Background of some heavy metals on the Croatian Carst

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Abstract
The aim of the research is to prove the influence of air pollution with heavy metals on the Carst area of Croatia. The following heavy metals were monitored: lead (Pb) copper (Cu), zinc (Zn) and cadmium (Cd). At 55 localities in the Croatian carst the organic layer (0-3 cm) and mineral soil of cambisols (5-25 cm) were collected and analyzed. On average 1 kg of soil was collected from each locality for analysis. On the mountain Velebit 4 samples from a deep pit-cave were also collected (Lukina jama-Trojama pit) as a reference point. During sampling maximum caution is required in order to avoid errors when taking 'natural' and pure sediment samples in "Lukina jama" pit. Research was undertaken in the carst forest ecosystem area in the Mediterranean region of Croatia. From the results obtained, it can be concluded that there is a higher level of lead, and especially cadmium, in the upper layers of the soil (0-3 cm), while in the mineral layer (5-25 cm) this level is somewhat lower. The amount of cadmium is close to the boundary value of 2,0 mg/kg. The mean value for lead in the upper layer is 43,1 mg Pb/kg while for the mineral area of the soil it is 29,8 mg Pb/kg, for cadmium the mean value in the upper layer is 1,7 mg Cd/kg while for the mineral layer it is 1,8 mg Cd/kg. The mean values for copper are 9,9 mg Cu/kg for the upper layer and 10,1 mg Cu/kg for the mineral layer of the soil; while for zinc they are 19,0 mg Zn/kg for the upper layer and 7,6 mg Zn/kg for the mineral layer of the soil. Copper and zinc can be found in low concentrations in the carst area of the Mediterranean region of Croatia. Samples from deep pit Lukina jama-Trojama (-1343m) have low concentration of heavy metals compared with the soil on the carst area.

Key Words
Heavy metals, Croatian carst, cambisol, "Lukina jama-Trojama" pit.

Introduction
The forest ecosystem in central Europe has been exposed to pollution for decades, some forest stands have even been exposed for more than a century. Gases such as SO_2 and NOx not only pollute the leaves but also acidify the soil. At the same time, acid in the soil mobilizes heavy metals that have accumulated through atmospheric accumulation. Less mobile heavy metals such as lead and to a certain extent copper accumulate through a long period of time in the upper layers of the soil. Depending on the distance from the pollution's source heavy metals pollution can be measured in lower or higher concentrations. The way that any heavy metal moves within an ecosystem depends on the biogeochemical cycle. There are a number of ways of circulation between the atmosphere, hydrosphere, geosphere and biosphere. The transmission of heavy metals can be observed through atmospheric flows in the form of gases as well as sedimentation of dry and wet deposits in the forest ecosystem and soil.

Materials and methods
A soil pit was dug at each location in order to define the soil type. During the procedure only cambisols was taken (the brown soil on the limestone or calcocambisol). The external morphological profile of the soil was described and samples were taken at two depths, each weighing one kilogram, in plastic bags. They were then taken for physical and chemical analysis in the laboratory. The basic ecological characteristics of each locality were also described (altitude, exposure, incline, depth, etc.). For comparison samples were collected in four different parts of Lukina jama-Trojama pit, from bottom (-1392m) to Camp II (-928 m). The heavy metal content (lead, copper, zinc and cadmium) per mg/kg was analyzed. Heavy metals were determined by an atomic absorption spectrophotometer AAS Perkin Elmer 3001 S, using the extracting method with a 2N HC1 (Brune-Ellinghaus 1981). This procedure separates the total amount of lead and cadmium, 75% of the copper and 30% of the zinc from the soil. Other soil analysis was undertaken using routine methods that are prescribed for analysing soil samples. Analysis was carried out in the laboratory of the Forestry Research Institute Jastrebarsko. The following was determined: The reaction of the soil upon applying glass electrodes in H_2O and M-KCl, the amount of carbonate, the amount of humus, particle size distribution and texture classification of the soil samples.

Results and discussion

Upon analysing the soil samples for the amount of heavy metals it was established that in certain areas of the carst there were higher amounts of lead in the upper layers of the soil. The largest amounts of lead were found near major roads, but also at high altitudes. According to data from literature, the values are varying for unpolluted soils. Nrigau (1978) states mean values of approximately 17 mg Pb/kg, Ure & Berrow (1982) states 29 mg Pb/kg. According to Reaves *et al* (1984) the humus layer has a mean value of 30 mg Pb/kg, while the mineral area of the soil has 13 mg Pb/kg. Zinc values are also variable (depending on the parent material). The natural content of lead is 10-35 mg/kg of soil, zinc 70-90 mg/kg of soil while copper is 20-30 mg/kg soil (Smith 1990). However, according to Kabata-Pendias *et al* (1992) they are between 10 and 300 mg Zn/kg soil with a mean value of approximately 50 mg Zn/kg. For copper and cadmium, according to Alloway (1995) mean values for carst soils (lime) are around 40 mg Cu/kg, while for cadmium they are 0,53 mg Cd/kg. In sediment samples taken in cave systems and deep carst pits that are not under the influence of dry and wet deposits, it was determined that values in the mineral area for lead were 9-13 mg Pb/kg, copper 10-22 mg Cu/kg, zinc 22-29 mg Zn/kg and cadmium 0,10-0,80 mg Cd/kg. Research was undertaken in the carst forest ecosystem area in the Mediterranean region of Croatia. Cambisol was monitored while other soil types such as calci-molic leptosol, rendzic leptosol and chromic-cambisol were omitted. Cambisol covers 10.53% of the total forest soils that are present in Croatia. Analysis results taken at 55 localities of cambisol and 4 samples from Lukina jama-Trojama pit. In Table 1 and Table 2 the mean values of heavy metals as well as the minimum and maximum values are reported. One can conclude from the results obtained that a higher level of lead and especially cadmium are present in the upper layers of soil, at depths of 0-3 cm, while in the mineral area at depths of 5-25 cm there is a slightly higher level of lead while cadmium is still close to boundary value of 2,0 mg/kg.

Table 1. Some chemical and physical properties of soil samples and heavy metal content

Sample Deep (in cm)	Cambiol samples	pH in H_2O	M-KCl	$CaCO_3$ %	Humus g/kg	Clay %	Heavy metals (mg/kg) Pb	Cu	Zn	Cd
0-3 humus layer	Min.	5.2	3.9	0.0	49.7	20.0	23	4	4	0.4
	Max.	7.7	7.4	32.99	639.5	43.3	86	36	78	4.0
	n	40	40	40	40	40	40	40	40	30
	Mean	6.9	6.2	2.60	181.1	32.7	43.1	9.9	19.0	1.7
5-25 mineral layer	Min.	5.7	4.6	0.0	31.3	26.9	15	5	4	0.4
	Max.	8.0	7.5	35.54	126.5	70.1	56	16	17	3.7
	n	53	53	53	53	53	53	53	53	40
	Mean	7.4	6.9	3.59	73.3	39.9	29.8	10.1	7.6	1.8

Table 2. Some chemical and physical properties of pit samples and heavy metal content

Sample Deep (in cm)	Pit samples	pH in H_2O	M-KCl	$CaCO_3$ %	Humus g/kg	Clay %	Heavy metals (mg/kg) Pb	Cu	Zn	Cd
5-25 Lukina jama-Trojama	Min.	8.3	7.1	22.3	5.9	7.9	9	10	22	0.1
	Max.	9.0	7.9	49.9	18.3	48.9	16	22	31	0.8
	n	4	4	4	4	4	4	4	4	4
	Mean	8.7	7.6	31.9	18.1	21.1	12.3	16.5	26.8	0.6

Conclusion

According to the content of heavy metals in samples taken from 55 localities, it can be concluded that there is a higher content of lead, and especially cadmium, in the Mediterranean area of Croatia with a parent material of lime. The mean value for lead for the upper layer is 43,1 mg Pb/kg, for the mineral area of the soil 29,8 mg Pb/kg, and while for cadmium the mean value in the upper layer is 1,7 mg Cd/kg in the mineral layer Cd concentrations was 1,8 mg Cd/kg on average. According to data from literature these are boundary values for the content of cadmium in soils. In the light of this analysis, the soil is likely to be contaminated with cadmium. Mean values for copper are 9,9 mg Cu/kg in the upper layer and 10,1 mg Cu/kg in the mineral layer, while for zinc they are from 19,0 mg Zn/kg for the upper layer and 7,6 mg Zn/kg for the mineral layer of the soil. Copper and zinc are present in low concentrations in the carst area of the Mediterranean region of Croatia. The results show the various values of lead, copper, zinc and cadmium content, depending on the structure and position of samples in the carst area. According to the content of heavy metals in the samples collected from Lukina jama-Trojama pit on the "Velebit" National Park, it can be concluded that the sediments in the speleological objects have natural content of heavy metals in

comparison to the soil samples taken from the humus horizon and mineral part of soil in the carst area under the limestone parent material.

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