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Levels of Polychlorinated Biphenyls, Organochlorine Pesticides, and Chlorophenols in the Kupa River Water and in Drinking Waters from Different Areas in Croatia

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As a consequence of a serious contamination with polychlorinated biphenyls (PCBs) of a relatively narrow karst area in Slovenia (Brumen et al. 1984) the presence of those pollutants was established also in the water, suspended particles, sediments and fish from the Kupa River in Croatia. The PCB levels in unfiltered river water samples collected during 1985 near the town of Sisak, 200 km downstream from the primary contaminated area, ranged from 1 to 52 ng/L (Šmit et al. 1987). Sisak is the center of an industrialized region in continental Croatia, in which the water for the public network comes from the Kupa River after purification involving coagulation, ozonization, activated carbon and chlorination. The purity of the Sisak drinking water depends on the pollution of the Kupa River and on the efficacy of the purification procedures. In this paper the results are presented of a monitoring study on the levels of not only PCBs but also of selected organochlorine pesticides and chlorophenols in the Kupa River water and drinking water from the nearby town of Sisak. The study was performed during the years 1988/1989 in order to evaluate if the residue levels of persistent organochlorine compounds in the river and drinking waters were within the recommended limits (Regulatory Act 1984). The organochlorine pesticides analysed were hexachlorobenzene (HCB), the hexachlorocyclohexane (HCH) group of isomers, and DDT-complex. The chlorophenols analysed were 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,5- and 2,4,6-trichlorophenols (2,4,5- and 2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) and pentachlorophenol (PCP).

The species and levels of organochlorine compounds in the Sisak drinking water were compared with those determined in drinking water samples from two other urban areas in Croatia: Zagreb, the capital and major industrial center located also in the continental part of Croatia, and Labin, a small town on the Istrian peninsula in Northern Adriatic. In Zagreb the ground waters, which are partly recharged through the Sava River water, and in Labin the karst spring waters are used as the municipal drinking water supplies.

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MATERIALS AND METHODS

Samples of the Kupa River water were collected monthly from March 1988 to April 1989 at two locations: 35 km upstream from Sisak (Location A) and in the Sisak area (Location B).

Drinking water samples collected in Sisak (16 samples), Zagreb (10 samples) and Labin (10 samples) were all tap water samples from the municipal drinking water supplies. The sampling was performed in the following way: in Sisak, always at the same location, 1-2 times monthly from March 1988 to April 1989; in Zagreb, in different city districts, during a period of 10 d in October 1988; in Labin, in different parts of the town, on one day in February 1989. Drinking water samples from Sisak and Labin were analysed for all three groups of organochlorine compounds and those from Zagreb were analysed for PCBs and organochlorine pesticides. The presence of chlorophenols in drinking water from the Zagreb city area was investigated earlier (Fingler and Drevenkar 1988).

Organochlorine pesticides and PCBs were extracted from unfiltered 2-L water samples (pH 5-9) in a separatory funnel, three times with 60 mL of n-hexane. All extracts were combined and evaporated to 1 mL under a stream of nitrogen. The concentrated extract was washed with 1.0 mL conc. H_2SO_4. The organic layer was separated, evaporated to dryness under a stream of nitrogen and redissolved in 1.0 mL of n-hexane immediately before gas chromatographic analysis.

For analysis of chlorophenols the water samples (500 mL for acetyl derivatives and 100 mL for pentafluorobenzoyl derivatives) were treated by an analytical method described previously (Fingler et al. 1987). Four parallel samples were prepared. After C_{18} reversed-phase adsorption enrichment on Sep-Pak C_{18} cartridge, the chlorophenols present in the acetonic eluate were converted in two duplicate samples to acetyl and in the other two duplicate samples to pentafluorobenzoyl derivatives.

Gas chromatographic analyses were performed with ^{3}H Sc (column I) and ^{63} Ni (columns II and III) electron capture detectors. Column I (glass, 1.8 m x 2 mm i.d.) was packed with 1.3% GE SF 96 + 5.3% QF 1 on 0,13-0.16 mm Supelcoport. Column II (glass, 2.5 m x 2 mm i.d.) was packed with 5% OV-101 on 0.16-0.20 mm Chromosorb W/DMCS/AW. Column III (21 m x 0.25 mm i.d.) was a WCOT SE-52 glass capillary column with a 0.1 μm film thickness. All samples were chromatographed on two different columns: the organochlorine pesticides and PCBs on columns I and II and chlorophenols on columns I and III. The compounds were identified by their retention times as compared to known standards on both columns.

Quantitation was done by comparing either the peak heights or peak areas in the sample with those of known standard mixtures. The standards for the determination of organochlorine pesticides and

PCBs were prepared by dissolving known amounts of analysed compounds in n-hexane. For PCBs determination Aroclor 1260 and Aroclor 1254 standards were used. The PCBs concentration was calculated by summation of 9 and 14 major peaks present in Aroclor 1260 on columns I and II, respectively, and of 7 and 9 major peaks present in Aroclor 1254 on columns I and II, respectively. The standards for the determination of chlorophenols were prepared by spiking the Sep-Pak C_{18} cartridge with known amounts of chlorophenols and by subsequent treatment of the acetonic eluate using the same procedure as for the samples. 2,4,6-Tribromophenol was used as internal standard.

All results were corrected for reagent blanks (values near or at detection limits of analysed contaminants) and for the accumulation recoveries of compounds from water. Recoveries were determined by spiking the water samples with mixtures of investigated contaminants. Recoveries of organochlorine pesticides at concentrations 1-8 ng/L were 42% for HCB, 66-87% for alpha-, beta-, and gamma-HCH, and 88-104% for 4,4'-DDE, -DDD and -DDT. At concentrations of 2-20 ng/L the PCBs were recovered with 63% as Aroclor 1254 and with 83% as Aroclor 1260. Chlorophenols were recovered almost quantitatively (Fingler et al. 1987). The only exception was 4-CP with a recovery of 42%. The detection limits in water were 0.5 ng/L for organochlorine pesticides and PCBs and 1 ng/L for chlorophenols. The determination limits were 1 ng/L for organochlorine pesticides and PCBs, 2 ng/L for 4-CP, 2,4-DCP, 2,4,5- and 2,4,6-TCP and 4 ng/L for 2,3,4,6-TeCP and PCP. The differences in frequencies of appearance and in median concentrations of investigated compounds in water samples were statistically tested by chi-squared test and Mann-Whitney test, respectively.

RESULTS AND DISCUSSION

The concentrations of organochlorine pesticides, PCBs and chlorophenols measured in the Kupa River water are given in Table 1. The distribution of the results was not normal and therefore medians were calculated as central values.The trace concentrations of PCBs were detected in all analysed samples being of the same order of magnitude as those measured in samples collected during the last four months in 1985 (Šmit et al. 1987). Although the investigations performed in 1985 indicated the possibility of periodical appearance of highly contaminated river water waves as a consequence of changes in hydrological conditions, in the present study no seasonal variations were observed and the concentrations were not dependent upon the flow rate of the Kupa River. The maxima in the PCBs load profiles in the river water were measured at highest flow rates. The average value of load profile at Location B was not significantly lower than that at Location A (Table 2).

The PCB pattern was evaluated by comparison of chromatograms of river water extracts with those of the Aroclor 1260 standard. No difference was found between the two sampling locations and

Table 1. Concentration of organochlorine compounds in the water of the Kupa River at Location A (11 samples for PCBs and organochlorine pesticides and 9 samples for chlorophenols) and at Location B (13 samples for PCBs and organochlorine pesticides and 12 samples for chlorophenols).

Compound	Concentration, ng/L			
	Location A		Location B	
	Median[a]	Range[b]	Median[a]	Range[b]
PCBs as				
Aroclor 1254	3 (11)	2 - 8	2 (12)	2 - 8
Aroclor 1260	3 (11)	1 - 6	2 (13)	<1 - 4
HCB	2 (10)	<1 - 3	<1 (9)	<1 - 3
alpha-HCH	0 (1)	<1	0 (5)	<1 - 1
beta-HCH	0 (0)		0 (0)	
gamma-HCH	6 (11)	2 -20	6 (13)	1 -17
4,4'-DDE	0 (5)	1 - 4	0 (3)	<1 - 2
4,4'-DDD	0 (4)	1 - 4	0 (2)	1 - 2
4,4'-DDT	0 (4)	2 - 6	0 (3)	2 - 3
4-CP	0 (3)	<2 -50	0 (2)	<2 - 5
2,4-DCP	<2 (5)	<2 -18	<2 (6)	<2 -11
2,4,6-TCP	0 (4)	3 -15	<2 (6)	<2 - 6
2,4,5-TCP	<2 (6)	<2 -23	0 (5)	2 - 8
2,3.4,6-TeCP	0 (4)	<4 -42	0 (5)	<4 - 8
PCP	28 (9)	<4 -95	11 (12)	<4 -51

[a]0 stands for values below detection limits; the number of positive samples is given in brackets. [b]Ranges apply to positive samples.

results obtained for a total of 24 river water samples were combined. The qualitative and quantitative comparisons of extract chromatograms statistically indicated the predominance of earlier eluting peaks which corresponded to penta- and hexachlorobiphenyls According to relative retention times to 4,4'-DDE multiplied by 100 (RRT_{DDE}) the most frequently detected peaks were those at RRT_{DDE} 70 and 146 (22 samples) and the peak at RRT_{DDE} 84 (18 samples). They were followed by peaks at RRT_{DDE} 125 (13 samples), 203 and 232/244 (9 samples), 280 (7 samples), 117 (4 samples), 160 and 360/372 (1 sample). According to Sawyer (1978) the peaks at RRT_{DDE} 70 and 84 belonged to pentachlorobiphenyls, those at RRT_{DDE} 125 and 146 to penta- and hexachlorobiphenyls, at RRT_{DDE} 117 to hexachloro-biphenyls and at RRT_{DDE} 160 to penta- and heptachloro-biphenyls. The later peaks belonged to heptachlorobiphenyls. The peak at RRT_{DDE} 70 was the major peak in 18 samples comprising on average 47% of total PCB concentration. The PCB concentrations

Table 2. Load profiles of PCBs, gamma-HCH and PCP in the Kupa River at Locations A and B

Compound	Load profile, mg/sec	
	Location A	Location B
	Mean ± S.D.	Mean ± S.D.
PCBs as		
Aroclor 1254	0.67 ± 0.50	0.39 ± 0.35
Aroclor 1260	0.37 ± 0.22	0.24 ± 0.25
gamma-HCH	1.42 ± 1.32	1.09 ± 1.39
PCP	5.41 ± 4.38	1.81 ± 1.49

found in the Kupa River were two orders of magnitude lower than those found in the heavily contaminated river waters like those of the Hudson (Bush et al. 1985) and the Niagara rivers (Maguire and Tkacz 1989). However, in most analysed samples the PCB concentration exceeded the maximum limit of 1 ng/L permitted by relevant Croatian regulation in freshwaters of the I and II categories, used as drinking water or drinking water supplies after an appropriate treatment (Regulatory Act 1984).

Gamma-HCH was the only organochlorine pesticide present in all samples of the Kupa River water and beta-HCH was not detected in any sample. The second pesticide most frequently present at both locations was HCB followed by traces of alpha-HCH at Location B and of DDT-complex at both locations. The highest concentrations were measured for gamma-HCH, which is still widely used for public health care. Its concentrations in the river water were comparable at both locations; they were slightly lower than those reported by Hernandez et al. (1991) in Gallego River (Spain) near an industrial source. The maximum gamma-HCH concentrations in the Kupa River were higher than 10 ng/L at both sampling locations which is the prescribed maximum concentration limit for freshwaters of the I and II categories in Croatia (Regulatory Act 1984). However, they were still significantly below the ecotoxicologically acceptable level for gamma-HCH in freshwaters which was taken to be 100 ng/L (United Nations Environmental Programme 1989). The average loading of the Kupa River water with that pesticide was not significantly higher at Location A (Table 2).

The frequency of appearance of the six measured chlorophenols in the Kupa River water was not statistically different at two sampling locations. The maximum concentrations of chlorophenols were approximately two to ten times higher at Location A than at Location B but still far below the maximum limits of 100 ng/L for

2-CP, 300 ng/L for 2,4-DCP and 1 μg/L for 2,4,5-TCP, 2,3,4,6-TeCP and PCP established by the relevant Croatian regulation (Regulatory Act 1984). The highest concentrations were measured for PCP which was present in all river water samples. The average loading of the river with PCP seemed to be higher (the difference is marginally significant: P=0.07) at Location A (Table 2). Although the highest PCP concentration was measured at a low flow rate, the PCP concentration in the river water in general was not dependent on the river flow rate.The PCP concentrations and the frequency of appearance in the Kupa River were comparable to those determined earlier in the Sava River water before the Zagreb city area, in the area and after it (Fingler and Drevenkar 1988). Unlike the Kupa River, in the Sava River, traces of 2,4,6-TCP and 2,3,4,6-TeCP were detected more frequently while 4-CP and 2,4,5-TCP were not detected at all.

The results of analysis of organochlorine compounds in drinking water samples from Sisak, Zagreb and Labin are compared in Table 3. PCB concentrations in all positive samples were at or near the determination limit. The highest incidence of PCBs, comparable to that measured in samples of the Kupa River water, was determined in samples from Sisak, possibly as a consequence of drinking water preparation from the contaminated river water. Out of the seven analysed organochlorine pesticides, six were detected in drinking water samples from Sisak, three in samples from Labin and two in samples from Zagreb. Gamma-HCH was the only organochlorine pesticide present in all samples. With the exception of the gamma-HCH concentrations measured in several samples of the Sisak drinking water the concentrations of other organochlorine pesticides were mostly at or near the determination limit. The maximum concentration of gamma-HCH in the Sisak drinking water was three times higher than that determined during the same period of time in the Kupa River water, but it was still much lower than the maximum admissible concentration of 0.1 μg/L established by the European Communities for single pesticides in water intended for human consumption (Council of the European Communities 1980) or the maximum contaminant level of 0.2 μg/L proposed for gamma-HCH in drinking water by the US Environmental Protection Agency (US Environmental Protection Agency 1990).

The results of chlorophenol analysis in the Zagreb drinking water, compared in Table 3 with those obtained for the Sisak and Labin drinking waters, are from our previous study (Fingler and Drevenkar 1988). The chlorophenol which was determined most frequently in all drinking waters and in highest concentrations was PCP. The highest concentrations were measured in the Labin samples where maximum concentration was four times higher than that in Zagreb and one order of magnitude higher than in Sisak. In Labin samples PCP was followed only by 2,3,4,6-TeCP. In Sisak and Zagreb samples the traces of chlorophenols with three and two chlorine atoms were also detected.

Although the levels of organochlorine compounds detected in drinking water samples from Sisak were generally lower than those

Table 3. Concentration of organochlorine pesticides, PCBs and chlorophenols in drinking water from Sisak (16 samples for PCBs and organochlorine pesticides, 13 samples for chlorophenols), Zagreb (10 samples) and Labin (10 samples). Results for chlorophenols in Zagreb drinking water refer to our previous study (Fingler and Drevenkar 1988).

Compound	Concentration, ng/L					
	Sisak		Zagreb		Labin	
	Median[a]	Range[b]	Median[a]	Range[b]	Median[a]	Range[b]
PCBs as						
Aroclor 1254	<1 (12)	<1- 5	0 (3)	<1- 5	0 (5)	1- 3
Aroclor 1260	<1 (11)	<1- 3	0 (2)	2	0 (4)	<1- 2
HCB	1 (13)	<1- 4	2 (10)	1- 3	0 (0)	
alpha-HCH	<1 (11)	<1- 1	0 (0)		0 (1)	2
beta-HCH	0 (0)		0 (0)		0 (0)	
gamma-HCH	3 (16)	1-59	1 (10)	<1- 1	1 (10)	1- 6
4,4'-DDE	<1 (9)	<1- 2	0 (0)		0 (1)	<1
4,4'-DDD	0 (3)	<1- 1	0 (0)		0 (0)	
4,4'-DDT	0 (6)	<1- 3	0 (0)		0 (0)	
4-CP	0 (0)		0 (1)	6	0 (0)	
2,4-DCP	0 (2)	<2- 2	0 (1)	17	0 (0)	
2,4,6-TCP	0 (2)	2	0 (4)	5- 9	0 (0)	
2,4,5-TCP	0 (3)	<2 -3	3 (5)	5- 22	0 (0)	
2,3,4,6-TeCP	0 (2)	<4- 4	0 (1)	10	4 (7)	<4- 5
PCP	5 (12)	<4-39	13 (5)	26-123	34 (10)	9-474

[a]0 stands for values below detection limits: the number of positive samples is given in brackets. [b]Ranges apply to positive samples.

in the Kupa River, the frequency of their appearance indicated that the procedures for purification of raw water were not always sufficiently efficacious. The ground waters in Zagreb serving as drinking water supplies can be contaminated by improper industrial and domestic waste discharge and occasional chemical spills as well as by the infiltration of the polluted waters of the Sava River and of a number of streamlets in the city area. The natural filtration through the subsurface sediment layers is the main purification step followed in most pumpstations only by chlorination. In Labin, a town located in the karst area, the purity of spring waters greatly depends on possible migration of micropollutants through a network of karst surface and ground water streams. In this area the elimination of pollutants from the water by natural filtration is insignificant and even highly lipophilic compounds may be transported not only from adjacent but also from very distant contaminated industrialized and

agricultural regions to the water sources.

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