Original scientific paper

Heavy metals in lysimetric solution of pseudogley soils in the Kupa and Česma river areas

BORIS VRBEK IVAN PILAŠ NIKOLA PERNAR TOMISLAV DUBRAVAC DARKO BAKŠIĆ JASNICA MEDAK TAMARA JAKOVLJEVIĆ

Croatian Forest Research Institute Cvjetno naselje 41 10450 Jastrebarsko, Croatia

Correspondence:

Boris Vrbek Croatian Forest Research Institute Cvjetno naselje 41 10450 Jastrebarsko, Croatia E-mail: borisv@sumins.hr

Key words: heavy metals, soil solution, lysimeter, pedunculated oak and common hornbeam

Abstract

Background and Purpose: The concentration of heavy metals in the environment has increased due to, among other reasons, the influence of human activity. An increase in concentration is not at the same level for all metals and depends mainly on the amount and the way of transmission, as well as the source of pollution. 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

Materials and Methods: The following heavy metals were monitored: lead (Pb) copper (Cu), zinc (Zn) and cadmium (Cd). Sampling was performed by means of funnels (throughfall) and the amount of precipitation was measured in rain gauges with a surface opening of 60 cm². Rain gauges and funnels were placed diagonally by 6–9 items, each on 30x30m plot. On a control plot, where the impact of vegetation was excluded, funnels (bulks) were placed in a random order or circularly. Plastic zero tension lysimeters were placed in the soil at the depth of 20 cm or beneath the humus layer and in mineral part of the soil at the depth of 100 cm. They collected the seeped liquid (seepage) in the soil. Sampling was carried out once a month. According to data obtained by monitoring, our forests and soils absorb more deposited heavy metals (wet and dry sedimentation) compared to the control samples in the open area.

Results: Concentration of lead and cadmium in some samples in lysimeters at a depth of 10 cm was increased and according to drinking water standards in Croatia (Pb>2.0 $\mu g L^{-1}$, Cd>0.20 $\mu g L^{-1}$) was t00 high. In lysimetric liquids, a slightly increased amount of heavy metals was observed. The average content of cadmium in lysimeters (spring, summer and autumn) was 0.13–0.36–0.37 $\mu g L$ –1, lead 4.3–4.2–5.1 $\mu g L$ –1, copper 3.3–5.3–4.6 $\mu g L$ –1, zinc12.7–8.9–17.6 $\mu g L$ –1, respectively.

Conclusions: The forest ecosystems of Pedunculate oak and common hornbeam, with its bio-mass surface, allow increased dry deposition of substances which, by means of precipitation, become leached through tree-crowns. These results are in agreement with other investigations (Bretchel, 1989; Van Breemen at al. 1988; Lindberg at al.1988;) which demonstrate that the deposition under forest tree-crowns is greater than in a open space, away from the influence of vegetation. This influences forest soils and soil solution in forest soils. There was an increased input of heavy metals into our forest ecosystem at all monitored sites. At control locations (bulks), where impact of vegetation is excluded, the amounts of heavy metals are always

Received July 10, 2009.

lower. On the basis of these investigations it can be concluded that problems of constant accumulation of heavy metals in soils are present in the region of lowland forests. In this process the types of soil play a significant role in buffering deposition substances which fall as precipitation.

INTRODUCTION

he atmosphere is and important medium for trans-■ port of heavy metals from various sources and over large distances. Soils could be very distant, over hundreds kilometers away and still become objects of pollution by persistent precipitation of heavy metals (1). Paritcles reach toposil by accuulmation from distant sources in air as aerosols, diemnsions from 5 nm to 20 μ m but mostly from $0.1-10 \,\mu\text{m}$ in dimaeter and are perisstent in the air from 10-30 days (2). Nowadays a large amount of heavy metal precipitation is of anthropogenic sources. Even before the massive use of metals in industry, the use of fossil fuel contributed to increase of heavy metals in the atmosphere and soil. The increase in heavy metals is not uniform for all elements; it the depends of quantity and types of sources. The emissions of heavy metals can be distinguished to emissions of gasses, dry and wet deposition into forest ecosystems and further seepage into the groundwater what is a primary aim of this research. Accumulation of heavy metals for prolonged period in organic parts of soils can contaminate soil organisms important for future soil development. Contents of cadmium up to (1 mgkg⁻¹ Cd), lead (150 mgkg⁻¹ Pb), zinc (100 mgkg⁻¹ Zn) and copper (20 mgkg⁻¹ Cu), according to (3), (4), (5) and (6) are still not sufficient to destroy soil organisms. However, 4-10 times of these concentrations can indirectly reduce the production of biomass, decomposition of litter and enzymatic activity in forest ecosystems in dependence of acidity, clay content and organic carbon of soils so that respective soil properties shouldbe taken into account in evaluation of toxicity of heavy metals.

GOAL OF RESEARCH

Precipitation causes dilution of substances in soils. They precipitate into deeper soil horizons or move into groundwater and further to watercourses and finally to seas. The sensitivity of a particular forest ecosystem depends on its soil buffering capacity. For forest association of common oak and hornbeam it was determined that the predominant soil type is pseudogley of level terrain.

This soil type was studied in detail in the area of Central Croatia, i.e. particularly in forest complexes of Pokupsko basin and Česma where permanent research plots for have been established assessment of heavy metals inputs into ecosystems. (Figure 1.). Consequently the goal of the research was to determine by means of lysimetric methods, the impact of precipitation on heavy metal composition of soil solution on plots of Pokupsko and Česma forests, estimate the amount of heavy metals (Pb, Cu, Zn, Cd) in soil solution in organic and mineral soil layer, and determine the amount of heavy metals in kg/ha which are deposited in the common oak and hornbeam forest.

MATERIAL AND MEHTODS

Plots were established in natural forest stands of common oak and hornbeam managed by close to nature forestry through regeneration cuttings with short rotation period. The dimension of plots was 1 ha, plots were not specially protected, i.e. forests were regularly managed according to management plan. Plots were located in lowland area in the forest of common oak and common hornbeam (Figure 1). The soil type was pseudogley of level terrain. The average values of chemical and physical parameters are given in Table 1. Forest stands inside plots were old and belonged to the same age group (from



Figure 1. Plot locations in Pokupsko and Česma area

 TABLE 1

 Mean values of chemical and physical parameters of pseudogley on the level terrain.

Horizon	Thick.	рF	I in	P ₂ O ₅	K ₂ O	Humus	ıs Total N	C : N	Clay %
HOLIZOII	cm	H ₂ O	n-KCl	mg/	100 g	%	%	C:N	< 0,002
Aoh,g	6.35	4.60	3.80	13.70	13.60	6.90	0.33	11.10	18.09
Eg	23.65	4.80	3.80	4.90	4.50	1.27	0.06	10.82	17.33
Btg	37.03	5.50	4.30	4.10	6.20	0.49	0.03	9.26	23.60
С	77.31	7.30	6.90	1.20	2.90	0.24	0.01	14.02	18.37

	IABLE 2
Т	he description of plots with main geographical characteristics.

Plot No	Forest department	Management unit	Area	Altitude	Latitude	Longitude
6	Čazma	Česma	4b	103	45°43′50?	16°34′43?
15	Vrbovec	Česma	86a	107	45°50′16?	16°39′07?
23	V. Gorica	Šiljak. dubrava	100a	125	45°39′36?	16°01′09?
36	Jastrebarsko	Jastr. lugovi	8c	120	45°38′48?	15°41′36?

81 to 120 years, 5th age class) (Table 2). Once a month the amounts in the vegetation period (eight samples per plot) of precipitation and throughfall liquid were measured in lysimeters on plots in mm (L/m²) in order to establish mgL⁻¹ values for ions to be converted into kgha⁻¹ for corresponding region and plot. The vegetation period involved from 54.5 to 56.5% mm of precipitation in relation to the whole year. Precipitations in the form of snow, outside of vegetation period, were not sampled and analyzed, as well as rain, hoar-frost, etc. Thus, the data shown the Table 13 include only a part of approximately 56% of substances brought about by dry and wet deposition

The small plastic lysimeters as parts of the system for seepage monitoring were placed into soil (7, 8, 9, 10, 11, 12). Plastic vessels were installed inside soil pits at two depths: 20 and 100 cm. The following heavy metals were monitored: lead (Pb) copper (Cu), zinc (Zn) and cadmium (Cd). Sampling was performed by means of funnels (throughfall) and the amount of precipitation was measured in rain gauges with a surface opening of 60 cm². Rain gauges and funnels were placed diagonally by 6-9 items, each on a 30x30m plot. On a control plot, where the impact of vegetation was excluded, funnels (bulks) were placed in a random order or circularly. For the collection of soil solution, the zero-tension lysimeters, the vessels connected to the container for collecting percolate, were installed at two soil depths: at 20 cm below the organic layer and at 100 cm depth. They collected the seeped liquid (seepage) in the soil. Sampling was carried out once a month. According to the data obtained by monitoring, our forests and soils absorb more deposited heavy metals (wet and dry sedimentation) compared to the control samples in the open area.

Determination of heavy metals in soil solution

Heavy metals in soil solution can be found in very small concentrations, which makes sampling very difficult because of the risk of contamination of samples. All sampling tools should be washed and isolated in plastic bags before sampling. Also, special care should be taken (rubber gloves) to avoid contamination of samples by hand manipulation. For determination of trace elements as heavy metals, various spectroscopic and electrochemical methods can be used. X-ray fluorescence and atomic emission spectroscopy (AES) are multielement methods by which various spectrums of substances could be deter-

mined but not applicable for determination of heavy metals in natural water. For that purpose fast non destructive methods with great sensitivity are used. For the analysis of heavy metals, various electroanalytical methods (polarigraphy, voltimetry) are used with high sensitivity which allows direct determination of heavy metals in natural waters. The disadvantage of these methods is their destructive character, i.e. total decomposition of organic matter is needed (13). Cyclical and pulse-differential voltimetric measurements are performed the instrument PAR-174 (Princeton Applied Research). The used amplitude of pulse-differential voltmetric the measurement was 50 mV and change of potential velocity 5 mV/s. Maximal sensitivity of intsrument was $0.002 \mu A$. Voltimetric method which is used for trace elmeents in natrual waetrs is difefrential pulse voltametry with andoe disoslvent (DPASV). This method should be adapted for deetrmination of metlas which contsruct amalagms with mercury. With this method very low concentrations of trace metals (ng/L) can be assessed in sample. This method is based on the reduction of metals from solution (which can form ions or labile complexes) on mercury electrode. The time of deposition based on potential of 200–300 mV, depends of heavy metal concentration and volume of the electrode. After deposition phase there follows the stagnation phase (20-30 sec) during which amalgamate is homogenized. These phases are followed by anode dissolution (the change of potential into positive), which leads to oxidation of the amalgam and newly occurred ions revert into solution. Anode dissolution of metals causes immediate increase in electricity followed by pike on histogram whose extent is proportional to quantity of deposited metals in the solution. With the aim of reaching accurate results in trace metal determination, care should be taken to avoid the contamination of glassware. For that purpose all glassware were washed out by 10% nitrogen acid and redestiled water.

For analysis, composite samples were taken in the field. From each bulk, 2 dcL of subsample were taken, and subsequently all subsamples from one plot were mixed into the sample. The sampling of heavy metals was performed during three time periods in April, June and September. All equipment was specially pretreated to avoid contamination at the Institute Ruđer Bošković where analysis was also undertaken. The data of chemical analysis were further assessed on PC using software packages EXCEL and Statistica 5.0 and Microsoft Access (Table 3).

TABLE 3Correlation coefficients for heavy metals.

	Pb	Cu	Zn
Plot no. 25			
Cd	0.613399	0.331721	-0.16201
Pb		0.389178	0.097346
Cu			0.047458
Plot no. 36			
Cd	0.255073	0.35687	0.560162
Pb		0.345391	0.451615
Cu			0.653194
Plot no. 6			
Cd	0.731523	0.235964	-0.06709
Pb		0.15669	0.279748
Cu			-0.16975
Plot no. 23			
Cd	0.78854	0.078261	0.505817
Pb		0.15669	0.360453
Cu			0.250749
All plots			
Cd	0.5211	0.232161	0.081222
Pb		0.379261	0.222873
Cu			0.276676

RESULTS

The results of analysis are presented in Table 4 where the average values and ranges of heavy metal concentrations are shown either as a througfall, bulk precipitation or soil solution at two depths, 20 cm and 100 cm. In Table 5, mean concentrations of heavy metals in vegetation period a presented according to soil type and in Table 6 average concentrations of heavy metals in vegetation period on all plots in gha⁻¹. In Tables 7–9 the results are reported are reported of partial analysis of lead, copper, zinc, and cadmium in collected samples in bulks and lysimeters. The estimated concentrations were related to annual precipitation so that yearly fluxes the of the above mentioned elements were obtained. According to results of statistical analysis, significant correlation was determined between cadmium and lead; otherwise no other significant correlation between was found elements was found. Concentration of lead and cadmium in some samples in lysimeters at a depth of 10 cm were increased and according to drinking water standards in Croatia (Pb>2.0 $\mu g L^{-1}$, Cd>0.20 $\mu g L^{-1}$) they were too high. In lysimetric liquids, a slightly increased amount of heavy metals was observed. The average content of cadmium in lysimeters (in spring, summer and autumn) was $0.13-0.36-0.37 \ \mu g L^{-1}$, lead $4.3-4.2-5.1 \ \mu g L^{-1}$, copper $3.3-5.3-4.6 \mu g L^{-1}$, zinc12.7-8.9-17.6 $\mu g L^{-1}$, respectively.

TABLE 4

Average values of heavy metal content and ranges of heavy metal concentrations.

Heavy	Pb	Cu	Zn	Cd				
metal								
Throught	metal $\mu g L^{-1}$ Throughfall (KŠ)							
range	0.2-5.1	1.8-8.7	3.4-44.1	0.02-0.30				
$X \pm \sigma$	2.1 ± 1.5	4.5 ± 2.0	21.9±15.5	0.13 ± 0.11				
Bulk (KC))							
range	0.3-1.3	0.7-4.3	3.5-28.7	0.02-0.34				
$X \pm \sigma$	1.6±1.5	2.2 ± 1.1	14.7±6.9	0.11 ± 0.09				
Lysimeter	20 cm (L ₂₀)							
range	1.0–19.7	1.9-17.5	7.6–26.8	0.02-0.80				
X±σ	5.2 ± 5.0	5.4±3.6	16.0±4.9	0.34 ± 0.22				
lysimeter	100 cm (L ₁₀₀))						
range		0.6–11.3	4.0-40.0	0.02-0.84				
$X \pm \sigma$	3.6±4.6	3.1 ± 3.2	11.3±11.0	0.23 ± 0.27				
Al sample	Al samples							
range		0.6–17.5	3.3-66.1	0.02-0.84				
X±σ	3.2±2.5	4.0 ± 2.2	17.9±10.5	0.19 ± 0.14				

TABLE 5

Mean concentrations of heavy metals in vegetation period.

Vegetation	Pb	Cu	Zn	Cd			
period	$\mu \mathrm{gL}^{-1}$						
Bulk (KO)	Bulk (KO)						
Spring	2.4 ± 0.09	3.1 ± 0.05	19.3±4.8	0.21 ± 0.07			
Summer	1.0 ± 0.6	2.0 ± 0.7	9.2 ± 4.4	0.08 ± 0.05			
Autumn	2.2 ± 1.1	1.7 ± 0.1	15.5 ± 2.8	0.03 ± 0.01			
$(L_{100})+(L_{20})$	₀)						
Spring	4.3 ± 4.4	3.3 ± 3.1	12.7 ± 3.8	0.13 ± 0.11			
Summer	4.2 ± 2.7	5.3 ± 2.5	8.9 ± 4.5	0.36 ± 0.17			
Autumn	5.1 ± 3.1	4.6±3.2	17.6±9.5	0.37 ± 0.19			

TABLE 6

Average concentrations of heavy metals in vegetation period in all plots.

A111-6-	Pb	Cu	Zn	Cd	
All plots	gha ⁻¹				
Throughfall	8.388	15.652	81.843	0.336	
Bulk	8.740	12.070	67.056	0.519	
L_{100}	5.964	7.606	19.349	0.458	
L_{20}	16.520	17.708	51.814	1.281	

TABLICA 7

Heavy metal ranges and average content on plots.

Plots -	Pb	Cu	Zn	Cd			
Piots		$\mu \mathrm{g}$	L^{-1}				
Plot No. 6							
range	0.3-12.6	0.7-12.3	4.3-44.1	0.02-0.84			
$X \pm \sigma$	2.5 ± 1.9	3.7 ± 1.8	18.8±9.6	0.27 ± 0.18			
Plot No 2	Plot No 23						
range	0.3-6.9	1.4-6.7	3.3-27.7	0.02-0.60			
$X \pm \sigma$	2.3 ± 1.5	2.7 ± 1.0	15.1±5.4	0.13 ± 0.14			
Plot No 1	5						
range	0.5-11.6	1.9–17.5	4.0-66.1	0.02-0.66			
$X \pm \sigma$	2.3 ± 1.5	2.7 ± 1.0	15.1±5.4	0.13 ± 0.14			
Plot No 36							
range	0.2-19.7	1.1-8.2	2.9-28.7	0.02-0.55			
$X \pm \sigma$	3.7 ± 3.0	3.2 ± 1.8	11.4±7.0	0.18±0.13			

According to the results of analysis, the highest concentrations of lead, copper and zinc were found in plots 23 and 36 in Pokupsko basin, the highest concentrations of cadmium in plot 6 in Česma. The lowest variation of results was found for cadmium and the highest for zinc. The total amount of respective metals assessed in plots show somewhat different picture that can be simply obtained by analysis of their concentration. Table 6 present differences in mean values of heavy metal fluxes (gha⁻¹) on plots and in throughfall, bulk precipitation and soil solution. In Tables 8–11 all concentrations are presented

TABLE 8Heavy metal content in gha⁻¹ for throughfall.

Troughfall	Pb	Cu	Zn	Cd
plots		gł	na ⁻¹	
P-6	6.63	14.50	104.21	0.72
P-15	6.98	11.40	30.01	0.09
P-23	10.82	22.26	96.85	0.28
P-36	10.79	13.09	31.48	0.32

TABLE 9Heavy metal content in gha⁻¹ for bulk area.

Bulk	Pb	Cu	Zn	Cd
plots		gh	ıa ^{–l}	
P-6	4.77	5.12	73.99	0.39
P-15	4.23	15.52	19.48	0.21
P-23	10.80	15.63	145.50	1.33
P-36	13.48	11.86	41.94	0.52

TABLE 10Heavy metal content in gha⁻¹ in lysimeters 20 cm deep.

L ₂₀ lysimeter	Pb	Cu	Zn	Cd	
20 cm	gha ⁻¹				
P-6	10.46	23.08	61.80	2.23	
P-15	7.53	14.56	30.77	0.76	
P-23	22.33	11.43	76.21	1.44	
P-36	32.92	12.96	74.04	1.41	

 $\begin{tabular}{ll} \textbf{TABLE 11} \\ \textbf{Heavy metal content in gha}^{-1} & \textbf{in lysimeters 100 cm deep.} \\ \end{tabular}$

L ₁₀₀ lysimeter	Pb	Cu	Zn	Cd
100cm		gh	ıa ^{–1}	
P-6	3.54	2.28	22.58	0.23
P-15	3.43	9.29	10.13	0.70
P-23	4.57	8.04	42.24	0.35
P-36	3.78	4.00	15.86	0.43

separately (throughfall, bulk, lysimeters) for each plot. Multiple increase in zinc of 81.843 g/ha was found for samples under stand canopy and for samples in control plots (bulk precipitation) of 67,056 g/ha.

The highest amounts of heavy metals were found in lysimeters in organic soil depth (20 cm).

DISCUSSION

Heavy metals were deposited on tree foliage during vegetation season through dry deposition, seepage and deposit in soils, and after the litter fall in autumn as leaves also decompose and return the nutrients and heavy metals into the biogeochemical cycle. Comparative assessments for Central and Eastern Europe shows that Croatia is categorized as a low polluted country (14). According to the above source, concentrations for cadimum vary bewteen $0.05 - 0.8 \mu g L^{-1}$, for lead between $2.5-20 \,\mu\mathrm{gL^{-1}}$ and for zinc $2.5-22.5 \,\mu\mathrm{gL^{-1}}$. Similar results were obtained in the study conducted by (15) around area of Zagreb some researches (16). concluded that the level of heavy metals in organisms in Pokupsko basin are directly related to the content of heavy metals in soils. Other studies (17, 18, 19, 20, 21) confirmed a significant increase in heavy metals (lead, coper, zinc and cadmium) in soils of floodplain forest areas of northern Croatia. The reason for that is in increasing pollution of watercourses. According to the results for the river Sava watershed, only 27% of waste water is treated by simplest mechanical treatment. According to (18), highest concentrations of pollutants in water occur during long periods of lowest water levels. After the prolonged seasons without precipitation, accidental showers cause increased seepage from agricultural areas and roads. The seepage from roads can

TABLE 12Sources of pollution with lead because of human activity in agriculture (mgkg⁻¹) according to (1), (source 38).

Heavy metal	Phosphate manure	Nitrate manure	Cattle manure	Calcification	Compost
			${\sf mgkg}^{-1}$		
Pb	7–225	2–27	1.1–27	20-1250	1.3-2240
Cu	1-300	_	2–172	2–125	13-3580
Zn	50-1450	1–42	15–566	20-1250	1.3-2240
Cd	0,1-170	0.05-8.5	0.1-0.8	0.04-0.1	0.01-100

have significant effect on pollution of watercourses, groundwater (22) and soil solution of nearby areas. According to (23) direct influence of road traffic is evident on the chemical composition of rainwater. Exhaust gasses from traffic are directly involved in environmental water cycling and thus they can increase pollutants in precipitation. The movement of heavy metals in soils also depends on intensity of percolation water through soils, physical processes as diffusion, adsorption, ion exchange, creation of surface complexes on soil aggregates, permeability and porosity of soils and also of the character of pollutants (24). When heavy metals are mobilized in soils they can again be released into the soil solution when changes occur in acidity of soils (pH) due to acid rains, application of de-icing salts and decreasing of redox conditions in soils (heavy metals are transformed into soluble components). Soils enriched with clay minerals have large specific areas and large ion exchange capacity, similar to organic compounds in soils (humus). When saturated, these compounds have no more the possibility of buffering, which resulted in the content of heavy metals in soils above threshold values. In lowland forest soils, increased inputs of heavy metals in some areas is due to the flooding in addition to wet and dry deposition. There is also significant input of heavy metals from surrounding agricultural areas. In Table 10 sources of pollution by lead in agriculture are presented. In soils with increased clay content as in Pokupsko basin and somewhat less significantly in Česma, where vertical permeability of upper soil layers is low (11), the increased accumulation of heavy metals is very certain, which can cause disturbance of forest nutrition. Higher concentration of heavy metals has been measured during the summer season than in winter (25). Summer rainfalls are much rarer and with shorter duration. Heavy metals deposited in the atmosphere and on tree canopy are washed out and increased the concentration of the sample. In autumn and spring seasons, certain dilution of the solution is common. From results in Table 4 it can be concluded that no significant difference exists between heavy metal concentrations in various seasons but the differences are more obvious if a total flux of elements, which also depends on precipitation is taken into account. According to Table 6, it is evident that lysimetric samples have an almost double amount of lead and cadmium compared to the control plot.

The examples of high pollution with heavy metals in precipitation and throughfall can be found in Solling, Germany (Wohldorf), in area under vegetation cover (26) and in lysimetric soil solution samples (27). Pollution was measured to be, respectively, between 160-192 g/ha lead, 472–1262 g/ha zinc, 113–138 g/ha copper and 2.88-5.58 g/ha cadmium under the tree canopy. In lysimetric samples (27) under beech stand between 320–840 g/ha lead was found and 200-470 g/ha zinc, 1.3-4.7 g/ha copper and 2.4-5.9 g/ha cadmium. Results of lysimetric studies in northwestern Croatia indicated significantly smaller amount of lead and zinc and cadmium but increased amount of copper. Studies of (28) proved that in today's world about 0.2–15 mg/kg of cadmium is brought in by various artificial fertilizers. Heavy metals from agricultural fields can be easily transported into the forests. The load of lead in forest and surrounding fields was elaborated in the studies of (29), and influence of nitrite and pesticides on groundwater in studies of (30) and (31). The increased concentrations of lead in surface ho-

TABLE 13

Total and average annual amount of precipitation in mm (L/m²) on four plots beneath tree crowns (throughfall), on the control site without the effect of vegetation (bulk) and soil solution in lysimeters.

Sample	Locality	Total	Average	– Locality –	Total	Average
		mm		Locality	mm	
Throughfall	ČESMA	1028.55	68.57	POKUPSKI	1449.13	96.61
Bulk	(P-15 P-6)	1300.97	86.73	BAZEN (P-36 P-23)	1685.80	112.39
Lysimeter 100 cm		532.14	35.48	(F-30 F-23)	1232.34	82.16
Lysimeter 20 cm		1034.25	68.95		1397.41	93.16

rizons of Žutica forest were shown to be displaced from a nearby agricultural area (21). Research of (32) showed that average yearly cadmium concentrations in urban areas can range between 0.14 and 0.37 μ gL⁻¹, lead between 7.95 and 12.9 μ gL⁻¹, zinc between 8.88 and 20.0 μ gL⁻¹ and copper between 1.30 and 3.49 μ gL⁻¹. Very small particles of heavy metals ranging between 0.1 and 5 μ m are together with gases transported from sources of pollution to forest ecosystems where they then precipitate.

Plants absorb heavy metals from soil liquid phase, i.e. soil solution, which according to (33, 3, 34) has negative effects on plants and trees if it conatins $>50~\mu g L^{-1}$ Pb, $>20~\mu g L^{-1}$ Cu, $>200~\mu g L^{-1}$ Zn, $>10~\mu g L^{-1}$ Cd. Direct damages especially affect enzymes and cell metabolism. Heavy metlas can find path through plant cell and cause seevre damgaes. When plant tisuse, esepcially leaves and fine roots, conatin a quanitty of heavy metlas bewteen $20{\text -}35~\mu g g^{-1}$ Pb, $15{\text -}20~\mu g g^{-1}$ Cu, $200{\text -}300~\mu g g^{-1}$ Zn, $5{\text -}10~\mu g g^{-1}$ Cd, the damage of the plant can be noticeable.

Increase in heavy metals in soil solution results in their increase in drinking water resources. In EU, there are strong regulations of drinking water quality. In Germany for example, the limiting concentrations of heavy metlas in drinknig waetr are $10~\mu g L^{-1}$ Pb, $50~\mu g L^{-1}$, $500~\mu g L^{-1}$ Zn, $5~\mu g L^{-1}$ Cd. Natural waters contain very low concentrations of ecotoxic elements so that even a small anthropogenic pollution can endanger natural system and its functions (35). The most dangerous pollutants are toxic, non disintegrating substances with long persistence in watercourses which show a high level of bioaccumulation, and can incorporate in organisms and through further food chain can be transported to human population

CONCLUSIONS

The forest ecosystems of Pedunclate oak and common hornbeam, with its bio-mass surface, allow larger dry deposition of substances which subsequently, by means of precipitation, become leached through the tree-crowns. These results are in agreement with other investigations (36, 37, 25) demonstrate that the deposition under forest tree-crowns is greater than in open space, away from the influence of vegetation. This influences forest soils and soil solution in forest soils. There was an increased input of heavy metals into our forest ecosystems in all monitored sites. At control locations (bulks), where impact of vegetation is excluded, the amounts of heavy metals are always lower. On the basis of these investigations it can be concluded that problems of constant accumulation of heavy metals in soils are present in the region of lowland forests. In this process the types of soil play a significant role in buffering deposition substances which are brought about by of precipitation

REFERENCES

 ALLOWAY B J 1995 Heavy Metals in Soils. Blackie Academic and Professional. London, 123–305

- BOWEN H J M 1979 Environmental Chemistry of the elements. Academic Press, London.
- **3.** TYLER G, BALSBERG-PÅHLSSON A M, BENGTSSON G, BÅÅTH E, TRANVIK L 1989 Heavy metal ecolgoy of tererstrial plants, mircoorganisms and inevrtebrates. A reivew. *Water, Air, and Soil Pollution 47*: 189–215
- BERGKVIST B, FOLKESON L, BERGGREN D 1989 Fluxes of Cu, Zn, Pb, Cd, Cr and Ni in temperate forest ecosystems – a literature review. Water Air Soil Pollut 47: 217–286
- ATANASSOV I, VASSILEVA V, SHEGUNOVA P 1999 Applications of data for background concentrations of Pb, Zn, Cu and Cd in soils for calculating critical loads. *In*: UBA. Effects-based approaches for heavy metals. Workshop Schwerin, 12–15 October 1999, Germany, p 137–140
- MAYER R 1984 Heavy metal accumulation in the root zone of forest soils. Wald und Wasser, Nationalpark Bayer. Wald. 5 Tag. Bericht, p 343–351
- VRBEK B 1992 Metoda pedoloških istraživanja u projektu ekonomsko-ekološke valencije. tipova šuma (EEVTŠ). Rad Šumar inst (Jastrebarsko) 27(1): 65–75, Zagreb
- 8. VRBEK B 1993 Praćenje depozicije taloženih tvari u zajednici hrasta lužnjaka I običnoga graba na području Uprave šuma Bjelovar. Rad Šumar inst (Jastrebarsko) 28(1–2): 129–145
- VRBEK B 1996 Small lysimeter monitoring in a forest of Pedunculate Oak and Common Hornbeam in North-West Croatia. Bericht Über die 6. Lisimetertagung im Dienste des Grundwasserschutzes« am 16 und 17 April 1996. Irdning.
- VRBEK B 1998 Lizimetrijska istraživanja kvalitete vode u tlu nekih šumskih zajednica, Rad Šumar inst (Jastrebarsko) 33 (1): 59–72
- VRBEK B 2000 A Method for monitoring deposited matter in forest Ecosystems. Arh Hig Rada Toksikol 51 (2): 207–216
- 12. VRBEK B 2002 Utjecaj padalina na kemijski sastav tekuće faze tala šumske zajednice hrasta lužnjaka i običnoga graba (Carpino betuliquercetum roboris, Anić 1956 ex. Rauš 1969) u sjeverozapadnoj Hrvatskoj. Disertacija. Sveučilište u Zagrebu, Šumarski fakultet.
- MIKAC N 1991 Određivanje alkil derivata olova u vodenom sustavu. Disertacija. Sveučilište u Zagrebu, Institut »Ruđer Bošković«.
- BOZÓ L, ALCAMO J, BARTNICKI K, OLENDRZYNSKI K 1992 Total deposition and budgets of heavy metals over Eastern Europe. IDÓJÁRÁS 2: 61–80
- MIKAC N, BRANICA M 1990 Unos ukupnog i organskog olova u rijeku Savu otpadnim vodama grada Zagreba. Zaštita voda '90, JDZV, Bar, p 386–389
- OLUJIĆ Z 1991 Sadržaj kadmija, olova i žive u flori, fauni i tlu bazena Kupčine. Disertacija, Veterinarski fakultet, Zagreb.
- MAYER B 1987 Rezultati prvih istraživanja olova, kadmija, sumpora i fluora u tlu nizinskih šuma bazena Kupčina. Šumar list (Zagreb)1–2: 19–27
- 18. MAYER B 1991 Važnost pročišćavanja otpadnih voda u sprečavanju ekotoksičnosti posebno za tla nizinskih šuma sjeverne Hrvatske. Rad Šumar inst 26(1): 95–104, Zagreb.
- MAYER B, PEZDIRC N 1990 Teški metali (Pb, Zn, Cu) u tlima nizinskih šuma sjevero zapadne Hrvatske. Šum list 6–8: 251–260, Zagreb
- KOMLENOVIĆ N, MAYER B, RASTOVSKI P 1991 Unos teških metala onečišćenim poplavnim vosdama u tla nizinskih šuma istočne Slavonije. Šum list 11–12: 131–149, Zagreb.
- **21.** VRBEK B, PILAŠ I 2000 Pedoekološke značajke šume »Žutica«. *Rad Šumar inst (Jastrebarsko) 35(1)*: 13–36
- 22. VRHOVAC A, EŠKINJA I, ŠOJAT V, RAMIĆ-MATEJAŠ I 1986 Razmatranje utjecaja oborina i dionice obilaznice Buzin-Ivanja Reka auto-ceste »Bratstvo i jedinstvo« na zagađenje podzemnih voda. Suvremeni promet (Zagreb) 4–5: 221–276
- ŠOJAT V, ŠOLJIĆ Z, VRHOVAC A 1988 Razmatranje utjecaja automobilskog prometa na kemijski sastav oborina. Suvremeni promet (Zagreb) 10: 5113–517
- MUSANI L J, KOZAR S, VERTAČNIK A 1990 Interakcija sedimenata s anorganskim zagađivalima. Zaštita voda ^ž90, JDZV, Bar, p 136–140
- **25.** LINDBERG S E, TURNER R R 1988 Factors influencing atmospheric deposition stream export, and landscape accumulation of trace metals in forested watersheds. *Water and Air and Soil Pollution 39*: 123–156
- RASTIN N, HEINRICHS H, ULRICH B, MAYER R 1985 Belastung der Landesforsten Hamburg durch Deposition von Schwer-

- metallen: I. Verteilung von Schwermetallen in den Waldokosystemen. Berichte des Forschungszentrums Waldokosysteme/Waldsterben, Bd. 10. 234–321
- MAYER R, RASTIN N, ULRICH B 1985 Belastung der Landesforsten Hamburg durch Deposition von Schwermetallen: II.
 Depositionsraten und Austrag mit dem Sickerwasser. Berichte des
 Forschungszentrums Waldokosysteme/Waldsterben, Bd. 10. 322–343.
- **28.** NRIGAU J O, PACYNA J M 1988 Nature (London) 333: 134–139
- PRPIĆ B, SELETKOVIĆ Z, ŽNIDARIĆ G 1994 Ekološki i biološki uzroci propadanja stabala hrasta lužnjaka (Quercus robur L.) u nizinskoj šumi Turopoljski lug. Glas šum pokuse (Zagreb) 30: 193–222
- VUKELIĆ Z, VUKELIĆ M 1994 Utjecaj nitrata i pesticida na podzemnu vodu. Bizovačke toplice, p 105–110
- 31. BAČANI A 1989 Utjecaj poljoprivrede na kvalitetu podzemnih voda s osvrtom na stanje u istočnoj Slavoniji. Zbornik radova sa savjetovanja u Zagrebu od 10–12 studenog 1987. Rijeka Sava zaštita i korištenje, p 114–120
- **32.** NGUYEN V D, MERKS A G, VALENTA P 1990 Atmospheric deposition of acid, heavy metals, dissolved organic carbon and nutrients in the Dutch delta area in 1980–1986. *Sci Tot Environ* 99: 77–91

- BALSBERG-PÅHLSSON A M 1989 Toxciity of heavy metlas (Zn, Cu, Cd, Pb) to vasuclar plants. A litreature reivew. Water, Air, and Soil Pollution 47: 287–319
- 34. ANDREAE H 1996 Ecological impacts of some heavy metals related to long-range atmospheric transport. Bacground Report UN/ECE International Co-operative Program on Assessment and Monitoring of Air Pollution Effects (ICP-Forests) 24 S.
- BRANICA M 1999 Tragovi metala u prirodnim vodama, 2. Hrvatska konferencija o vodama. Dubrovnik 19.–22. svibnja, Dubrovnik, p 43–52
- **36.** BRECHTEL H M 1989 Monitoring wet deposition in forests; quantitative and qualitative aspects. *In:* Monitoring Air Pollution and Forest Ecosystem Research, Report No.21 in the Air Pollution Report Series of The Environmental Research Programme of the European Communities, Brussels, p 39–63
- 37. VAN BREEMEN N, WISSER, W F J, PAPE T H 1988 Biogeochemistry of an oak-woodland ecosystem in the Netherlands affected by acid atmospheric deposition. Agricutural Research Report 930, Pudoc, Wageningen.
- KABATA-PENDIAS A, PENDIAS H 1992 Soil and Plants, 2nd Edition Lewis Publ. Ic. Boca Raton, Florida, USA.