

Article

Assessment of Heavy Metal Pollution Using Forest Species Plantations of Post-Mining Landscapes, Ptolemais, N. Greece

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Abstract: The main purpose of the study was the absorption of heavy metals in the leaves of forest tree species, which were planted in two different plots for forestry use and environmental restoration. Four species were studied *Pinus brutia*, *Robinia pseudoacacia*, *Quercus trojana* and *Fraxinus ornus*. Forty-eight leaf samples were collected which consisted of six samples from each species at each plot. The heavy metal concentrations in the leaves were measured for the following nine heavy metals: iron (Fe), copper (Cu), chromium (Cr), nickel (Ni), cadmium (Cd), manganese (Mn), zinc (Zn), cobalt (Co) and lead (Pd). The determinative estimation of metal concentration was carried out in the clear filtrate, using ICP-OES. Statistically significant differences in the concentrations of the heavy metals were found among the species, as well as between the two plots. It was only in *Robinia pseudoacacia*'s leaves that the cadmium concentration showed a statistical difference among the other species. The same applied for manganese in *Quercus trojana*'s leaves and zinc for *Pinus brutia*. The careful selection and planting of the appropriate forest tree species provides for an overall improvement in the environment in heavy metal polluted sites, such as those resulting from thermal power plants.



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1. Introduction

Lignite is the most common type of coal in Greece, occurring in more than 60 sedimentary basins [1]. Lignite is exclusively used in Greece for electrical power regeneration and has led to the production of the most cost-effective kilowatt hour within the European Community [2]. Four Thermal Power Stations (TPSs) with more than 4000 MW total installed capacity are located in the Ptolemais-Amynteon basin, which is the most important natural lignite basin in south Europe and is located in west Macedonia, Greece [3].

The main potential source of air and soil pollution in this area are the four TPSs, which release fly ash into the atmosphere [4]. Fly ash is the main waste residue produced during pulverized lignite combustion and is collected by electrostatic precipitators. Despite the fact that most thermal power plants have been equipped with electrostatic precipitators in recent years, significant amounts of fly ash are still emitted into the atmosphere because of the high rate of lignite combustion [5]. Several studies have demonstrated the environmental impacts of fly ash air pollution [5–11]. This fly ash contains heavy metals in concentrations comparable to, and in some cases greater than, those found in the upper continental crust [4].

With the construction and operation of the four TPSs, the vegetation of the area has been exposed to pollution emissions. As a result, the environmental situation has been additionally complicated by the designation of special areas with reclaimed soils where lignite has been exhausted. Such reclaimed soils have led to extremely harsh stress conditions for plant survival [12].

The restoration of old mine areas, where lignite has been exhausted, is one of the goals of the Public Power Corporation (PPC). To achieve this, the PPC has selected woody

species to remove pollutants from the environment or to render them harmless [11]. The absorption and accumulation of heavy metals in plants are the result of the influence of some external factors, such as the concentration of heavy metals in fly ash, atmospheric deposition, rainfall, plant growth stage, and soil properties. The solubility of heavy metals generally increases with the decrease in the pH of soil; the high values of soil pH could represent a reduced metal transfer from soil to plants [13].

Table 1 represents the concentrations of important heavy metals in fly ashes and soils that were measured in the same area [2,14–16]. The pollution of the area's soils from fugitive fly ash emissions is minimized, however, due to the alkalinity of the Greek soils and the alkalinity of the fly ash [14]. The main pathway of heavy metal accumulation by plants is via atmospheric position.

Table 1. Concentrations, in ppm, of heavy metals of environmental interest in fly ashes and reclaimed soils.

Heavy metals	Fly ashes	
	(Foscolos et al., 1998) [15]	(Fillipidis et al., 1997) [16]
Cd	0.4	1.6
Co	17	31
Cr	317	451
Cu	24	59
Ni	218	449
Pb	29	36
Zn	-	205

Heavy metals	Soils	
	(Pentari et al., 2006) [2] With the addit. of top soil	(Pentari et al., 2006) [2] Without the addit. of top soil
Cd	0.3	0.2
Co	33.4	15.2
Cr	312	99.7
Cu	34.2	30.8
Ni	209	66.5
Pb	63	59.6
Zn	69	43

Uptake and accumulation of heavy metals in woody species follow two different pathways, one via the root system and the second via the leaves [11,17–19].

Trees via their leaves reduce air pollution in two ways: with direct removal of pollutants from the air, and with indirect reduction through preventing the creation of secondary air pollutants. Direct reduction is carried out through pollutant absorption by the stomata of leaves. In addition, the crown of the trees stops pollutant movement and diffusion [20] by absorbing them, via the wet surface of their leaves [21]. Indirect pollution reduction occurs due to the tree's cooling effect of the atmospheric temperature (via shading and evapotranspiration mechanisms), which in turn leads to lower rates of chemical reactions in the atmosphere and reduces secondary pollutant production by interfering with VOC production by the leaves/needles [22,23].

The aim of this study was to determine the levels of airborne heavy metal contamination (Cu, Fe, Mn, Zn, Cd, Co, Cr, Ni, Pb) in trees leaves at reforestation locations (four forest species and two planting distances) with reclaimed soils in post-mining landscapes.

2. Materials and Methods

2.1. Study Area

The Ptolemais region is in northwest Greece, where the biggest lignite deposits of Greece are found. Four Thermal Power Stations (TPSs) are located in this basin. About 64 Mt of lignite, produced by open-cast mining, is used in the TPSs. Knowing that around 15% of the fuel is converted to ash, and assuming 99.9% collection efficiency for the electrostatic

precipitators, the total amount of fly ash which is released into the atmosphere is about 9.6 Kt annually [5,24,25].

The climate is continental Mediterranean, characterized by low temperatures during winter ($-1.3\text{ }^{\circ}\text{C}$ to $6.3\text{ }^{\circ}\text{C}$) and high temperatures during summer ($20.1\text{ }^{\circ}\text{C}$ to $28.5\text{ }^{\circ}\text{C}$). Prevailing winds are weak to moderate, and their direction is NW/SE [8,26,27].

2.2. Methods

The research was conducted in the main lignite field of PPC-Ptolemais. There were two different plantation locations, with one being utilized for forestry and the second for environmental restoration. The main purpose of plantations in the first area was the production of timber. Three broad-leaved trees were planted there: *Robinia pseudoacacia* L. (Black Locust), *Quercus trojana* Webb. (Macedonian Oak) and *Fraxinus ornus* L. (Flowering Ash). These were planted in a $2.5\text{ m} \times 2.5\text{ m}$ planting joint, and one conifer species *Pinus brutia* Ten. (Calabria or Turkish Pine) was planted in a $2\text{ m} \times 3\text{ m}$ planting joint.

The main purpose of plantations in the second area was for environmental restoration, in order to shape the landscape of the area in such a way that it is directly related to its natural features. The forest tree species used for the creation of areas for the purpose of environmental restoration was the conifer *Pinus brutia* in a $5\text{ m} \times 5\text{ m}$ planting joint, the broadleaf species *Robinia pseudoacacia* L., *Quercus trojana* Webb. and *Fraxinus ornus* L. in a $5\text{ m} \times 5\text{ m}$ planting joint. It is important that in such plantations, the species selected for planting (in addition to forestry use or ecological-aesthetic restoration) is firstly to survive, and secondly to have the ability to retain pollutants.

A variety of forest species have been planted in the past in the study area. However, three species, *Pinus brutia*, *Quercus trojana* Webb. and *Fraxinus ornus* L. were planted for the first time. Therefore, we decided to study these species. The leaf morphology differs among the four species, i.e., *Pinus brutia*'s needles are rough, while *Robinia pseudoacacia* and *Fraxinus ornus* leaves are compound and *Pinus brutia*'s leaves are lamina [27–33].

We collected leaves from six trees of each species at each plot ($n = 48$). The samples were collected from the same part of the plants, since the content in heavy metals varies depending on the part of the plants [34]. Leaves were sampled uniformly around the lower foliage (1.5 to 2.0 m) [26] and from the four points of the horizon [35,36].

The sampled trees were selected using systematic sampling [37]. The repetitions are of vital importance, since pollutant concentration may vary among different species and even for the same species [34]. The sampling was carried out after a prolonged rainless period (end of summer), [37,38].

All samples were collected following Kováč's suggestion [37]. At both plantation locations, 48 foliage samples were taken, with 24 samples from each location and 6 samples taken from each species. Leaves were sampled uniformly from the four points of the horizon [35,36] and at a fixed height of around 2 m from the ground [26]. Leaf samples (approximately 200 g) were collected in the morning, placed in paper bags and oven-dried at $80\text{ }^{\circ}\text{C}$ for 24 h . All samples were washed with distilled water, desiccated at room temperature to constant weight, ground and sieved with a 2 mm mesh (0.2 mm Culatti 220 Model, 301122). All measurements were carried out on fully developed leaves, undamaged by insects, and with no color differentiations. For evergreen coniferous species, biennial needles were selected [39–42].

Chemical analyses were carried out to determine of copper (Cu), iron (Fe), manganese (Mn), zinc (Zn), cadmium (Cd), cobalt (Co), chromium (Cr), nickel (Ni) and lead (Pb) levels. Specifically, 1 gr of sieved foliage matter samples were heated overnight (16 h) at $550\text{ }^{\circ}\text{C}$ in a muffle furnace and cooled in a desiccator to room temperature. Afterwards, 5 mL HCl 6N was added to the samples to dissolve the ash. The supernatant was placed in 50 mL volumetric flasks, topped up with water. The metal concentration was determined in the diluted ash by using an ICP-OES (Perkin Elmer Optical Emission Spectrometry, Optima 2100 DV), an inductively coupled plasma optical emission spectrometer [15,39–46]. The respective wave lengths which were used and the lowest detectable metal concentration

according to instrument's specifications were: (1) for Cu 0.0097 ppm, (2) for Fe 0.0046 ppm, (3) for Mn 0.0014 ppm, (4) for Zn 0.0059 ppm, (5) for Cd 0.0027 ppm, (6) for Cu 0.0097 ppm, (7) for Cr 0.0071 ppm, (8) for Ni 0.015 ppm and (9) for Pb 0.042 ppm, respectively.

2.3. Statistical Analysis

A statistical analysis was conducted to determine the differences in the heavy metal levels of the samples using analysis of variance/General Linear Models [39,40]. The experimental design was a 2×4 factorial completely randomized design (two plots \times four tree species). Significant differences among means were detected by the Tukey's test. The Tukey test was chosen to reduce the expansion Error Type I cumulative rate [41]. Statistical analysis was performed using the SPSS statistical package v 17.0 (SPSS Inc., Chicago, IL, USA). Prior to analysis, the metal concentrations of Mn, Zn, Cd, Ni and Pb were log transformed, in order to homogenize error variances. A value of $p < 0.05$ was considered significant.

3. Results

Metal Retention

The mean concentrations of copper, iron, manganese, zinc, cadmium, cobalt, chromium, nickel, and lead of the tree leaves and needles are given in Table 2.

Table 2. Heavy metal concentration in forestry use landscape and in the environmental area (ppm)¹.

Plot	Heavy Metals	Species			
		<i>Pinus brutia</i>	<i>Quercus trojana</i>	<i>Fraxinus ornus</i>	<i>Robinia pseudoacacia</i>
Forestry use	Cu	2.139	3.081	3.395	2.670
	Fe	76.823	90.140	127.363	101.607
	Mn	66.227 (1.715)	24.519 (1.389)	24.911 (1.408)	21.918 (1.353)
	Zn	12.915 (1.143)	17.677 (1.268)	17.055 (1.254)	15.181 (1.190)
	Cd	0.087 (0.036)	0.260 (0.095)	0.178 (0.068)	0.131 (0.052)
	Co	0.114	0.085	0.081	0.077
	Cr	0.427	0.442	0.547	0.456
	Ni	1.115 (0.318)	0.695 (0.227)	0.666 (0.219)	0.550 (0.188)
	Pb	0.433 (0.153)	0.315 (0.115)	0.487 (0.167)	0.271 (0.102)
Env. restoration	Cu	6.622	5.967	4.791	5.791
	Fe	167.778	166.090	181.301	195.950
	Mn	45.380 (1.663)	97.397 (1.806)	22.138 (1.319)	27.669 (1.452)
	Zn	24.400 (1.366)	18.357 (1.277)	19.421 (1.308)	21.985 (1.353)
	Cd	0.160 (0.060)	0.117 (0.046)	0.222 (0.082)	0.602 (0.171)
	Co	0.102	0.101	0.091	0.098
	Cr	0.674	0.721	0.739	0.881
	Ni	2.759 (0.563)	4.058 (0.683)	1.705 (0.430)	2.154 (0.494)
	Pb	0.618 (0.207)	0.765 (0.243)	0.690 (0.224)	0.832 (0.260)

Note: ¹ The values in parentheses correspond to the $\log_{10}(X + 1)$ transformed values.

The concentrations of the heavy metals depended on the species and the plot from which they were collected.

The higher manganese (Mn) and nickel (Ni) mean concentrations were measured in *Quercus trojana*'s leaves, and the higher copper (Cu) concentration was measured in *Pinus brutia*'s leaves at the forestry use plot. In addition, the higher concentrations of iron (Fe), zinc (Zn), chromium (Cr) and lead (Pb) were measured at the forestry use plot. Furthermore, the higher concentration of iron (Fe) was measured on the leaves of *Fraxinus ornus* trees (Figure 1).

Except for nickel, all the other heavy metals showed higher concentrations in the leaves of the trees that were planted for environmental use. For example, the mean copper concentration in the tree leaves that were planted in the forestry use plot was 2.821 ppm, rather than 5.793 ppm in the environmental use plot. The corresponding concentrations for

iron was 98.983 ppm (first plot) and 177.780 ppm (second plot), for manganese 34.394 ppm and 48.146 ppm, for zinc 15.707 and 21.041 ppm, for cadmium 0.164 and 0.275 ppm, for cobalt 0.089 and 0.098 ppm, for chromium 0.468 ppm and 0.754 ppm, and for lead 0.376 and 0.726 ppm, respectively.

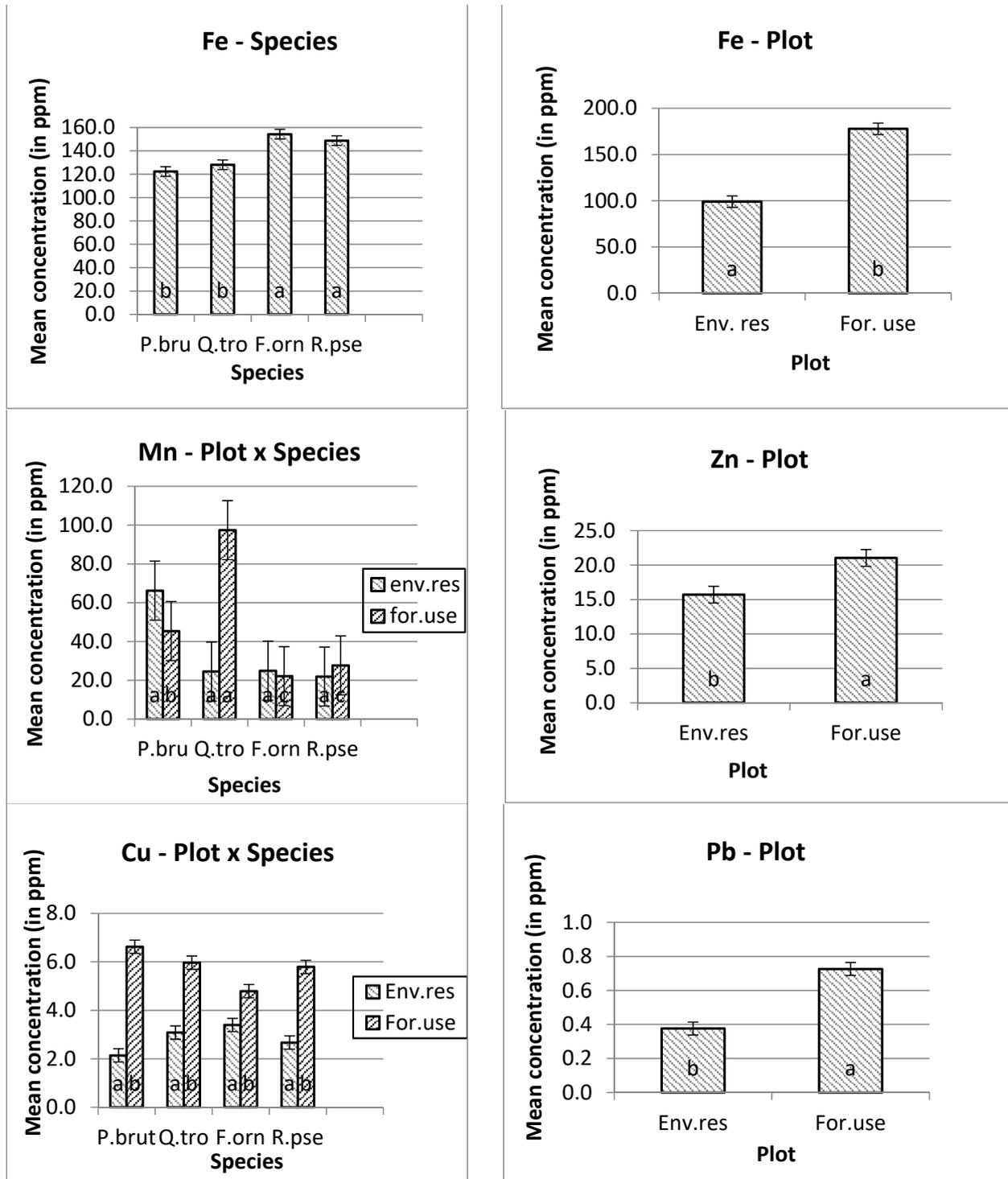


Figure 1. Cont.

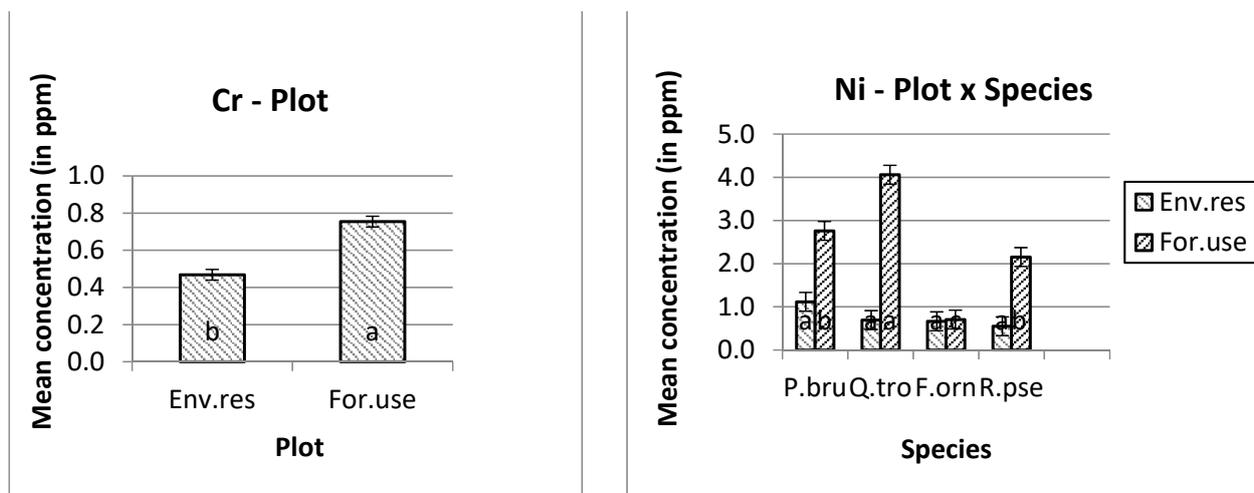


Figure 1. Mean and s.e. of the studied heavy metals concentrations. The differences in the mean values of the heavy metal concentration with different letters are significantly (ANOVA, $p < 0.05$ and the Bonferroni Test of multiple comparisons).

4. Discussion

An environmentally sustainable development approach for coal mining activities, reclamation, and reforestation of depleted and/or abandoned coal mines is essential. The concentration of heavy metals in the fly ashes and their solubility in water in the reclaimed soils, hence their absorption or retention by plants, are of great importance. Although there are many studies about the presence of heavy metals in the fly ashes originating from Greek power stations [46–51], there are few studies on the retention of heavy metals by plants [11,52].

Plant biomonitoring and retention of heavy metals has been widely applied as a complementary approach to conventional methods [53–55]. Trees are very efficient at trapping atmospheric particles. Leaves of various tree species, both evergreen and deciduous, have been studied for this purpose [11,56,57].

In the present research, the average concentration of heavy metals in the leaves of the forest species was $Fe > Mn > Zn > Ni$ for all of the species. The descending order for the rest metals was $Cr > Pb > Cd > Co$ for *Pinus brutia* and *Fraxinus ornus*. For *Quercus trojana* the descending order was $Pb > Cr > Cd > Co$ and for *Robinia pseudoacacia* was $Cd > Cr > Pb > Co$. Similar results were also obtained in other studies on trees and other vegetation types (mosses, lichens, sea plants) [29,58–62].

Likewise, not one species that displayed the maximum concentration for all of the measured heavy metals. *Pinus brutia*, for example, showed the highest copper, zinc, and cobalt concentration. As in most coniferous trees, the needles of *Pinus brutia* remain in the tree from two to five years. Therefore, they are exposed to the polluted air for a longer period in relation to the leaves of deciduous trees. The sunken stomata of *Pinus brutia* borne in longitudinal bands and its rough surface are among the reasons for the high heavy metal concentration in its leaves [30].

Beckett et al. [62] stated that coniferous trees have higher air pollutant concentration than broad-leaved trees, but in this study the broadleaves species showed maximum concentrations for some of the heavy metals that were studied. Oak leaves remain on the trees during winter, whereas the other broadleaves trees lose their leaves in the winter season. During this period the leaves are dry and accumulate heavy metals in a high capacity, derived from dry and wet deposition from the atmosphere [63]. *Quercus trojana*'s leaves retained the highest manganese and nickel concentration.

Fraxinus ornus is a tall tree species which is readily distinguished by its light-grey bark and its large compound leaves. It is also considered to be a pioneer tree due to the fact that it is tolerant to the wide ranges of most environmental factors, except a shortage of light [64].

Fraxinus ornus is the only species that didn't display the maximum concentration of any of the studied heavy metals. The reason for this may be due to the fact that *Fraxinus* sp., such as *Alnus* sp. and *Sorbus* sp. can be considered to be heavy metal excluders. These three plant species may have a mechanism to avoid metal uptake by stabilizing it in the rhizosphere or excluding it from their above-ground tissues by keeping it in their roots [65–67]. Thus, the other three species that were studied could potentially uptake metals from the soil and translocate them to their above-ground tissues like leaves. Unfortunately, root analyses could not be performed at that stage of the experiment. This suggests that the heavy metal concentrations that were measured in *Fraxinus ornus* leaves may have originated primarily from atmospheric deposition.

Robinia pseudoacacia is used as a pioneer species to reforest the degraded land where other species fail to succeed [68,69]. It also has good adaptability to dryness, fast growth, and the ability to fix nitrogen [70]. It can survive under a wide temperature range and grows in almost any type of soil [64]. Tzvetkova and Petkova [71] suggested that *Robinia pseudoacacia* may be considered a bioaccumulator species for Pb, Zn and Cd, and can be used as a bioindicator of pollution with these metals. The strong correlation between the degree of contamination and concentrations in all plant leaves that were assessed, demonstrate that the leaves of *Robinia pseudoacacia* reflect the environmental changes accurately and that they seem to act as an effective biomonitor of environmental quality in areas subjected to industrial and traffic pollution [68]. The *Robinia pseudoacacia* showed the highest concentrations of iron, cadmium, chromium and lead. Leaf accumulation for lead and chromium only depends on the direct uptake of atmosphere particulates by foliar absorption, rather than from their translocation from the soil to the leaves [72]. In many cases, plants seem to accumulate high concentrations of heavy metals such as lead in their cell walls [63].

Cadmium concentrations of tree leaves range between 0.015 to 1.686 ppm. All the studied species had a cadmium concentration below 1 ppm except for *Robinia pseudoacacia*.

Copper concentrations ranged between 1.672 and 8.083 ppm with no strong differences among the studied species. It must be noted that copper concentrations in all of the trees studied are in adverse proportion to iron, because these heavy metals show an antagonistic interaction.

Iron was the heavy metal with the highest concentration in all the studied species, a maximum being observed in the case of *Robinia pseudoacacia* (337.574 ppm) while *Pinus brutia* (50.699 ppm) accounted for minimum values. The systematically higher iron concentration in *Pinus brutia* in relation to the other species makes it a satisfactory indicator of iron pollution [4]. Iron concentrations are, as a rule, in inverse proportion to manganese concentrations, which can be attributed to the antagonistic action of the two elements. This is especially evident for *Fraxinus ornus* and *Robinia pseudoacacia*.

Foliar zinc concentrations in the studied area ranged from 9.022 ppm to 40.164 ppm which is within the normal range [17].

The manganese concentrations of tree leaves ranged from 9.632 and 224.016 ppm with strong differences among the studied species. *Pinus brutia* and *Quercus trojana* had manganese concentrations above 100 ppm, while *Fraxinus ornus* and *Robinia pseudoacacia* had less than 38 ppm. The same differences were shown between species measured by Sawidis et al. [52] for the same area studied.

The average chromium concentration varies between 0.256 ppm and 1.669 ppm. The highest values of chromium in *Robinia pseudoacacia* were accompanied by low values for Mn and Ni, which is normal since these elements have an antagonistic relation with chromium [4]. The same matter could not be confirmed for Cu where *Robinia pseudoacacia* retained high concentrations. It is important to note that in none of the studied species did the chromium concentration exceed the toxicity limits which range from 5–30 ppm [17].

The nickel average concentration ranged from 0.356 ppm in *Robinia pseudoacacia* to 6.191 ppm in *Quercus trojana*. The toxicity limits for nickel in plants ranges from 10–100 ppm [17]. Concentrations higher than 10 ppm have not been observed.

Average cobalt concentration varied between 0.042 ppm and 0.179 ppm. The maximum cobalt concentration was observed in *Pinus brutia*, while *Quercus trojana* displayed minimum cobalt concentration values.

Finally, lead concentrations of tree leaves range between 0.046 ppm for *Quercus trojana* and 1.328 ppm for *Robinia pseudoacacia*. Lead is one of the heavy metals which has very low translocation capability from soil to leaves. Thus, leaf accumulation for lead only depends on the direct uptake from the atmosphere rather than translocation from the soil [19]. For this reason, in descending order lead holds one of the last positions.

The differences that were observed between the two plots may be due to the different planting joints in which the trees were planted. The higher concentrations of heavy metals found in the tree leaves of the second plot suggests that this may be due to much easier air flow between the crowns of the trees.

5. Conclusions

The Ptolemais basin region is in the northwest of Greece. The lignite beds of this basin are under intense exploitation by open cast mining [4]. The depleted or abandoned mines are reclaimed and revegetated after being filled with a mixture of fly ash, overburden and inter-bedded sediments removed from the working mines [25,73]. Before a plantation is initiated, it is essential to consider the existing vegetation, ecological and climatic factors. It is important to note that the trees not only play an important role in the retention of heavy metals on their leaves, but also plays an important role in protecting the terrain from wind erosion [12].

It was only in *Robinia pseudoacacia* leaves that the cadmium concentration showed a statistical difference among the other species. The same applied for manganese in *Quercus trojana*'s leaves and zinc for *Pinus brutia*. Therefore, the selection of forest species for plantations in the post-mining area of Ptolemais basin should be with different forest species (coniferous and broad-leaved) which contributes to the enhancement of the environment and the remediation of post-mining areas.

Only three (Mn, Cd, Co) of the nine heavy metals didn't show a statistical difference between the two plots. The two plots were planted with the same species but with different planting joints. Thus, further research must be carried out to determine the effect of the planting joints in the ability of forest trees to retain heavy metals.

Overall, the selection and planting of the appropriate forest species is critical in order to ensure improvement in the environment in the vicinity of thermal power plants.

Author Contributions: "Heavy metal retention by different forest species used for restoration of post-mining landscapes, N. Greece" conception and experiment design: T.S., I.S., P.P. and T.G.P. Laboratory chemical analyses and analyses and interpretation of the data: T.S. Critical revision of the article: I.S., P.P. and T.G.P. T.S. takes responsibility for the integrity of the work from the inception to the finished article. All authors have read and agreed to the published version of the manuscript.

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