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HEAVY METALS IN THE CYPRESS TREE BARK (*CUPRESSUS SEMPERVIRENS* L.) IN THE VIRPAZAR AREA – SKADAR LAKE NATIONAL PARK – MONTENEGRO

SUMMARY

Determination of heavy metals contents (Cd, Cu, Mn, Ni, Pb and Zn) was carried out from the bark of cypress trees, which were collected at two locations in the area of Virpazar (Virpazar and Fortress Besac). Content of heavy metals in the cypress tree bark from the study sites was dependant on the proximity of pollution sources. The results of this study show that cypress bark can be a good bioindicator of air pollution.

Key words: Heavy metals, cypress bark, Virpazar, national park

INTRODUCTION

Virpazar, with the Skadar Lake national park, has great tourism potential because of its natural and cultural resources. Its position is a significant element of tourist valorization, i.e. easy access – crossing of roads from the north-south (Podgorica-Bar) and east-west (Cetinje-Skadar). Also of significance is the proximity of Vranjina, one of the main tourist sites of Lake Skadar. Virpazar is one of the largest settlements on the Montenegrin side of the lake, with the most tourist facilities and infrastructure, including a dock that is used as a starting point for a lake cruise.

Intensive technical and technological development in all branches of the economy is a major cause of environmental pollution (Dragović et al., 2012); however, there are areas that are exempt from intensive anthropogenic pollution.

Determination of heavy metal concentration in the environment is of special importance for toxicology. Elements such as Fe, Mn, Cu and Zn are necessary (essential elements) in the physiological processes of plants, animals and humans. However, Pb, Cd and Hg belong to the group of elements that can have a toxic effect. No matter which group they belong to, an increased level of these elements can result in toxic effects.

Investigation of the presence of heavy metals in the bark of different trees points to the fact that their concentration in the investigated species depends on traffic intensity; that is, on the anthropogenic sources of pollution (Satake et al., 1996; Odukoya et al., 2000; Tayel El-Hasan et al., 2002). The bark of over 40 different tree species has been used in biomonitoring studies in Europe. The most

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commonly used tree species are *Acer platanoides, Aesculus hippocastanum, Fraxinus excelsior, Quercus robur, Tilia cordata, Picea abies* and *Pinus sylvestris* (Poikolainen, 2004). Apart from the above-mentioned tree species, cypress tree bark has also been used in biomonitoring of the presence of heavy metals (Tayel El-Hasan et al., 2002; Roganović and Đurović, 2012; Roganović et al., 2013), in addition to moss, lichen, herbaceous plants, etc. (Lippo et al., 1995; Poikolainen, 1997). The aim of this study is to determine if the heavy metal content of cypress bark is a good indicator of their presence in the wider part of Virpazar.

MATERIAL AND METHODS

Sampling of the plant material**:** Bark samples (5 grams weight) were taken from cypress trunks by means of a sharp knife, at 1.8 meters height, and were then placed in paper bags and marked according to the regulations. The average age of the trunks was around 50 years. The samples were collected in May 2012. The bark samples were stored in paper bags in standard boxes in the individual storage rooms in the sample bank. The boxes are located on movable shelves that afford easy access to the samples for use in future research. Information about the samples was stored in the database. This includes data such as information on sample species, sampling sites, time of collection, and the location of the samples in the storage facility.

The sampling sites cover around 1 sq km on each of t–he localities. The concentration of cadmium, copper, manganese, nickel, lead and zinc were determine on 20 samples from two locations in the area of Virpazar.

Preparation of the samples for analysis: the biological material was first washed in distilled water and subsequently divided into small pieces and dried into well aired, clean rooms which had not been in contact with evaporative or powdery substances that could affect the composition of the samples. In the preparation procedure, a precisely determined quantity of bark sample (1 g) is rendered well homogenised by dry burning – method AY-4 and, afterwards, it is gradually and carefully dried and smoked on a well heated thermal hot plate until it is carbonised (Perkin Elmer-Analytical methods-AY-4). When the smoking has stopped, the sample is placed into the furnace with a graduate increase of temperature up to 450 ºC and is left at this temperature for 24 hours. All this is carried out with a great caution to make sure that the sample will not catch fire. Following the set period of time, the sample is taken out and examined. If the ashes are white or pale yellow, they are ready to be dissolved. If the ashes are grey or if there are some black unburnt particles, then they are further processed by adding 30% of H_2O_2, by additional heating and drying on a burner and by additional burning in the furnace. After the burning, the ashes are dissolved by 20% of HCl and transferred into a regular 25 ml bowl. It the ashes are not dissolved, a few drops of concentrated HCl may be added. The sample thus prepared is ready for the analysis.

Blank tests are prepared in the same way as the samples, by means of adding all the necessary chemicals in the same proportion as in the sample preparation procedure, but without adding the samples.

Determining the concentration of lead, cadmium, copper, zinc, nickel and manganese using ICP method – Laboratory testing of the plant material samples on the heavy metals content (Pb, Cd, Cu, Zn, Ni and Mn) has been carried out by means of applying the instrumental technique ICP-OES– inductively coupled plasma – optical emission spectrometry.

Standard solutions of lead, cadmium, copper, zinc, nickel and manganese, of the concentration 1000 mg/dm^3 and manufactured by LGC, have been used for the preparation of calibration solutions. All other chemicals used in the preparation of the samples are of a special purity degree, marked "for determination of the metal residues" and produced by J. T. Baker.

RESULTS AND DISCUSSION

Investigation of the content of cadmium in Cypress tree bark samples showed its range from 0,07 mg/kg to 0,28 mg/kg (Table 1.). The average concentration of cadmium was 0,134 mg/kg (Figure 1.). In the previous research into Cd concentration in Cypress tree bark showed the low concentration (0,133 mg/kg) at locality Vranjina (Roganović et al., 2013). Low concentrations of cadmium showed a small presence of this element in the air of this area and that there is no source of pollution of this element.

Table 1. Total and average concentrations of heavy metals contents in the Cypress tree bark at the investigated area

Locality/ mg/kg	**Cd**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
Virpazar 1	0,10	4,05	15,44	0,92	8,30	19,01
Virpazar 2	0,07	2,76	13,57	0,70	4,58	19,03
Virpazar 3	0,13	2,99	21,10	1,10	8,58	23,04
Virpazar 4	0,12	4,13	23,28	1,38	8,49	28,37
Virpazar 5	0,07	3,11	23,41	0,89	6,68	21,34
Virpazar 6	0,13	3,38	27,03	0,92	7,34	30,85
Virpazar 7	0,19	5,25	20,14	2,06	19,10	60,65
Virpazar 8	0,28	4,09	25,86	0,95	18,49	33,42
Virpazar 9	0,10	4,65	15,15	0,60	11,71	34,37
Virpazar 10	0,07	4,42	13,68	0,64	9,43	32,17
Besac 1	0,20	4,80	24,53	1,67	22,10	43,75
Besac 2	0,09	4,53	13,89	0,86	13,01	26,11
Besac 3	0,14	3,37	18,71	1,47	8,35	33,05
Besac 4	0,09	4,61	14,54	1,21	5,87	39,23
Besac 5	0,08	3,25	11,98	1,05	4,23	23,41
Besac 6	0,14	4,53	21,79	1,26	16,02	32,66
Besac 7	0,11	4,12	16,60	1,44	10,27	25,27
Besac 8	0,22	4,84	31,08	1,80	13,15	48,20
Besac 9	0,14	2,87	16,10	0,94	9,46	30,62
Besac 10	0,21	4,01	26,86	1,71	13,70	37,20
Mean concentrations	0,134	3,988	19.737	1,178	10,943	32,087

Copper content in the samples of cypress tree bark ranges from 2,76 mg/kg to 5,25 mg/kg (Table 1.). The average concentration recorded at this site amounted 3,988 mg/kg (Figure 1.). In previous research the lowest average copper concentration in cypress bark has been found at Vranjina site (3,972 mg/kg), while copper concentrations were significantly higher in the locality Zeta (14, 528) (Roganović & Đurović, 2012; Roganović et al., 2013). Researches into concentration of Cu in the scots pine bark in Finland have registered extremely high concentrations (867 mg/kg) in the industrial zone of the smeltery in Monchegorsk city (Poikolainen, 2004).

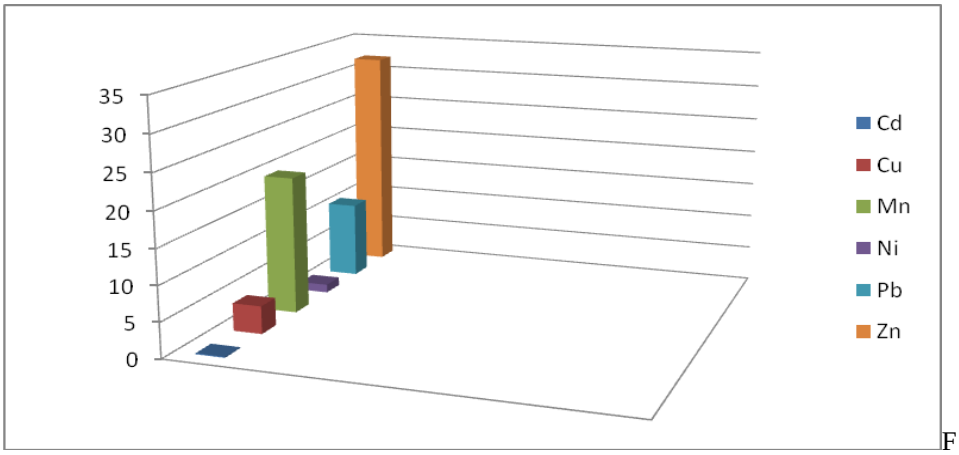

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Figure 1: The average concentrations (in ppm) of heavy metals contents in the Cypress tree bark at the investigated area

The concentration of manganese in cypress bark ranges from 11,98 mg/kg to 31,08 mg/kg (Table 1). The average concentration was 19,737 (Figure1). At the site Vranjina manganese contained in the samples of cypress bark ranges from 5,69 to 37,30 mg/kg (Roganović et al., 2013). Relatively high concentration of manganese in Cypress tree barks sampled at the investigated sites is due to the additive (MMT) which is added into the unleaded petrol, serving as octane booster. It can be assumed that this may be a cause for the relatively enlarged concentration of this metal. It should be borne in mind that Virpazar is one of the largest settlements on the Montenegrin side of the lake, with largest tourist facilities and infrastructure, the dock that is used as a starting point for a lake cruise.

Investigations of the nickel contained in the Cypress tree bark samples collected on this site has shown low concentrations. Its range was from 0,60 mg/kg to 2,06 mg/kg (Table 1). The average concentration was 1,178 mg/kg (Figure 1). In previous research on the locality Vranjina, the average content of nickel in the samples of cypress bark also was low - 1,114 mg/kg (Roganović et al., 2013). Analyses of Ni contained in the scots pine bark in Finland have revealed extremely high concentration of nickel in the industrial zone of the

smeltery in the city of Monchegorsk (303 mg/kg), also proving a significant decline of this concentration westward (Poikolainen, 2004). The results of the research into the concentration of nickel in the soil of six different locations on the territory of Podgorica in 2009 point to an increased level of this metal in the soil (EPA Montenegro, 2011).

Content of lead in the samples of cypress bark ranges from 4,23 mg/kg to 22,10 mg/kg (Table 1). The average concentration is 10,943 mg/kg (Figure 1). At the site Vranjina average content of lead in the cypress bark samples were 10,700 mg/kg (Roganović et al., 2013). The average concentration of lead in the bark of *C. japonica* tree in Nikko - Japan (Satake et al. 1996) was around 150 mg/kg, whereas the average lead concentration in Cypress tree bark (*Cupressus sempervirens* L.) in Aman (Jordan) ranged from 257,4 mg/kg to 330,3 mg/kg (Tayel El-Hasan et al. 2002). The concentration of lead found in the cypress bark samples indicate that, apart from the bioaccumulation of the lead absorbed by a plant from the soil, the upper parts of the plant are significantly contaminated by the lead from the atmosphere. Relatively high singly lead concentration resulting from proximity to the local road from which the samples were collected.

Concentration of zinc in the Cypress tree bark samples ranges form 19,01 mg/kg to 60,65 mg/kg. The average concentration was 32,087 mg/kg (Figure 1). At the site Vranjina, the content of zinc in the samples covers the scope from 16,00 mg/kg to 64,80 mg/kg (Roganović et al., 2013). Research into concentration of zinc in the bark of seven tree species (Abeokuta, Nigeria) has indicated that it depending on anthropogenic sources of pollution (Odukoya et al. 2000). For a relatively higher concentration of zinc in the cypress bark (which are significant below the allowable concentration) should bear in mind that the area Virpazar is agricultural (viticulture) area which includes the use of agricultural measures for growing plants such as the use of fertilizers and insecticides which is a common component of Zn.

CONCLUSIONS

The results of this research have shown low concentrations of heavy metals in the area of Virpazar. The lead content at the study site indicates that the concentration of this element in the bark of cypress trees depends on the proximity of the local road to the area samples were taken, as the sample trees were lower and away from the sources of pollution

The relatively high concentrations of manganese that were recorded during the study suggest the presence of sources of pollution such as cars and boats, because Mn is added as an additive in unleaded gasoline, serving as an octane booster.

When it comes to zinc, relatively higher concentrations in the bark of the cypress trees indicates the use of chemicals in agriculture (viticulture) that contain zinc.

The results of this research indicate that cypress tree bark can be a reliable bioindicator of air pollution.

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TEŠKI METALI U KORI ČEMPRESA (CUPRESSUS SEMPERVIRENS L.) NA PODRUČJU VIRPAZARA – NACIONALNI PARK SKADARSKO JEZERO – CRNA GORA

SAŽETAK

Određivanje sadržaja teških metala u kori čempresa (Cd, Cu, Mn, Ni, Pb and Zn) obavljeno je iz dvadeset uzoraka koji su sakupljeni na dvije lokacije na području Virpazara (Virpazar i utvrđenje Besac). Koncentracije teških metala u kori čempresa na istraživanim lokalitetima su zavisile od blizine izvora zagađenja. Rezultati ovih istraživanja ukazuju da kora čempresa može da posluži kao dobar bioindikator aerozagađenja.

Ključne riječi: Teški metali, kora čempresa, Virpazar, Nacionalni park