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Comparison of Ambient Air Levels of PCBs and Organochlorine Pesticides at Two Sites in Zagreb, Croatia

S. Herceg Romanić, B. Krauthacker

Biochemistry and Organic Analytical Chemistry Unit, Institute for Medical Research and Occupational Health, Ksaverska c. 2, Post Office Box 291, 10001 Zagreb, Croatia

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Polychlorinated biphenyls (PCBs) and organochlorine pesticides are persistent environmental pollutants. Their properties are excellent concerning application, but because of their hazardous effects on environment and biota, their usage has been banned or reduced in many industrialised countries for many years. Organochlorines are still present as environmental pollutants, but thanks to usage restrictions, levels of many organochlorines have been considerably reduced in the biotic and abiotic environment.

This study continues follow-up measurements of the levels of PCBs and organochlorine pesticides at two sites in Zagreb, which began in 1997. One site was chosen in a residential, non-industrial part of Zagreb, and the other close to a landfill and the industrial zone. The results were also analysed with respect to seasonal variations.

MATERIALS AND METHODS

Zagreb is a northwestern Croatian city situated at the foot of mountain Medvednica with about 1 000 000 inhabitants. Samples were taken at two different sites, the first, Ksaver, is a residential area to the north and second, Jakuševec, is an area near a landfill and the industrial zone to the south of the city. The air distance between these two sites is about 9 km. From June 1999 to February 2000, 47 consecutive air samples were collected from Ksaver and from June 2000 to June 2001, 33 consecutive air samples were collected from Jakuševec. Data on ambient temperature and pressure were obtained from the Meteorological and Hydrological Service of Croatia. Samples ($\approx$ 1000 m^3) were collected on quartz fibre filter (for particulate matter) and polyurethane foam (PUF) (to absorb organochlorines in the gas-phase). The following organochlorines were analysed: 20 PCB congeners (PCB-28, PCB-52, PCB-60, PCB-74, PCB-77, PCB-101, PCB-105, PCB-114, PCB-118, PCB-123, PCB-126, PCB-138, PCB-153, PCB-156, PCB-157, PCB-167, PCB-169, PCB-170, PCB-180, PCB-189) and organochlorine pesticides/metabolites HCB (hexachlorobenzene), α-, β-, γ-HCH (alpha-, beta-, gama-hexachlorocyclohexane), DDT (1,1,1-trichloro-2,2-di(4-chlorophenyl) ethane, DDE (1,1-dichloro-2,2-di(4-chlorophenyl)ethene) and DDD (1,1-dichloro-2,2-di(4-chlorophenyl)ethane. The quartz fibre filter and PUF plugs were extracted

Correspondence to: S. Herceg Romanić

together in Soxhlet apparatus with 650 ml of 5% diethyl ether in n-hexane for 12 hrs. The extracts were reduced to ≈ 5 mL using a rotary evaporator. The concentrated extracts were treated with sulphuric acid and the organic layer was evaporated to dryness under a gentle stream of nitrogen (Herceg Romanić and Krauthacker 2000a). Method blanks were checked at a frequency of one blank for about 5 samples and impurities did not interfere with the compounds of interest.

The prepared extracts were analysed on an "ATI Unicam" 610 Series gas chromatograph equipped with electron capture detector (HRGC-ECD). Compounds were separated on two capillary columns 0.25 mm id and 0.25 μm film thickness ("Supelco" USA); the first column was 30 m long with SPB-1701 stationary phase, and the second column was 60 m long with SPB-5 stationary phase; the carrier gas was nitrogen; the column temperature programme started at 100 °C (second column) and 110 °C (first column) with ramp 4 °C/min to 240 °C and 50 min isothermally; the injector temperature was 250 °C, and the detector temperature was 270 °C. The external standard was used for qualitative and quantitative analysis. The standard solutions of PCB congeners in isooctane (35 μg/mL) were purchased from "Campro Scientific", Veenendaal, Netherlands. The determination limit was calculated using the analyte peak height to baseline noise ratio in the air sample chromatograms ≥ 3 and the determination limit in the air samples was 0.5 pg/m^3 per analyte. Method recovery and reproducibility were checked during three years of sampling (1999 – 2001). Eight samples were analysed per level. Known amounts of analysed compounds were added to PUF and quartz fibre filter paper prior to extraction at three fortification levels which correspond to the fortification levels listed in Table 1, for an air sampling volume of 1000 m^3.

Table 1. Mean method recovery and reproducibility expressed as relative standard deviation (RSD) of eight samples per level analysed between 1999 and 2001.

Polychlorinated biphenyls			Organochlorine pesticides		
Fortification level (pg/m^3)	Recovery (%)	RSD (%)	Fortification level (pg/m^3)	Recovery (%)	RSD (%)
0.93 - 1.40	62-86	23-50	0.56 – 2.93	43-91	18-54
4.65 – 7.00	56-76	15-40	1.41 – 9.39	60-86	22-41
18.0 – 21.0	55-98	15-39	3.67 – 24.4	60-81	20-49

RESULTS AND DISCUSSION

The results of analysis of 80 ambient air samples collected in Zagreb are presented in Table 2. All results are corrected for recovery and recalculated to normal conditions. Concentrations of organochlorine pesticides were in the range from below determination limit for β-HCH, DDD and DDT to 246.5 pg/m^3 for γ-HCH. HCB, α-HCH, γ-HCH and DDE were found in all samples at both sites and γ-HCH had the highest levels. The DDE/DDT ratio (often used as indicator of

DDT input) is lower at Ksaver than at Jakuševec (0.8 vs 2.2). This implies that DDT emission at Jakuševec is not higher than the emission of DDE (in spite of

Table 2. Organochlorine pesticides and polychlorinated biphenyls (pg/m^3) in ambient air collected in Zagreb in 1999/2001.

	Ksaver (N=47)			Jakuševec (N=33)		
	n (%)	range	median	n (%)	range	median
HCB	100	1.1-36.3	9.4	100	2.1-33.6	10.2
α-HCH	100	3.5-44.3	12.3	100	0.6-60.5	9.9
β-HCH	100	0.5-40	5.6	97	0-17.1	4.2
γ-HCH	100	11.5-246.5	53.1	100	5.6-246.3	74.7
DDT	83	0-36.4	16.6	79	0-32.2	8.4
DDD	83	0-101.0	7.5	82	0-26.9	5.0
DDE	100	2.3-63.3	11.5	100	0.8-142.5	23.6
PCB-28	100	3.0-312.2*	35.7*	100	4.7-204.1	80.6
PCB-52	100	1.6-65.2*	12.5*	100	2,2-172.6	13.7
PCB-60	98	0-23.2	8.0	100	1.1-32.9	10.2
PCB-74	49	0-18.5	2.2	80	0-23.0	8.3
PCB-77	0	/	0	19	0-7.9	0
PCB-101	100	1.6-222.8*	14.2*	100	1.2-162.5	26.8
PCB-105	65	0-35.5	1.9	88	0-30.0	5.5
PCB-114	49	0-13.8	0	82	0-13.4	2.5
PCB-118	88	0-23.3	2.6	91	0-24.1	8.4
PCB-123	100	0-11.7	2.6	83	0-17	6.9
PCB-126	13	0-3.6	0	30	0-9.9	0
PCB-138	100	1.5-128.3*	5.5*	100	0.7-71.5	12.6
PCB-153	100	0.5-91.7*	4.4*	100	1.3-54.7	9.1
PCB-156	4	0-1.3	0	33	0-2.5	0
PCB-157	0	/	0	3	0-1.1	0
PCB-167	11	0-3.9	0	27	0-3.4	0
PCB-169	13	0-2.9	0	0	/	0
PCB-170	21	0-2.2	0	36	0-5.6	0
PCB-180	64	0-6.8*	1.8*	70	0-22.9	2.2
PCB-189	6	0-1.7	0	0	/	0

N – number of analysed samples; n – percentage of positive samples (%);
0 – below determination limit; * Herceg Romanić and Krauthacker 2003

the neighbouring landfill) but the situation is opposite at Ksaver (which has no known emission sources). This could be the result of long-range air transport of DDT and its influence on the levels of DDT in Zagreb, which was also observed earlier. Low DDE/DDT ratios were observed in: particulate matter isolated from rain and snow samples collected from 1990 to 1992 (Fingler et al. 1994), pine needles collected in 1998 (Herceg Romanić and Krauthacker 2000b), air samples

collected in 1997 in Zagreb (Ksaver and Jakuševec) (Herceg Romanić and Krauthacker 2000a). The ratio α-HCH/γ-HCH, which is frequently used as an indicator of γ-HCH input, was 0.2 at both locations, which reflects the usage of γ-HCH. In all samples, the concentrations of 20 PCB congeners ranged between 0 (below determination limit) and 312.2 pg/m^3. We observed two differences between PCBs and organochlorine pesticides. First, the ratio between median concentrations at Jakuševec and Ksaver is higher than 1 for all PCB congeners whose median is > 0. The second difference is that the profiles of individual congeners are the same at both sites with the exception PCB-114 (at Ksaver the median is 0 pg/m^3, and at Jakuševec 2.5 pg/m^3). At both locations PCB-28, PCB-52, PCB-101, PCB-138 and PCB-153, which belong to a group of six indicator congeners, were found in all samples. Moreover, three of these had the highest concentration medians in the following order: PCB-28 > PCB-52 > PCB-101. The remaining three indicator congeners follow the same order of concentration medians at both sites: PCB-138 > PCB-153 > PCB-180. PCB-77, PCB-126, PCB-156, PCB-157, PCB-167, PCB-169, PCB-170 and PCB-189 were not found in all samples and median concentrations were 0 while order of other PCBs according to median concentrations is: PCB-60 > PCB-118, PCB-123 > PCB-74 > PCB-105. Higher levels at Jakuševec could be attributed to the proximity of a landfill, which is supported by Ruokojärvi and co-workers (1995) who found that an uncontrolled, spontaneous landfill fire might result in the emission of tetra- and penta-chlorinated biphenyls.

Our earlier measurements at Ksaver and Jakuševec in October – November 1997 and November – December 1997, respectively, were focused on organochlorine pesticides and six indicator PCBs (Herceg Romanić and Krauthacker 2000a). In order to compare this study with our new results, we filtered the data for samples collected in October - November 1999 at Ksaver (N=13 out of 47) and November – December 2000 at Jakuševec (N=5 out of 33). The comparison is presented in Table 3. Temperature ranges in both studies were similar (Ksaver: 0.9 – 14.3 °C in 1997 vs -0.6 – 14.6 °C in 1999; Jakuševec: -2.6 – 6.3 °C in 1997 vs 3.3 – 10.5 °C in 2000). Median air levels of all compounds at Ksaver decreased except for DDE and DDT, which remained unchanged. At Jakuševec, however, only HCB, α-HCH and β-HCH levels dropped. The comparison shows that the median levels (pg/m^3) of six indicator PCBs at Ksaver decreased slightly (Herceg Romanić and Krauthacker 2003), which is not case with PCB medians in the air of Jakuševec (Table 3) as only PCB-52 and PCB-180 showed decrease. A comparison of present results revealed differences in seasonal variations of organochlorines (with frequency of appearance > 50%) between the two sites, with exception of HCB. At Ksaver the concentrations of pesticides (except HCB) in ambient air increased with temperature while at Jakuševec their levels were similar throughout the sampling period regardless of air temperature. This is illustrated by Figure 1 with the sum of DDT, DDD and DDE concentrations. The same applies for PCBs. Their concentrations (sum of 20 PCB congeners) at Ksaver showed a temperature-dependent behaviour reaching their maximum in the summer, which

is not the case with concentrations measured in air samples collected at Jakuševec (see Figure 1). In addition, although Table 2 shows that the concentration ranges of organochlorines at these two sites overlap, the seasonal concentration variations suggest that compounds sources might occur at Jakuševec. It should be noted that temperature ranges at Jakuševec (-2.5 °C –27.8 °C) and Ksaver (-10.2 °C

Table 3. Comparison of levels (median, pg/m^3) in ambient air collected in this study with data obtained in1997

	Ksaver		Jakuševec	
	1997 (N=14)**	1999 (N=13)	1997 (N=10)**	2000 (N=5)
HCB	29	9	31	22
α-HCH	25	10	28	11
β-HCH	8	6	15	5
γ-HCH	49	42	77	110
DDE	10	10	19	22
DDD	11	4	7	16
DDT	12	12	9	12
PCB-28	29	19*	36	118
PCB-52	19	9*	21	13
PCB-101	10	7*	14	21
PCB-138	8	3*	10	15
PCB-153	7	2*	12	13
PCB-180	5	2*	13	4

N-number of samples; *Herceg Romanić and Krauthacker 2003;
**Herceg Romanić and Krauthacker 2000

– 24.5 °C) were similar, which rules out differences in temperature as the reason for differences in concentrations of pollutants. The air concentration of HCB depends on temperature and follows a curve, which was similar for both sites (Figure 1). Unlike other organochlorine pesticides HCB shows higher concentrations in winter. The reason may be inadequate incineration of chlorine-containing wastes (WHO/IPCS 1997). Kaupp and co-workers (1996) investigated seasonal variations of HCB concentrations and observed higher levels in warmer season, but they also mentioned that this was somewhat unexpected because an earlier study in Germany showed constant concentrations of HCB throughout the year. A comparison of our data with literature (Iwata et al. 1995; Karlsson et al. 2000; Babu Rajendran et al. 1999; Lee et al. 2000) shows that the concentrations of organochlorine pesticides in Zagreb follow the global environmental pollution trend. The comparison of the levels of six indicator PCBs in Croatia and in other countries showed that they were not high for cities; in fact, they could be characterised as typical for semi-urban areas (Kaupp et al. 1996; Haugen et al. 1999; Lee and Jones 1999; Panshin and Hites 1994). The concentrations of coplanar PCBs measured in Zagreb were higher than in some non-industrial areas

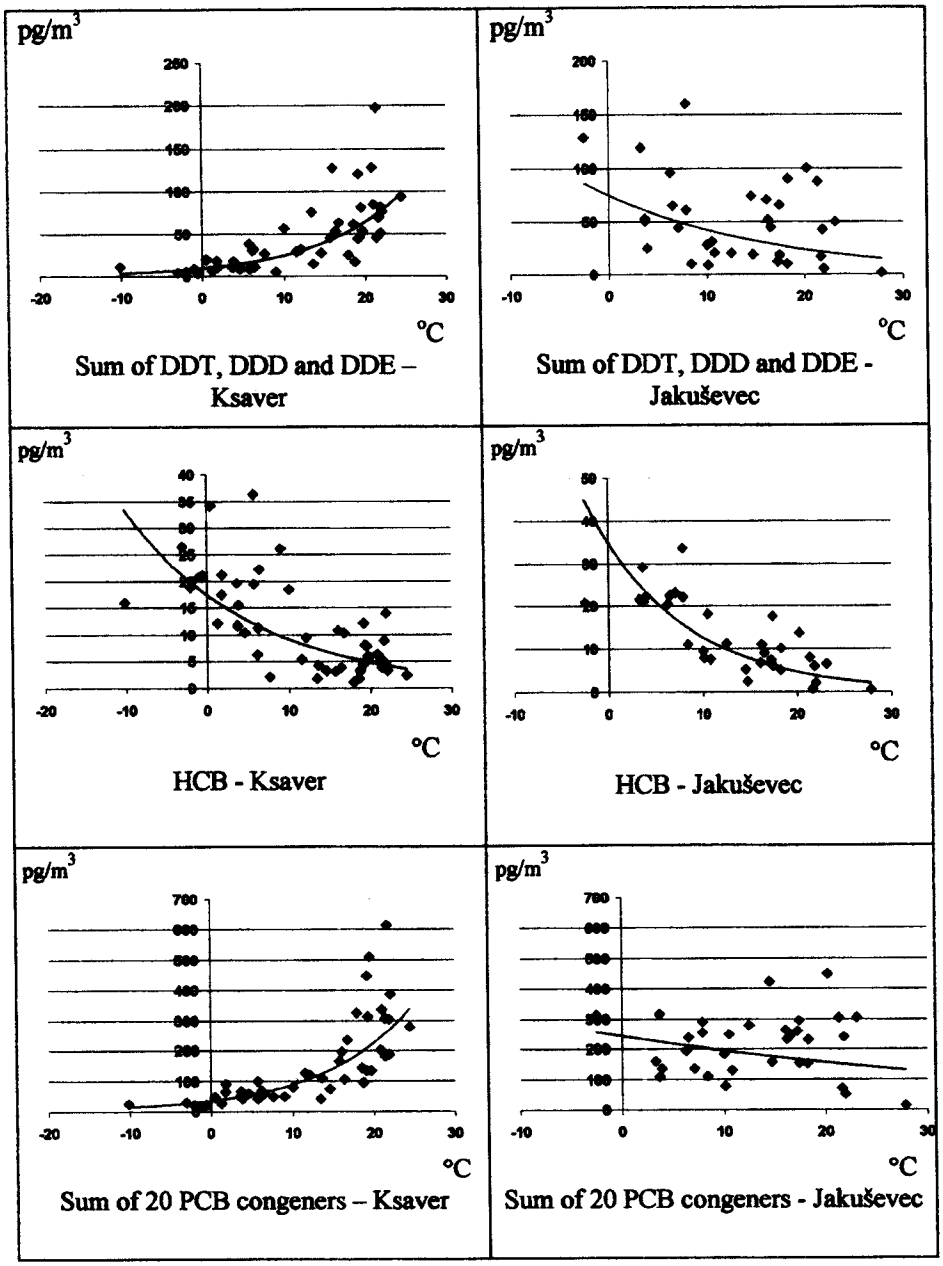

Figure 1. Temperature dependence of DDT, DDD and DDE sum, HCB and sum of 20 PCB congeners levels (pg/m^3) in air samples collected at Ksaver and Jakuševec in 1999/2001.

(Garcia et al. 1996, Harner et al. 1998), but are comparable to the levels in rural areas neighbouring industrial areas in Bavaria (Kerst et al. 2002) and in Chicago (Harner et al. 1998). However, the levels of PCB-77 and PCB-118 measured in urban areas such as London are higher (Halsall et al. 1995). According to literature data, and our results, it could be concluded that the levels of PCB-105 and PCB-118 are the highest among coplanar PCBs. In our study, PCB-123 also stood out with its high concentration in comparison to other PCBs.

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