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State of Forest Plantations Used for Afforestation of Heavy Metals Polluted Lands Around Former Metallurgic Plant "Kremikovtsi" (Bulgaria)

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Abstract. A study was carried out on the sustainability of forest plantations established on soils contaminated with heavy metals in the vicinity of the former "Kremikovtsi" metalurgic plant. Soils and forest vegetation near the village of Buhovo (black pine *Pinus nigra* Arn.) and Lokorsko I (red oak *Quercus rubra* L.) and Lokorsko II (winter oak *Quercus sessiliflora* Salisb.) were studied. The soils of the area are geochemically enriched with lead, reaching up to 136 mg/kg for Pb under the Black Pine Plantation. The lowest levels of assimilation have the red oak leaves, as evidenced by the analysis of the heavy metals content: Zn, Cu, Pb, Cd and the biological absorption coefficient Ah, and it is recommended that for the soil reclamation to be used this tree species.

Key words: red oak, black pine, biological absorption coefficient.

Introduction

In the conditions of intense industrialization and active technogenic impact, afforestation with forest plantations on contaminated lands is proved to be a stable, lasting and cheap opportunity to rehabilitate ecosystems, to improve hygienic and sanitary conditions and microclimate of the environment. For many years, defensive or meliorative afforestations have been widely used in combating erosion, natural disasters and for providing a healthy, clean and aesthetic environment in cities and other settlements (Zahariev, 1977; Popov *et al.*, 2018). The tree vegetation is successfully applied around roads and highways to reduce soil pollution with heavy metals (Chulgijan & Petrov, 1985; Kachova & Atanassova, 2014). By forest vegetation are improved the structure and properties of the soil, and by the fall and decomposition of the dead forest litter (DFL) is improved soil nutritional status (Sokolovska *et al.*, 2001). Forestry-biological restoration is successfully used and around a number of industrial enterprises (Gencheva & Geleva, 1984; Malinova, 1998). Significant aesthetic, mitigating and meliorative effect of the forest plantations makes the forest-biological restoration particularly effective. Forest vegetation improves the hydro-thermal regime and the fertility of disturbed lands, creating more favorable growing conditions in future land uses (Prokopiev, 1967; Alexandrov *et al.*, 2001). Forest vegetation used for restoration is also considerable reservoir of carbon in the ecosystem (Zhiyanski *et al.*, 2014). Of particular

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importance is the choice of species for afforestation. Individual tree species thanks to their biological, physiological and morphological features are distinguished by different adaptability and resistance to contaminated lands. Less sensitive species are recommended for industrial areas: acacia (*Robinia pseudoacacia* L.), american ash (*Fraxinus americana* L.), elms (*Ulmus spp.*), sycamore (*Acer negundo* L.), simple dogwood (*Cornus mas* L.), oaks (*Quercus spp.*), silver spruce (*Picea pungens*), douglas- fir (*Pseudotsuga menziesii* (Mirb.) Franco), west tuya (*Thuja occidentalis* L.), juniper (*Juniperus spp.*) (PROKOPIEV, 1967; TSAKOV & DIMITROVA, 2002). The lands around the former "Kremikovtzi" plant are remarkable with poor quality, mainly with the presence of heavy metal pollution (HM). Questions such as: "Which are the most suitable forest plant species for afforestation around the former plant?"; "What is the adaptability of plantations to the specific pollution of the soils in the area?", remain open yet.

The aim of this study is to analyze the accumulation of heavy metals in the leaves of several tree species, used for afforestation in the area of former Kremikovtsi plant; to assess the state of the established plantations and to recommend forest species suitable for future afforestation.

Material and Methods

The sample plots (SP) are located in the pre-mountainous climatic region of the Sofia region with a typical temperate continental climate and an annual sum of precipitation ~ 600 mm. Western winds predominate (up to 2/3 of the cases).

The sample plots (SPs) in the following objects were used for study:

- *Buhovo* with altitude of 750 m, brown forest soil (Eutric Cambisols) and black pine plantation (*Pinus nigra* Arn.);
- *Lokorsko I* at altitude of 650 m, cinnamoric soils (Chromic Luvisols) and red oak plantation (*Quercus rubra* L.);
- *Lokorsko II* with altitude 650 m, cinnamonic soils (Chromic Luvisols) and a winter oak plantation (*Quercus petraea* Liebl.).

Soil samples were taken from 5 depths: 0-5, 5-10, 10-20, 20-40, 40-80 cm in 4 repetitions for each site. Laboratory analyzes were performed according to established methods (DONOV *et al.,* 1974): mechanical composition – by Kaczynski method; pH - potentiometrically with "Pracitronic MV 88"; total carbon – by Turin method. Total heavy metal content was determined on a "Perkin Elmer 370 A" atomic absorption spectrophotometer after treatment with aqua regia (HNO_3 : HCl 1: 3) (ISO 11466); mobile forms of HMs – by atomic absorption after treatment with 1N $CH3COONH_4$ at pH = 4.8.

Analyses of the elements in the leaves were made after processing with concentrated HNO_3 and was determined by AAC Method (ICP Forests, 2006). An average sample of 5 representative trees was taken.

Dendrometrical characterization of the trees from the SPs (20/50m = 0.1ha.) was carried out on the basis of measuring the diameters of the trees (with accuracy of 2 cm) and at 3 heights (0.5 m accuracy). To assess the general physiological state of the trees an entomological characteristic was made. Separately, plastid pigments: chlorophyll "a", chlorophyll "b" and carotenoids in leaves in deciduous trees and annual needles of coniferous trees were defined, through the method of MACKINNEY (1941). It was done in three repetitions for June and October.

The average diameter (cm) is obtained by the arithmetic basal area – formula:

$$DbH=SQRT(1.274*\sum G/n)*100$$

where: $G=\pi*d^2/4$ – is a basal tree area(m^2);

d - is the tree diameter(cm);

n - is number of trees;

DbH – is the average diameter (cm).

The average height (m) is calculated as a weighted average according the Lorey's formula. The average height was obtained as weighted mean from the heights of all trees in the relevant sample plots after the formula of LOREY (1878):

$$H = h_1 g_1 + h_2 g_2 + \ldots + h_n g_n / g_1 + g_2 + \ldots + g_n \text{ (m)}$$

where: h – is a height of each tree (1,2, ….n) (m);

g – is a basal area of each tree (m²).

Stand quality class is determined by interpolating and using the tables for determining the quality of black pine plantations according Tsakov (PORYAZOV *et al.,* 2004), of red oak plantations according Krastanov and Hristov (PORYAZOVPORYAZOV*et al.,* 2004) and of high-stemmed oak stands according Nendyalkov (KRASTANOV & RAYKOV, 2004).

Results and Discussion

Soil Analyses. When considering the condition of plantations on polluted lands, the specific characteristics of soils are of fundamental importance. Soil determines the quality of the growth environment. The results for the general characterization of soils and the content of total forms of heavy metals (HM) in SPs are given in Table 1.

The soil of Buhovo has an alkaline reaction (pH 7.85 - 8.10). The soils of the other SPs are defined as medium to strongly acid along the profile depth. According to data from the mechanical composition, the soil substrates under the wood pine plantation in Buhovo have the highest content of clay and fine clay. They are the most loamy along the profile compared to the rest. The majority of the soils in the surveyed areas are poor in organic carbon, especially those under the winter oak in Lokorsko II. This low content of organic matter shows, that the organic matter has no significant role in the sorption of HMs. The surface horizons of Buhovo are relatively richer in organic carbon. This shows a relatively higher level of buffer capacity of this soil towards toxic pollution. For the soils from the investigated area the Zn content is not high. These concentrations do not exceed the levels for precautionary concentrations and maximum permissible concentrations for industrial/production sites and also intervention concentrations for HMs adopted in the country (Regulation № 3 / 01.08.2008). This is applied for the medium sandy-loam soil from Buhovo too. In the soils of the SPs, the Cu content is within the range of this element's variation in the country. The content of Cu is within the frame of the adopted permissible concentrations (including the soils from Buhovo, where pH>6). The data for Pb show pollution with technogenic and geochemical origin along the entire depth of the soil from Buhovo. Precautionary concentrations of Pb in the soil (at the rate for sandy loam soil rate of 40 mg/kg) have been exceeded. But the maximum permissible and interventional concentrations (at the rate in pH > 7.4 of 150 mg/kg) are not exceeded. For the soils from Lokorsko I and Lokorsko II there are a technogenic contamination of the surface layers of 0-5 cm with exceeding of the precautionary values (concentrations > 40 mg/kg for sandy clay soils). The analysis of the obtained results shows presence of HM contamination in the soils from Buhovo. But these exceeding concentrations are also associated with higher pH values, which in the other hand makes these soils more resistant to pollution. The Cd values vary below the regulatory concentrations adopted in the country. There is one with exception: the surface layer 0-5 cm of the soil from Buhovo, where the concentration is equal to the precautionary value for sandy loam soils (0.6 mg/kg).

For the specific clarification of the accumulation of HMs into tree species and in particular to clarify their toxicity, the amo-acetate extractable mobile forms of HMs in the soils were determined. The results are given in Table 2.

Table 1. Characteristics of soils and total contents of Cu, Zn, Pb, Cd (mg/kg).

SP	Depth, cm	Mechanical composition (%)			pH	C g/kg	Zn mg/kg	Cu mg/kg	Pb mg/kg	Cd mg/kg
		clay	sand	fine clay						
Buhovo	0 -5	31.18	68.82	8.29	7.85	22.0	67	42	136	0.6
	5 – 10	29.22	70.78	8.29	7.95	16.8	60	38	108	0.5
	10– 20	31.36	68.64	8.31	8.00	14.9	94	34	82	0.5
	20 - 40	30.68	69.32	8.31	8.00	12.3	63	35	84	0.5
	40 - 80	36.38	63.62	8.29	7.80	9.7	59	29	110	0.6
Lokorsko I	0 -5	25.74	74.26	4.05	5.20	15.8	25	21	48	0.05
	5 – 10	21.27	78.73	4.05	4.50	6.5	22	18	23	0.1
	10– 20	20.60	79.40	8.08	4.45	5.2	17	10	16	0.06
	20 - 40	25.30	74.70	4.06	4.85	3.8	21	20	21	0.06
	40 - 80	21.25	78.74	8.10	5.10	1.9	20	19	21	0.06
Lokorsko II	0 -5	20.97	79.03	8.06	6.40	11.0	17	20	64	0.1
	5 – 10	35.35	64.15	4.03	5.40	7.1	13	14	26	0.1
	10– 20	17.12	82.88	8.06	4.70	5.8	10	10	17	0.02
	20 - 40	17.32	82.68	4.03	4.65	4.5	14	13	19	0.02
	40 - 80	25.08	74.92	8.09	4.90	1.3	20	17	29	0.07

Table 2. Mobile forms of Cu, Zn, Pb, Cd (mg/kg) and % of their total content.

SP	Cu		Zn		Pb		Cd	
	mobile	% of total	mobile	% of total	mobile	% of total	mobile	% of total
Buhovo	2	5	2.5	4	15.5	11	0.45	75
	2.5	7	1.5	3	10	9	0.4	80
	2.5	7	1.5	2	12	14	0.35	70
	3.5	10	4.5	7	13	15	0.35	70
	3	10	2	3	14	18	0.5	83
Lokorsko I	1	5	1	4	3.5	7	-	-
	2	11	0.5	2	1.5	6	-	-
	2	12	0.5	3	5	31	-	-
	2.5	12	0.5	2	4.5	21	-	-
	2	10	1	5	4	19	-	-
Lokorsko II	2	10	1	6	9.5	15	-	-
	1	7	0.7	5	5	19	-	-
	1	10	1	9	5	29	-	-
	2	15	1	7	5	8	-	-
	2	15	1.5	7	4.5	15	-	-

Table 3. Total content of heavy metals in leaves of the trees.

SP species	Age	Zn	Cu	Pb	Cd
		mg/kg			
Buhovo - black pine	1	77	38	249	1.4
	2	29	16	28	0.3
	3	20	7	28	0.3
Lokorsko I - red oak		24	4	5	0.2
Lokorsko II – winter oak		18	8	19	0.4

Data show that despite the increased total concentrations of HMs in the soil of Buhovo, due to the alkalinity of the medium (pH ~ 8) their solubility and mobility, and hence their accessibility to plants is low. The percentage of mobile forms to the total forms of Cu and Zn is below then the other more acidic soils, which is the reason for the poor suppling of this soil with plant-accessible mobile forms of these two elements. Concerning Pb where there are high total concentrations the concentration of the mobile forms slightly higher than those of the more acidic soils. The major buffering factor is again the alkalinity of the medium. In relation with Cd there is the opposite fact: the alkaline medium is not a buffering factor, and the movable forms of this element are high as a percentage of the total concentrations.

Foliar analysis is also used to determine the level of nutrition of plants, which also affects their overall general condition. The background concentration of Pb in white pine needles for Western Europe is 2.45-3.90 mg/kg, but according to our data (YOROVA & KUCHUKOV, 1996) for the Western Stara Planina Mts. it is up to 4 mg/kg. In terms of critical levels the values, indicated in the literature vary widely: Pb 3-300 mg/kg, and for Cu 2-100 mg/kg. In most cases the data reported are higher than the tolerant dose (10mg/kg for Pb). The data from the present study show too high Pb content in the black pine needles in Buhovo. Concerning Cu and Zn there are also higher contents of these elements in the black pine needles. Cd is within background content. According to the literature, the background concentrations of trace elements in oak trees are: Pb - 6mg/kg, Zn - 25mg/kg, Cu - 10 mg/kg, Cd – 0.5 mg/kg. In this sense, there is only contamination with Pb in the needles of the winter oak from Lokorsko II. Low values of HMs are found in the leaves of the red oak (*Q. rubra* L.) of Lokorsko I, especially with respect to Cu, Pb and Cd.

To elucidate the absorption of HMs in the woody vegetation, depending on their concentrations in the soil, a bio-absorption coefficient was calculated. This coefficient shows the intensity of biological uptake of HMs, and is calculated by the formula:

$$Ah = Lx / Nx,$$

where: Lx is the content of a chemical element in the ash residue of the plant;

Nx is its content in the surface layer of the soil (GIGOV *et al.*, 1998).

If: 10 > Ax > 1 there is a high degree of biological absorption of the element; 1 > Ax > 0.1, an average bioavailability of the element is achieved and at Ax < 0.1 a low bioavailability of the element is showed (Table 4).

The lowest degree of absorption of all HMs (Zn, Cu, Pb, Cd) is found in the leaves of the red oak (*Q. rubra* L.) from Lokorsko I.

In order to compare the tree species growth peculiarities in the studied plantations, some dendrometrical indicators were defined (Table 5).

The determined stand quality class of each of the studied plantations is a complex dendrometrical indicator for the quantitative productivity of the respective tree species for a given age and under the appropriate habitat conditions. The results show, that the trees of the winter oak (Lokorsko II) is the most productive, followed by the red oak (Lokorsko I) and last but not least the black pine plantation (Buhovo).

In Table 6 are shown the more important types of pest disease-causing agents, as a part of the entomological characterization of the test areas from Buhovo and Lokorsko. With the "+" sign, the following degrees of distribution of pests are differentiated: + - rarely encountered; ++ - commonly encountered; +++ - encountered very often.

A pathogenic fungus, cancer agent was discovered in Buhovo, which could cause major damage. But it was too low met, which gives grounds for assertion, that it could hardly develop. No insect pests were found in the same SP. In the Lokorsko I, in only one single case wounds were found on the stem of a single tree from the wood decomposing fungi *Stareum hyrsutum*. No pathogenic fungi and pests were found in in Lokorsko II. But part of the lower leaves of the winter oak were attacked by flour mana (fungi of the family Peronosporaceae and Pythiacea), and up to 10% of the leaves were damaged by insect pests (Torticidae, Geometridae, Noctuidae).

Quantitatively were determined plastid pigments. The results are given in Table 7.

Table 4. Biological absorption coefficient.

SP	Age	Ax			
		Cu	Zn	Pb	Cd
Buhovo – black pine	1	0.9	1.2	1.8	2.3
	2	0.4	0.4	0.2	0.6
	3	0.2	0.3	0.2	0.5
Lokorsko I – red oak		0.2	1	0.09	2
Lokorsko II – winter oak		0.4	1.05	0.3	4

Table 5. Dendrometrical indicators in studied SPs.

SP	Composition	Age	$H_{av.}$ m	$D_{av.}$ cm	Stand quality class	Number trees/ha
Buhovo	Black pine (*Pinus nigra* Arn.)	38	11.5	13.2	IV	2130
Lokorsko I	Red oak (*Quercus rubra* L.)	43	18.0	14.7	III	5150
Lokorsko II	Winter oak (*Quercus petraea* Liebl.)	43	15.5	17.5	I	2050

Table 6. Species composition and occurrence of major fungus disease.

SP	Find	Species	Importance	Meeting
Buhovo *Pinus nigra* Arn.	branches	*Gremmenilla abietina*	+++	+
Lokorsko I *Quercus robur* L.	trunk	*Stereum hyrsutum*	+	+

Table 7. Plaster pigment content.

Tree species SP	Month	Chlorophyll "a"	Chlorophyll "b"	"a"/ "b"	"a"+"b"	Carotene	a+b/ Carotene
P. nigra	VI	0.980	0.471	2.08	1.451	0.280	5.18
Buhovo	X	0.817	0.361	2.26	1.178	0.242	4.86
Q. rubra L.	VI	1.125	0.407	2.77	1.532	0.320	4.78
Lokorsko I	X	0.917	0.402	2.28	1.319	0.378	3.49
Q. sessiliflora S.	VI	1.080	0.471	2.29	1.552	0.352	4.09
Lokorsko II	X	0.870	0.399	2.18	1.269	0.480	3.05

The biosynthesis of green pigments: chlorophyll "a" and chlorophyll "b" is not impaired. Their total amount decreases in June - October. This decrease is mainly due to the reduction of chlorophyll "a", which is a more labile pigment. Its lability is more intense in case of a higher degree of atmospheric contamination and acid deposition. The ratio of chlorophyll "a"/chlorophyll "b" is considered an indicator determining the degree of gas resistance of tree species. It shows lower values than those considered as optimal 3:1. In our case, the results are about a 2:1 ratio. According this indicator, the studied tree species used for afforestation around the "Kremikovtsi" metallurgic plant can are considered sustainable. The amount of yellow pigments: the carotenoids are less varied, especially in deciduous species. The increase is regarded as a protective response under unfavorable conditions. Higher quantities have the leaves of winter oak in October. The quantities in leaves of black pine are stable. The ratio of green/yellow pigments is within the optimal 4:1 range, 5:1. Analogous analyzes were made for the plantations of black pine and white pine around metallurgic plant - Plovdiv (MIRCHEVA, 1996, Sofia, pers. comm.). Greater resistance of *Pinus nigra* Arn have been determined, compared to *Pinus sylvesstris* L. in terms of atmospheric pollution.

Conclusions

The studies conducted and the results obtained are a reason to say that although winter oak trees show greater productivity, the red oak plantations are best suited for establishing on technogenically contaminated terrains, especially those polluted with lead and low-acid pH of the soil. On so studded sample plots at these altitudes, red oak plantation has a low degree of uptake of leaf toxicanta with very good growth indicators and good entomological situation. It is in dependance of the meteorological and ecological conditions of the specific habitats: altitude, exposure, moisture and others.

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References

ALEXANDROV A., H. TSAKOV. P. DIMITROVA. 2001. [Structure of wood crown in plantations of *Rubinia Pseudoaccacia* L. planted on degraded terrains]. – *Nauka za gorata*. 1-2: 5-19. (In Bulgarian).

CHULGIJAN H., I. PETROV. 1985. [Automobile transport and contamination of soils in the country with lead]. - In: Proceedings of *National practical conference „Automobiles and the environment"*. 19-20 November. Razgrad, pp. 98-103. (In Bulgarian).

GANEV S., A. ARSOVA. 1980. [Method of determination of strongly acid and weakly acid cation exchange in soil]. – *Pochvoznanie and agrohimia*, 3: 21-28. (In Bulgarian).

GENCHEVA C., E. GELEVA. 1984. [Forestry-biological restoration of technogenic landscapes]. - In: *Balkan Sci. conference "Study. preservation and use of forest resources."*, II. Sbornik. Sofia. pp. 59 - 64. (In Bulgarian).

GIGOV N., E. NIKOLOVA. G. GELIAZKOV. S. NEDKOV. 1998. [Biogeochemical specific of landscapes in some of reserves in Strandga.] - In: *Proceedings of Scientific conference "70 years of the Forest research Institute"*. 6-7 October. 1998. Sofia. Acad. Publishing house "Marin Drinov", I, pp. 140-145. (In Bulgarian).

DONOV V.. S. GENCHEVA. K. YOROVA. 1974. [*Handbook of soil analyses.*] Sofia. Zemizdat, 220 p. (In Bulgarian).

ICP Forests. 2006. *International Co-operative Programe on Assessment and Monitoringf Air Pollution Effects on Forest. Manuals.* Available at: [icp-forests.net].

KACHOVA V., I. ATANASSOVA. 2014. Influence of forest vegetation on reduction of soil contamination with heavy metals. - *Silva Balkanica,* 15(2): 58-67.

KRASTANOV K., R. RAYKOV. 2004. [*Guide on dendrometry.*] Sofia. Bulprofor, 427 p. (In Bulgarian).

LOREY T. V. 1878. Die mittlere Bestandeshöhe. - *Allgemeine Forst- und Jagdzeitung,* 54: 149–155.

MACKINNNEY G. 1941. Absorption of Light by Chlorophyll solutions. - *Journal of Biological Chemistry*, 140 (2): 315-322.

MALINOVA L. 1998. [Content of Cu in forest soils from the region of Pirdop-Zlatiza valley]. - *Science for Forestry,* 1-2: 76-85. (In Bulgarian).

POPOV G., G. KOSTOV, I. MARKOFF, Y. DODEV, D. GEORGIEVA. 2018. [*Coniferous plantations in Bulgaria established out of their natural areal.*] Sofia. Publ. Avangard, pp. 5-10. (In Bulgarian).

PORYAZOV I., T. TONCHEV, I. DOBRICHOV. 2004. [*Handbook of the dendrometrics worker.*] Sofia. Bulvark. (In Bulgarian).

PROKOPIEV E. 1967. [*Afforestation of industrial regions.*] Sofia. Zemizdat, 144 p. (In Bulgarian).

SOKOLOVSKA M., M. NUSTOROVA, M. GAIFFE, A. DELKOV. 2001. Assessment of the chemical status of waste banks from open ore mining and soil biogenity. - *Silva Balkanica*, 1: 91-99.

TSAKOV H., P. DIMITROVA. 2002. [Growth and profile characteristic of the forest crowns of acacia plantation established with rehabilitation]. - *Nauka za gorata,* 3-4: 39-45. (In Bulgarian).

YOROVA K., E. KUCHUKOV. 1996. [Content of heavy metals – Pb. Zn. Cu. Mn. Cd in foliar mass of some wood plants]. - *Nauchni trudove of Forest Institute, secsion "Ecology and landscape architecture"*, XXXVII: 17-27. (In Bulgarian).

ZAHARIEV B. 1977. [Forest plantations with special functions]. - In: [*Forest Plantations*]. Sofia. Zemizdat, pp. 422-482. (In Bulgarian).

ZHIYANSKI M., A. FEREZLIEV, M. SOKOLOVSKA. 2014. [Characteristic of above-ground biomass and carbon storage in components of ecosystems, formed after afforestation with white pine in the region of North-Western Rodopi mountain]. - In: *Collection scientific publications of the Forest research Institute "145 years of Bulgarian Academy of Sciences".* Sofia. Forest Research Institute, pp. 224-238. (In Bulgarian).

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