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Polychlorinated Biphenyls in Residents around the River Krupa, Slovenia, Yugoslavia

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Polychlorinated biphenyls (PCBs) are ubiquitous environmental pollutants and are current constituents of the human body (Wassermann et al. 1979). In the general population predominant exposure to PCBs is via ingestion of food, water and from the air (Bennett 1983). In workers occupationally exposed to PCBs (in chemical synthesis, capacitor and transformer manufacturing and service, handling of chemical waste) dermal absorption is the major route of body entry (Baker et al. 1980; Maroni et al. 1981; Wolff et al. 1982; Lees et al. 1987). Increasing exposure to PCBs is observed in residents living around waste dump sites containing discarded PCBs (Stehr-Green et al. 1986).

In previous publication (Brumen et al. 1984) serious contamination of the river Krupa (Slovenia, NW part of Yugoslavia) produced from improper disposal of the waste discharge of a plant working with PCBs was reported. Since 1967 the plant has been using various technical PCBs (Clophen A-30 and A-50, Pyralene 1500 and 3010) which are similar to Aroclor 1242 and 1254. Pollution with PCBs in the river Krupa (Brumen et al. 1984) reached 55 µg/g in sediment, 0.3 µg/L in water and 117 µg/g in fish (Brumen et al. 1984a).

The present investigation reports fairly high levels of PCBs in human blood and skin in the residents of the river Krupa gorge. The population was not occupationally exposed to PCBs. It is suggested that the river Krupa is the source of PCB pollution. Dermal absorption could be the predominant route of entry of PCBs for residents of this region.The concentration of PCBs was determined by high resolution GL chromatography.

MATERIALS AND METHODS

Samples of human blood (10 g each) and skin (inner side of the thigh, approx. 0.5 g each) were collected in the autumn of 1984, the winter of 1985 and the autumn of 1986 from three groups of residents: Group A - residents of the river Krupa gorge; Group B- from a region between 1 to 3 km distant from the river Krupa; and

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Group C - at distances over 20 km of the river Krupa. Persons donating samples were not occupationally exposed to PCBs. All members of Group A lived at least 1 km distant from the contaminated waste landfill. Members of Groups A and B were settled in the same place for at least 10 years. In Group A of 10 blood donors three persons were selected three times and one twice in different periods. Human skin was donated from two persons twice. In Group B comprised. 19 blood samples, and in Group C 4. The sediment was collected from the upper 10 cm of the river sediment profile in 1985. Underwear of polyamide fibre was contacted with river water for 2 h in the spring of 1986. Air was sampled through an impinger filled with glass pellets and 2-propanol (Vannucchi and Berlincioni 1980). The air flow rate was around 2 L/min; 400 L of air passed through impinger.

Human skin samples were dried with anh. sodium sulfate and fat extracted with hexane in an ultrasonic bath for 15 min. Dry sediment was extracted with hexane in an ultrasonic bath for 15 min. Blood samples were digested with diluted sulfuric acid (1+1) and hexane extracted. Air dried underwear was hexane extracted for 15 min. in an ultrasonic bath. To 2-propanol from the impinger of the air sampler, water was added in a separatory funnel and extracted with hexane.

Hexane extracts were cleaned with concentrated sulfuric acid, hydrolysed for 1.5 h at 95°C with ethanolic 2.5 % potassium hydroxide and the hexane extract column chromatographed throug Florisil (Florisil, Fluka 60-80 mesh, deactivated with 1.25 % water). Hexane eluates were evaporated and chromatographed (Zell and Ballschmiter 1980).

A Varian GC Mod. 3700 with an EC detector (^{63}Ni) was used with a 30 m x 0.25 mm ID glass capillary column coated with SE-54 (Supelco Inc.). Chromatographic conditions were as follow: temperature of the injector 240 °C, of the detector 270 °C; the initial oven temperature 50 °C, held for 1.5 min. after the injection, than programmed from 50 °C to 190 °C at 15 °C/min.; from 190 °C to 220 °C at 2 °C/min.; at 220 °C isothermal. Splitless injection, volume injection 2 µL; purge activation time 1.5 min. Hydrogen velocity through the column 40 cm/sec; make-up gas nitrogen 21 mL/min.; injector purge 100 mL/min. The concentration of PCBs was calculated by relating peak areas of components No. 28,52,101,118,138, 153,170,180 assigned from IUPAC (Ballschmiter and Zell 1980) of the sample peak to the corresponding peak in the commercial mixture of Aroclor 1242-1254, 1 + 1.

RESULTS AND DISCUSSION

In Table 1. the PCB level of three groups of non-occupationally exposed residents at different distances from the river Krupa is presented. Group A living in the river Krupa gorge possess fairly high levels of PCBs in blood (mean value of 10 samples 155 ng/g) and skin (mean value of two samples 295 µg/g fat basis). This corresponds to the level found in occupationally exposed persons (Wolff et al. 1982). People of Groups B and C live outside the gorge. Their mean PCB blood concentration was 11 and 5 ng/g, resp. In Fig. 1 high resolution gas chromatograms of the PCB profile of hexane extracts of human skin and of air, sediment and clothes after washing in river water sampled in the environment of Group A are presented. PCB residues in human skin reached 320 µg/g fat, in river sediment 48 µg/g, in the air 0.5 µg/m³, and in underwear after washing in river water 0.8 µg/g. In human skin congeners with high lipophilic character predominate : these congeners are rather stable to transformation processes and possess "para substituted phenyl" rings (Zell and Ballschmiter 1980; Wolff et al. 1982a), such as No. 28, 74, 99, 118, 128, 138, 153, 156, 170, 180 (Fig. 1).

Table 1. PCB residues (ng/g) in non-occupationally exposed residents, Slovenia, Yugoslavia

Group A - residents of the river Krupa gorge

Type of sample	Age(yr)	Sex	PCB conc. in 1984	Decline in PCB level after ceasing to use the river water	
				18 months after	25 months after
Blood	62	F	144		
Blood	30	M	38		
Blood	70	F	320		
Blood	28	M	35		
Blood	12	F	76		
Blood	56	M	60		
Blood	10	M	41	15	9
Blood	34	F	135	46	
Blood	39	M	220	35	24
Skin fat	same	same	270,000		11,000
Blood	50	M	480	50	13
Skin fat	same	same	320,000		12,000

Total No of blood samples	PCB conc. range
10	35-480 (155)*

Group B - residents in the region from 1 to 3 km distant from the river Krupa in 1985

No of blood samples	Age (yr)	PCB conc. range
19	25-61	6-18 (11)*

Group C - non-exposed population from different parts of Slovenia (Črnomelj, Novo mesto, Ljubljana) in 1986

No of blood samples	Age (yr)	PCB conc. range
4	25-51	2-7 (5)*

* arithmetic mean

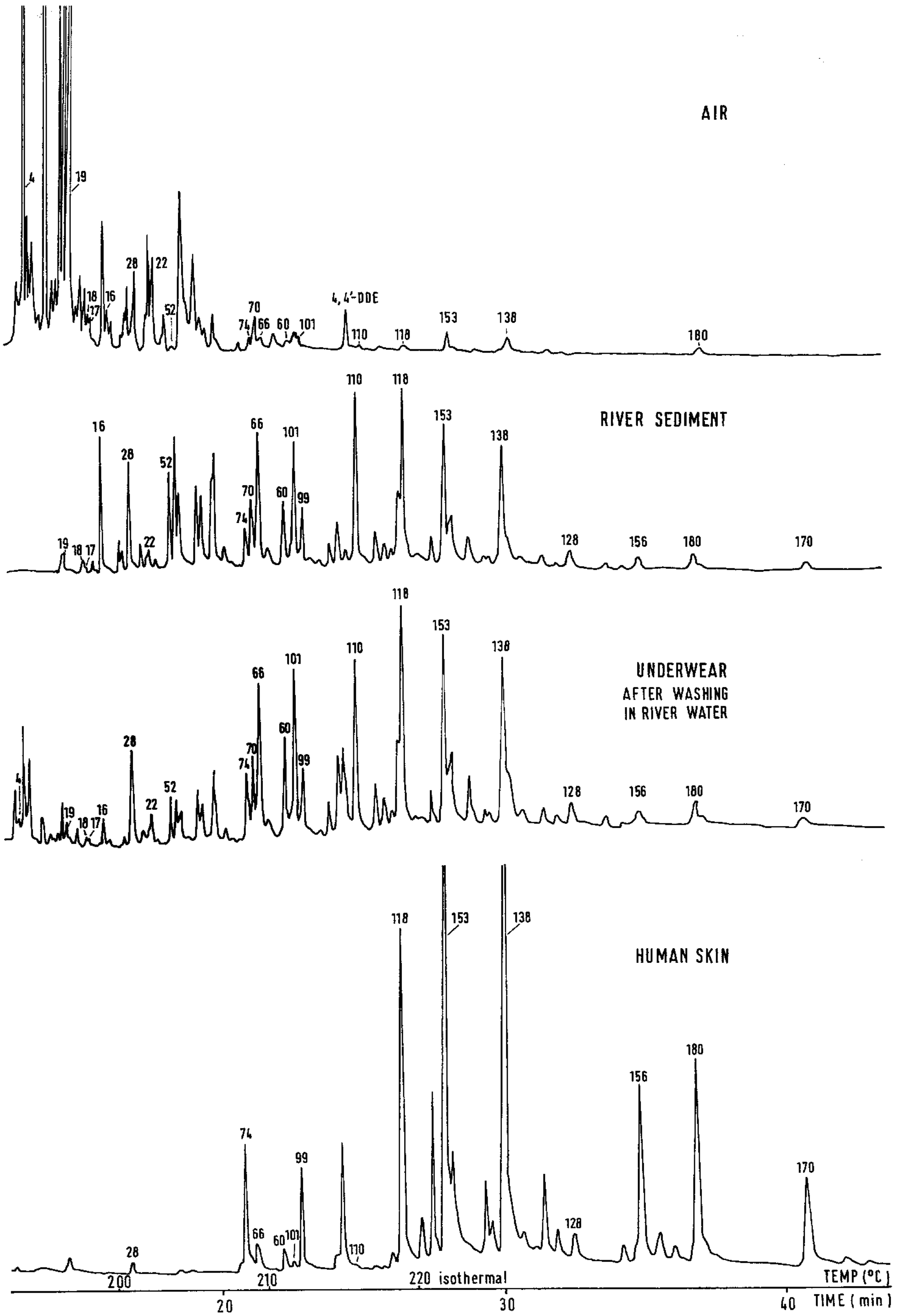

Figure 1. Capillary GL chromatographic profiles of hexane extracts in PCB region from human skin, underwear, sediment, and air. Samples from river Krupa gorge. PCB peaks are numbered according to Zell and Ballschmiter (1980).

The high PCB level in Group A of residents could not be explained by dietary intake and inhalation only. Groups A and B have equal nutritional habits and do not eat fish from the river Krupa. The daily intake of PCBs from breathing in residents of Group A calculated from 20 m^3 of air with a PCB concentration of 0.5 $\mu g/m^3$ is 10 μg PCBs. This is lower than the total daily intake reported for a non-exposed population (24 μg/day) (Bennett 1983). We suggest the predominant role of dermal absorption via:

a) direct uptake from air - (in summertime persons are partly uncovered);
b) direct uptake through skin by bathing in the river;
c) indirect transport through underwear: people used to wash underwear in river water. PCBs are trapped on polyamide fibres of underwear during washing. During wearing desorption od PCBs from clothes and absorption on human skin and further diffusion into blood could occur. Underwear acts as a transfer agent for PCBs between water and human skin. This transfer is promoted by human body temperature.

25 months after ceasing to use the river for bathing and washing the PCB levels declined in human blood from 247 to 15 ng/g (mean of three samples) and in human skin fat from 295 to 12 $\mu g/g$ (mean of two samples) (Table 1). This reduction of the PCB level is appreciable. It is a result of the biological half - life of PCBs in man (Chen et al. 1982; Steele et al. 1986). These data on decreasing PCB levels after ceasing to use river water for washing and bathing could confirm the suggested exposure pathway for residents around the river Krupa.

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