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Organochlorine Pesticides and Polychlorinated Biphenyls in Ambient Air Collected in Zagreb, Croatia

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Organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are persistent, lipophilic organic compounds, which have had extensive world-wide use in many agricultural and industrial applications. PCBs and OCPs are distributed in all compartments of the biosphere and accumulate in all lipid-containing specimens including adipose tissue of humans and animals (Jones and de Voogt, 1999).

Emission into the air is associated with the recent use and/or evaporation from earth sorbents. OCPs and PCBs can travel long distances via air, depending on wind velocity and direction which influence their global distribution (Ballschmiter, 1996).

Many countries monitor air quality, including the levels of OCPs and PCBs (Halsall et al. 1995; Oehme et al. 1996; Ballschmiter et al. 1991; Nerin et al. 1996). As there are no data on OCP and PCB distribution in the ambient air in Croatia we started an investigation of the occurrence and distribution of OCPs and PCBs in air. This paper presents an analysis of OCPs and PCBs in the ambient air collected at two different sampling points in Zagreb, the capital and the major industrial center of Croatia. Sampling points differed with respect to possible sources of OCPs and PCBs pollution.

MATERIALS AND METHODS

Ambient air samples were taken at two different locations in the Zagreb city area. Zagreb, the capital of Croatia is a continental, industrial city with about 1, 000, 000 inhabitants. The first location, the northern part of the city - Ksaverska c., lies beneath the slopes of the mountain Medvednica and this is residential, not industrialized part of Zagreb. The second location, the southern part of the city - Jakuševec is an area near a landfill. From October to November 1997, 14 consecutive air samples were collected at Ksaverska c., and from November to December 1997, 10 consecutive air samples were collected at Jakuševec. Air sampling(≈1000

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m^3, 14 m^3/h) was carried out using high volume air sampler. Samples were collected on quartz fiber filter QM-A ("Whatman International Ltd", UK) and polyurethane foam (PUF) plugs (supplied by US Environmental Protection Agency). PUFs were precleaned before use by Soxhlet extraction with 10% diethyl-ether in n-hexane (650 mL) for 12 hrs. The module and glass PUF holder were rinsed with n-hexane before assembling. After air sampling, PUFs and filters were extracted in Soxhlet with 5% diethyl-ether in n-hexane (650 mL) for 12 hrs. Extract volumes were reduced to ≈5 mL using rotary evaporator ("Büchi" R-114, Switzerland) and washed with 5 mL concentrated sulphuric acid. The organic layer was separated and evaporated to dryness under gentle stream of nitrogen. Before gaschromatographic (GC) analysis, samples were redissolved in 1,0 mL of n-hexane. Compounds investigated in this study are listed in Table 1. Standards of OCPs were kindly supplied from the US EPA. Standards of PCB congeners were purchased from Promochem GmbH, Wesel, Germany.

Table 1. Compounds measured in this study and purity of standards.

Abbreviation	Compound	Purity (%)
HCB	Hexachlorobenzene	99.70
α-HCH	alfa-hexachlorocyclohexane	99.70
β-HCH	beta-hexachlorocyclohexane	99.50
γ-HCH	gama-hexachlorocyclohexane	99.86
p,p'-DDE	1,1-dichloro-2,2-di(4-chlorophenyl)ethene	99.99
p,p'-DDD	1,1-dichloro-2,2-di(4-chlorophenyl)ethane	99.31
p,p'-DDT	1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane	99.70
PCB-28	2,4,4'-trichlorobiphenyl	99.00
PCB-52	2,2',5,5-tetrachlorobiphenyl	99.00
PCB-101	2,2',4,5,5'-pentachlorobiphenyl	99.00
PCB-138	2,2',3,4,4',5'-hexachlorobiphenyl	99.00
PCB-153	2,2',4,4',5,5'- hexachlorobiphenyl	99.00
PCB-180	2,2',3,4,4',5,5'-heptachlorobiphenyl	99.00

The GC analysis of OCPs and PCBs (Table 1) was carried out on gas chromatograph "Ati Unicam" 610 Series equipped with two ^{63}Ni electron capture detectors. Compounds were separated on two capillary columns of 0.25 mm I.D. with 0.25 μm film thickness ("Supelco", USA): The first column was 30 m long with stationary phase SPB-1701 and second was 60 m long with stationary phase SPB-5. Nitrogen was used as the carrier gas. The column temperature programme started at 100 °C (column 1) and 110 °C (column 2) with ramp 4 °C/min to 240 °C, and kept at 240 °C for 50 min. The temperature of injectors and detectors was 250 °C and 270 °C respectively. Qualitative and quantitative analysis were done by comparison with external standards.

RESULTS AND DISCUSSION

Prior to sampling the method recovery and reproducibility were estimated. Recovery was determined by addition of known amounts of analysed compounds to PUF and quartz fiber filter prior to extraction. Levels of added compounds were recalculated on the basis of 1000 m^3 of air. Analysed compounds were added at three fortification levels, which are given in Table 2. Five samples were analysed at each fortification level. At the second and third level, recoveries and RSD ranged between 50-95%, and 4-46% depending on the compound. At the first fortification level, recoveries ranged between 41% and 110% and relative standard deviations (RSD in %) for reproducibility ranged between 11% and 42% depending on the compound. Exceptions were HCB and α-HCH for which RSD were 78% and 59%, respectively. RSD was higher at the first level, which was close to determination limits, than at the other two fortification levels (Table 2). Determination limits were calculated using the peak height to baseline noise ratio of a particular analyte in air sample chromatograms ≥ 3. Table 2 shows average values for determination limits of analysed compounds. Considering the obtained results, it was concluded that method is suitable for OCPs and PCBs analysis in air samples.

Table 3 shows results of measurements of air samples collected at two different locations in Zagreb. PUFs and filters were extracted together and these results present the amount of compounds in the gas phase and bound on the particulate matter. In Ksaverska c. samples, OCPs levels ranged 0.5-80.0 pg/m^3 and PCBs levels ranged 1.0-57 pg/m^3. In Jakuševec samples, OCPs and PCBs ranged 3.0-91.0 pg/m^3 and 4.0-92.0 pg/m^3, respectively.

PCBs and OCPs levels varied between samples, but PCB and OCP distribution were similar on both locations. Median concentrations of HCB, α-HCH and γ-HCH are about four times higher than β-HCH and DDT complex (p,p'-DDT, p,p'-DDD and p,p'-DDE) on both locations. Among PCB levels, the highest concentrations were found for PCB-28 and PCB-52 on both locations. In Ksaverska c. samples, median concentrations of PCB-28 and PCB-52 were 29 pg/m^3 and 19 pg/m^3, and the median concentration of the other four PCB congeners were 5.0-10.0 pg/m^3. Median concentration of PCB-28 and PCB-52 in Jakuševec samples were 36 pg/m^3 and 21 pg/m', the range of the other four congeners was 10.4-14.0 pg/m^3. PCB-28 and PCB-52 are the most volatile PCB congeners and mostly influenced by long transport (Oehme et al., 1996) and this could be the reason for differences in PCB congener levels.

Comparison of OCPs and PCBs levels between locations reflect slightly higher levels at Jakuševec than at Ksaverska c. Exception are p,p'-DDE and p,p'-DDT. The sampling location at Jakuševec is near a landfill where

Table 2. Method recoveries at three concentration levels and determination limits for OCPs and PCBs. Five samples were analysed at each level. $\bar{x}$ – mean recoveries (%), RSD - relative standard deviations (%), DL - determination limit (pg/m^3), c - concentration of added compound expressed as pg/m^3

	LEVEL 1			LEVEL 2			LEVEL 3			
	$\bar{x}$	RSD	c	$\bar{x}$	RSD	c	$\bar{x}$	RSD	c	DL
HCB	41	78	0.56	86	23	1.41	67	32	3.67	0.50
α-HCH	59	59	0.69	70	24	1.73	75	35	4.49	0.50
β-HCH	89	38	2.59	83	23	6.48	78	46	16.8	2.00
γ-HCH	75	29	1.04	88	28	2.60	88	26	6.74	1.00
p,p'-DDE	85	21	2.92	95	23	7.30	70	39	19.0	1.50
p,p'-DDD	74	41	3.75	85	33	9.39	82	31	24.4	2.00
p,p'-DDT	89	43	2.33	81	19	5.83	75	24	15.1	2.00
PCB-28	110	40	0.91	82	23	4.57	73	13	22.8	0.50
PCB-52	81	36	0.83	89	26	4.16	50	20	20.8	0.50
PCB-101	72	13	1.06	75	16	5.13	61	16	26.5	0.50
PCB-138	94	11	0.85	82	9	4.24	67	37	21.2	0.50
PCB-153	106	22	1.02	89	12	5.12	56	4	25.6	0.50
PCB-180	84	13	0.82	78	18	4.10	56	20	20.5	0.50

Table 3. OCP and PCB levels (pg/m^3) in ambient air samples collected in Zagreb in 1997. Results are corrected for recoveries. N - number of analysed samples; n - number of positive samples

	Ksaverska c. (N=14)			Jakuševec (N=10)		
	n	range	median	n	range	median
HCB	14	0.5 - 49	29	10	15 - 61	31
α-HCH	14	2 - 52	25	10	14 - 61	28
β-HCH	14	3 - 22	8	10	5 - 35	15
γ-HCH	13	3 - 80	49	10	36 - 91	77
p,p'-DDE	14	2 - 26	10	10	8 - 29	19
p,p'-DDD	14	2 - 65	11	9	3 - 17	7
p,p'-DDT	13	4 - 32	12	8	4 - 40	9
PCB-28	14	17 - 57	29	10	15 - 92	36
PCB-52	14	9 - 36	19	10	10 - 44	21
PCB-101	14	4 - 28	10	10	5 - 36	14
PCB-138	14	2 - 21	8	10	4 - 24	10
PCB-153	14	3 - 16	7	10	9 - 20	12
PCB-180	14	1 - 13	5	10	10 - 51	13

occasional uncontrolled fire breaks out. It is known from the literature that uncontrolled fire may result in emission products different from those obtained by controlled bum of waste. Ruokojävi and w-workers (1995) analysed tri- to hepta-chlorinated biphenyls in the air samples collected during an uncontrolled spontaneously landfill fire and found that tetra- and penta-chlorinated biphenyls were the most abundant congeners. Inadequate incineration of chlorine-containing wastes are also known as a source of HCB (WHO/IPCS, 1997).

According to Haugen and w-workers (1998), α-HCH/γ-HCH concentration ratios correlate with air origin. In our study, this ratio is very low. The α–HCH/γ-HCH median concentration ratios were 0.5 and 0.6 at Jakuševec and Ksaverska c. locations, which implies a recent emission of the γ-HCH (lindane) into the atmosphere. This is in agreement with what is known about the use of lindane in Europe, which is not banned, but restricted (Voldner and Li, 1995). The ratio p,p'-DDE/p,p'-DDT is also very often used to distinguish any recent DDT input. High values of this ratio suggest remote pollution (Nerin et al., 1996). The p,p'-DDE/p,p'-DDT median concentration ratio is 1.0 in Ksaverska c. samples and 0.64 in Jakuševec samples. Low p,p'-DDE/ p,p'-DDT ratio has also been found by Fingler et al. (1994) in samples of rain and snow collected from December 1990 to June 1992 at urban and suburban/semi-rural locations in the Zagreb city area. The p,p'-DDE/p,p'-DDT median concentration ratio of 0.25 and 0.7 on particulate matter isolated from rain and snow samples were obtained. Also, low p,p'-DDE/p,p'-DDT has been determined in pine needles collected in March 1998 at Jakuševec and Ksaverska c., 0.27 and 0.24 (Herceg, 1999). These ratios indicated that there had been a recent input of DDT into the atmosphere. The use of DDT is banned or severely restricted in most countries, but in some African, Asian and south American countries DDT is still in use (Voldner and Li, 1995). Hence, the presence of DDT in Zagreb ambient air samples could be explained by long range transport via air.

Review of literature data reflects a broad range of PCBs and OCPs levels in ambient air. Levels of PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180 were measured in four UK urban centers, London, Stevenage, Cardiff and Manchester and reported atmospheric PCB concentration varied from nondetectable to 1770 pg/m^3 (Halsall et al., 1995). In Ny-Alesund, Svalbard, Norway, the range of OCPs (HCB, α-HCH, γ-HCH, p,p'-DDE, p,p'-DDD, p,p'-DDT) was 0.02-203 pg/m^3 and range of PCBs (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180) was 0.1-47.0 pg/m^3 (Oehme et al., 1996). In comparison with other findings, our results showed that the levels in the ambient air samples collected in Zagreb are at the lower end of published data range.

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