process in which the mass of substance decreased by 64%, registering a percentage of metal concentration of 243.9%. The percentage of ash resulted from the incineration of dry biomass was 14.3% and the percentage of metal concentration in the plant ash increased by values between 544.5 - 2282.1% (Table 4) The differences of metal concentration by incineration was because of volatilization of some elements or because of the adsorption on flying ash which was lost during the incineration. Because of that, future researches will be needed for the construction of an integrated system of plant biomass incineration, designed with filters and cyclone for the recovery of all particles of ash.

In this experiment, the ash was used for metal extraction by leaching. The results showed low effectiveness of this method, because the metals from ash were not fully extracted in the leachate. The weakest extraction in the leachate was for tin, only 16.3% from the total quantity of tin in the ash. A fair extraction was only for Ni and Cr which were extracted 92.6% and 87.8% respectively from the ash (Table 5).

Future research should be conducted to establish methods of metal extraction by leaching of ash with better results for the majority of heavy metals to be recovered.

Metal	Concentration in plants (mg/kg)			Percentage of concentration %	
	fresh biomass	dry matter	ash	by drying	by incineration
Cu	81.35	198.41	1454.08	243.9%	732.8%
Zn	172.87	421.63	2295.92	243.9%	544.5%
Sn	106.77	260.42	3367.35	243.9%	1293.0%
Pb	3.05	7.44	76.53	243.9%	1028.6%
Co	< LD	< LD	306.12	-	-
Ni	< LD	< LD	2142.86	-	-
Mn	179.99	438.99	3214.29	243.9%	732.2%
Cr	65.08	158.73	3622.45	243.9%	2282.1%

Table 4. Metal concentration in plant biomass by drying and incineration (%)

Metal	Ash concentration (mg/kg)	Solution concentration (mg/l)	Percentage of metal extraction into solution* (%)
Cu	1454.08	11.20	30.8%
Zn	2295.92	30.45	53.1%
Sn	3367.35	13.70	16.3%
Pb	76.53	1.25	65.3%
Co	306.12	< LD	-
Ni	2142.86	49.60	92.6%
Mn	3214.29	35.5	44.2%
Cr	3622.45	79.55	87.8%

* 10 g of ash were used to prepare 400 ml solution

Table 5. Heavy metal extraction by leaching of ash

In the process of electrolysis, the cathode layout has changed on the surface. At macroscopic level could be observed the metal deposition after the electrolysis - oxides spots and at the microscopic level could be observed a smoothing of the surface (Figure 6).

There was a difference in mass of the cathode of 0.7 mg, from 4.6242 g before to 4.6249 g after electrolysis.

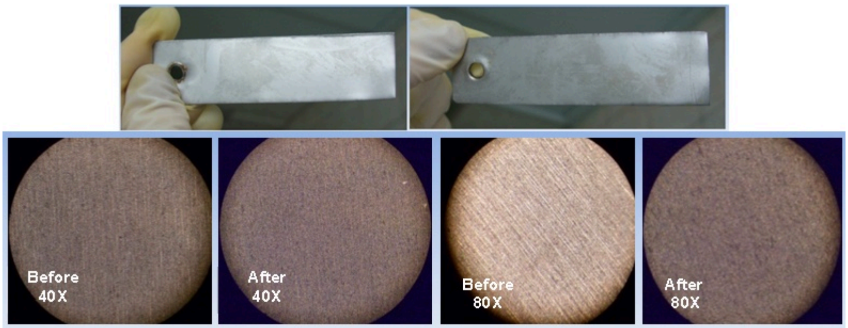

Figure 6. Metal depositions on electrode at 1x, 40x and 80x magnification [2]

The quantitative evaluation of metal deposition on cathode was made by EDXRF and different metal concentrations were observed. The most effective deposition was for Ni, Mn and Cr, which showed concentration of 3.07, 2.2 and 7.3 g/kg respectively.

6.4. Balance of phytoremediation and heavy metal extraction

The experiment of phytoremediation of heavy metal polluted soil in the vicinity of Targoviste city showed the results for one growth season of perennial grass *Lolium perenne* (Table 6). The metal concentration in soil as evaluated before and after the plant culture and after mowing the results showed a decreasing of metal concentration in soil with 0.3 – 5.9%. The concentration of cobalt and nickel had the lowest decreasing. The best accumulated heavy metals by plants were Zn and Pb. The accumulation of Pb was because of the high concentration of this metal in soil and the Zn accumulation was because of the synergic effect of the Pb concentration in soil on the accumulation of Zn [2].

Metal	**Metal concentration in soil (mg/kg dry matter)**		**Percentage of metal extraction by plants (%)**	**Metal content in plant (mg/kg dry matter)**	**BF**
	before	**after**			
Cu	313.54	303.62	3.2%	198.41	0.653
Zn	141.04	132.72	5.9%	421.63	3.177
Sn	107.36	102.78	4.3%	260.42	2.642
Pb	71.99	68.23	5.2%	7.44	0.109
Co	16.77	16.72	0.3%	< LD	-
Ni	52.93	52.63	0.6%	< LD	-
Mn	1176.02	1152.63	2.0%	438.99	0.381
Cr	90.66	87.56	3.4%	158.73	1.813

<LD – below limit of detection

Table 6. Results of the phytoremediation of heavy metal polluted soil near Targoviste

The synergic effect of the Pb concentration in soil can be observed also in the value of Zn bioaccumulation factor, 3.177. During the experiment of phytoremediation, *Lolium perenne* showed good accumulative capacity for chromium also.

By reporting the results to the quantity of ash used in the experiment, small quantities of heavy metals were obtained (Table 7).

According with the biomass quantity that can be harvested from one hectare cultivated with *Lolium perenne* species (40 tons) and ash content of raw material (5.1%), in a growing season of this species, can be extracted from soil about 0.13 g of Cu, 0.27 g of Zn, 0.07 g of Sn, 0.04 g of Co, 0.88 g of Ni, 0.63 g of Mn, and 2.09 g of Cr. The efficiency of heavy metals extraction by electrolysis can be improved by increasing the leaching efficiency.

Even if these amounts are very small and the economic value of process is almost nonexistent, the immense advantage of metal recovery is the extraction of these elements from soil and the decreasing of toxicity risk caused by the presence of heavy metals in the environment.

Metal	Metal concentration in leaching solution (mg/l)		Metal concentration in cathode deposit (mg/kg)	Recovered metal	
	before	after		µg/5 g ash	g per ha
Cu	11.20	7.40	445.92	0.31	0.13
Zn	30.45	22.40	946.39	0.66	0.27
Sn	13.70	11.45	260.91	0.18	0.07
Pb	1.25	0.55	< LD	-	-
Co	< LD	< LD	142.31	0.10	0.04
Ni	49.60	23.35	3076.37	2.15	0.88
Mn	35.5	16.935	2222.486	1.56*	0.63
Cr	79.55	17.70	7312.619	5.12**	<2.09

* 2% of Mn deposit is probably because of anodic dissolution

** The results were probably contaminated because of high content of Cr in the stainless steel (14%)

Weight of metal deposition – 0.7 mg; fresh biomass per hectare – 40 t; percentage of ash – 5.1%

Table 7. Results of heavy metal extraction from *Lolium perenne*, by electrolysis

7. Discussion

The present study concerned a novel approach of the phytoremediation process: phytoremediation followed by heavy metal extraction. The researches concerned first the analysis of soil to reveal the necessity of remediation, then researches concerned the species used for phytoremediation and methods of processing the resulted biomass. The treatment of biomass enriched with heavy metals led to the recovery of these elements as alloy, which can be economically exploited. Also, the resulted ash was characterized as material with low heavy metal concentration, which can be used in agriculture or can be disposed without the risk of toxicity.

Analysis of soil samples from the vicinity of metallurgical plant of Targoviste indicated an exceeding of alert threshold for Cu, Sn, Pb, Mn and Cr, with metal concentration levels that could be harmful for both the agricultural and industrial soil [49]. According to these aspects and because the land was used as pasture, the soil needed interventions for decreasing the heavy metal concentration. The best way to remediate this land was the use of wild growing perennial plants to extract heavy metals from soil and the resulted biomass to be mowed and disposed as hazardous material. The wild growing plants have the advantage of ecological adaptability and low costs for starting and maintaining the crop [2].

Metal concentration was evaluated for seven perennial grasses, regarding the bioaccumulation capacity of these species, to establish the most effective species to be used in remediation of studied area. Results indicated heavy metal concentrations for *Lolium perenne* similar to results from previous articles: chromium and copper concentration showed values similar to the results presented by Arienzo et al., 35 and 70 mg/kg for Cr and Cu respectively [50]. Instead, the results of present study indicated 2 and 6 times higher concentrations for Pb and Zn when compared with plants from unpolluted sites and similar results when compared with plants from metallurgical site [50]. The same values of Pb and Zn concentrations were obtained also by Bidar et al. [51] when have researched the behavior of *Trifolium repens* and *Lolium perenne* growing in a heavy metal contaminated field. This study indicated that the two metals, Pb and Zn, are accumulated predominantly in roots (269.98 mg/kg for Pb and 1511.18 mg/kg for Zn), and in lower concentrations in shoots (45.65 mg/kg for Pb and 218.15 mg/kg for Zn) [51]. The results of soil phytoremediation can be improved by the addition of chelates such as EDGA which lead to a 2 times increasing of heavy metal uptake by plant [52].

For a correct evaluation of the most efficient species to be used in phytoremediation, the bioaccumulation factor should be investigated because it indicated the metal accumulation ability of each species by comparing the metal concentration in plant with the metal content of the soil [7]. The results of present study indicated that, despite some species showed a high metal concentration in shoots, the metal uptake was caused by the high metal content of soil, not by the accumulation capacity of that species [2]. Only some of the studied species accumulated heavy metals in higher concentration than the metal content of soil (BF > 1) (Table 3).

For effective results of the phytoremediation, the process should be implemented for a long period of time, with many growing seasons followed by mowing of plants [7]. Therefore, from a phytoremediation process implemented at commercial scale will result huge quantities of plant biomass which should be treated as hazardous material because of the contamination with heavy metals [53]. The leaching test showed that the composting of this biomass is not efficient, because by composting process are formed soluble organic compounds that enhanced metal solubility and availability for plants [53]. Based on these requirements, the present study aimed the development of a novel method of thermal treatment of the biomass from phytoremediation to reduce the initial volume to 5.1%, by drying and incineration. A similar percent (2 – 5%) of mass reduction was indicated by Ghosh and Singh [53], after biomass combustion. Thereby, the much smaller quantities of ash can be properly disposed, but still with the risk of heavy metal toxicity. Also, the resulted ash can be used in phytomining process to recover the saleable heavy metals [53].

In 1994, the development of novel methods for metal recovery from ash resulted from the plant incineration have been referred as future research, known as extraction from bio-ore [54]. The recovered metals could reveal the secondary potential of hyperaccumulating species, the economic value besides the environmental benefits.

In the incineration process, the organic matter is destroyed, releasing metals as oxides [53]. At higher temperature, over 600ºC, the most toxic metals became volatile [37], and because of this reason the thermal treatment should not exceed this temperature [2]. Thus, by the incineration of plant biomass, the metal concentration is increasing by ash mass and the volatilization should be avoided. A very important factor that influenced the metal recovery efficiency was the leaching solution, which determined the metal solubility according with the pH of leachate. The use of nitric acid and sulfuric acid as leaching reagent had a positive influence on the nickel and chromium solubility. The lowest solubility showed tin and copper. The experimental results showed that the methods used for thermal treatment of plant biomass and the leaching method were efficient and a quantity of 0.7 mg of alloyed (Ni, Cr and Mn was majority) metals was obtained. For a selective recovery of heavy metals is necessary that the electrochemical process should be conducted according to the differences of deposition potential of each metal [42, 43].

The balance of phytoremediation and heavy metal extraction indicated that the thermal treatment followed by ash leaching and electrolysis was an efficient method of metal extraction from the phytoremediation by-products – the plant biomass. By this process could be recovered saleable heavy metals and the waste resulted from phytoremediation was a heavy metal low-concentration material, without toxicity risk.

8. Conclusions

For the studied area, in the vicinity of metallurgical plant of Targoviste city, the heavy metal concentration in soil for Cu, Sn, Pb and Mn exceeded the alert threshold for agricultural soil. For Zn, Ni and Cr, some of the results showed values that exceeded also the alert threshold for industrial soils.

The metal concentration in soil was according with the position against the pollution source.

The heavy metal concentration was widely different in the seven studied species of perennial grasses, and the bioaccumulation capacity was different according with the species and metal concentration in soil. Even a species accumulate high concentrations of metals, this could be because of the high content of metal in soil, not because the species showed accumulative capacity – BF higher than 1 (Table 8).

Metal	Maximal concentration in studied species (mg/kg)		Maximal value of bioaccumulation factor	
Cu	113,83	*Festuca pratensis*	1,12	*Cynodon dactylon*
Zn	921,67	*Lolium perenne*	1,36	*Cynodon dactylon*
Sn	379,23	*Festuca pratensis*	6,06	*Cynodon dactylon*
Pb	66,30	*Lolium perenne*	12,29	*Luzula campestris*
Co	4,6	*Agrostis tenuis*	0,40	*Agrostis tenuis*
Ni	60,23	*Agrostis alba*	1,63	*Agrostis alba*
Mn	703,93	*Lolium perenne*	0,33	*Lolium perenne*
Cr	191,99	*Stipa capillata*	2,67	*Agrostis alba*
Mo	25,63	*Festuca pratensis*	15,34	*Cynodon dactylon*

Table 8. The maximal values of heavy metal concentration and bioaccumulation factor for studied plant species

The thermal treatment of plant biomass was an effective method for metal concentration in the material which will be used in metal recovery.

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The leaching method should be improved for the extraction of a higher percentage of metals from ash. A quantity of 0.7 mg of metals deposition was obtained after the run of an electrochemical procedure for metal recovery.

By thermal treatment, leaching and electrolysis, small quantities of heavy metals can be recovered from plants used in phytoremediation of polluted soils. The extraction of these elements has advantage for environmental protection, by decreasing the risk of toxicity of heavy metals in soil.

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