Residue Levels of Polychlorinated Terphenyls, Polychlorinated Biphenyls and DDT in Human Blood

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Since 1966 when the environmental pollution by PCBs was detected by Jensen, many investigaters identified PCB residues not only in the samples from environment such as bird, fish and animal but also in human milk, blood and adipose tissue. These results indicate that PCBs are widely dispersed through the biota.

PCTs which are used in similar industrial application to PCBs may be expected to accumulate in biological systems because of the similar chemical properties which these two substances share.

While their presence in environment has been reported by several investigaters(1~6), PCTs have not recieved so far as wide attention as PCBs.

Zitko identified the PCT residues in the eggs and the fatty tissue of herring gull(1), and Freudenthal found its presence in the river water, oyster and human fat(2). It was shown by Thomas that paperboad and food packing material contained PCTs(3). Nishimoto identified PCT residues in human fat and milk, but not in such food materials as meat, dairy products, vegetable and fish, and in the samples of water and sludge(4). Minagawa reported the residues of PCTs in human fat, some food and food packing materials and wild birds(5). We reported the levels of PCT in human fat collected from the Tokyo area(6).

This paper describes the detection of PCTs as well as PCBs and DDT compounds in human blood.

Materials and Methods

The analyses were made with 27 samples of human blood offered by the volunteers, 19 males and 8 females from 21 to 57 years old, in Tokyo Metropolitan Research Laboratory of Public Health in November 1973. No occupational contacts with PCBs and PCTs were recognizable with these subjects.

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above.

We confirmed PCT residues in human blood using gas chromatograph-mass spectrometer, Simazu-LKB 9000, coupled to Simazu GC-MS PAC 300 computer. As the quantity of the sample blood collected from the subjects was not sufficient to allow confirmation using the mass spectrometer, the 600 ml of whole blood was purchased from Japan Red Cross Central Blood Center. This blood sample was shown to contain 3 ppb of PCT residues, when calculated from the peak heights in its chromatogram.

Results and Discussion

The gas chromatograms of PCT and PCB residues in the blood are shown in Fig.1 and Fig.2, respectively.

The peak profiles in the chromatograms of human blood and fat which we reported in the previous paper are quite similar to that of KC-C. No contamination of PCBs and PCTs during the analytical procedure was ascertained.

All the samples examined were found to contain substantial quantities of PCTs, PCBs and DDE (Table 1).

Table 1, Residue levels of PCBs, PCTs and DDE in Human Blood (ppb on whole blood basis)

Age	Sex	PCB	PCT	DDE	Age	Sex	PCB	PCT	DDE
24	M	3.1	7.0	7.9	38	M	5.8	1.3	13.8
"	"	3.4	5.7	12.2	40	"	3.0	4.0	12.2
25	"	2.8	4.5	18.2	42	"	2.5	7.2	6.7
26	"	3.0	11.8	7.9	"	"	2.5	4.2	8.5
"	"	5.1	0.7	17.2	54	"	5.7	2.0	19.6
27	"	3.0	4.9	10.1	21	F	2.3	7.8	9.3
"	"	2.2	1.1	6.4	22	"	4.0	19.6	12.8
29	"	5.1	1.8	12.1	"	"	2.7	4.2	6.0
"	"	2.7	4.0	3.8	23	"	3.2	2.6	9.6
30	"	3.5	1.9	14.0	25	"	2.5	5.3	8.5
31	"	2.3	2.9	12.4	35	"	2.9	10.5	3.2
35	"	1.9	3.3	9.8	36	"	2.7	3.2	10.3
"	"	2.8	4.9	18.2	46	"	3.1	4.0	18.9
36	"	2.4	5.4	13.7					

	PCB	PCT	DDE
Mean value	3.2	5.0	11.2
Max.	5.8	19.6	19.6
Min.	1.9	0.7	3.2
σ	1.05	3.95	4.5

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CT	DDE
.3	13.8
.0	12.2
.2	6.7
.2	8.5
.0	19.6
.8	9.3
.6	12.8
.2	6.0
.6	9.6
.3	8.5
.5	3.2
.2	10.3
.0	18.9

Ten grams of whole blood in a 50 ml centrifuge tube was shaken vigorously with 20 ml of ethanol. Five grams of potassium hydroxide was added to this and heated at 90°C for 1 h. After cooling, the content was extracted with 2 additional 20 ml portions of n-hexane. The hexane extract was separated by centrifugation and transferred to a 50 ml separate funnel and washed twice with 20 ml of sulphuric acid(96~98%), followed by passing through the column consisted of each 1 g of silicic acid, Florisil and anhydrous sodium sulfate piled on this sequence. PCTs, PCBs and DDE are eluted from the column with hexane and initial 100 ml of fraction was collected. The eluate was concentrated to 1 ml prior to gas chromatography.

The checking of possible contamination during the analytical procedure was made on the type of syringes which were used for blood collection by washing them with hexane which subsequently followed the same analytical procedure as the blood samples.

The gas chromatograph used was a Simazu GC-5AP3 instrument fitted with ^{63}Ni electron capture detector. The gas chromatographic operating conditions for PCB and DDE analyses were as follows :

Column dimensions : 2 m x 3 mm (i.d.) glass,
Column packing : 2% OV-1 on Gas-Chrom Q 80/100 mesh,
Column temp. : 200°C, Detector temp. : 250°C
The operating conditions for PCT analysis were as follows :
Column dimensions : 1.5 x 3 mm (i.d.) glass,
Column packing : 2% OV-1 on Gas-Chrom Q 80/100 mesh,
Column temp. : 280°C, Detector temp. : 320°C.

Quantitation of PCB residues was made by comparing respective height of several peaks in the sample with the height of corresponding peak in the chromatogram of a mixture of KC-500 and KC-600 in the proportion of 1:2 which showed a similar peak profile to that of sample blood. The calculation of PCB quantity in each peaks of the standard mixture followed the method presented by Ugawa et al(7) KC-500 and KC-600 are technical PCBs produced by Kanegafuchi Chemical Industry Co. in Japan, corresponding to Aroclor 1254 and 1260 respectively.

The PCT residues in the blood samples were quantified by comparison of total peak height of the 12 major peaks given by KC-C and those given by the samples. KC-C is a technical PCTs produced by the same company as described

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The mass spectrum shown in Fig.3 identifies some PCTs present in human blood.

The average concentrations of PCTs, PCBs and DDE were 5.0 ppb, 3.2 ppb and 11.2 ppb, respectively.

So far as we are aware, no one has reported presence of PCT resodues in human blood. Statistical analyses showed significant difference at the 5% level between residue levels of PCTs and PCBs, and no correlation between them.

It is of interest that the level of PCT residues in human blood is higher than that of PCBs in spite of lesser industrial output of the former ; the amount of PCBs produced and imported in Japan up to 1971 was 58,000 t (8) and that of PCTs is estimated as 2,000 ~ 3,000 t.

The levels of DDE obtained in this study consist of the sum of DDE originally present in the sample blood and those transformed from p,p'-DDT by alcoholic alkaline hydrolysis which converts p,p'-DDT to p,p'-DDE and p,p'-DDD to p,p'-MDE (10).

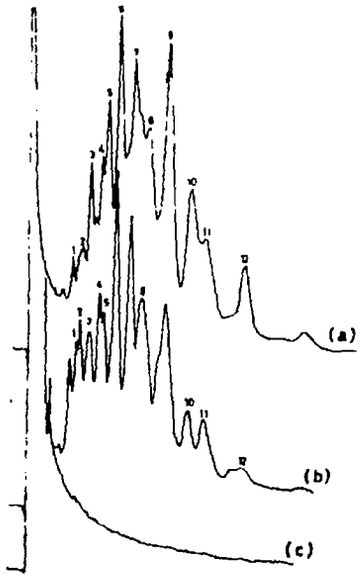


Figure 1. Gas chromatogram of PCT residues in human blood.
(a) : KC-C. (b) : Human blood. (c) : Reagent blank.

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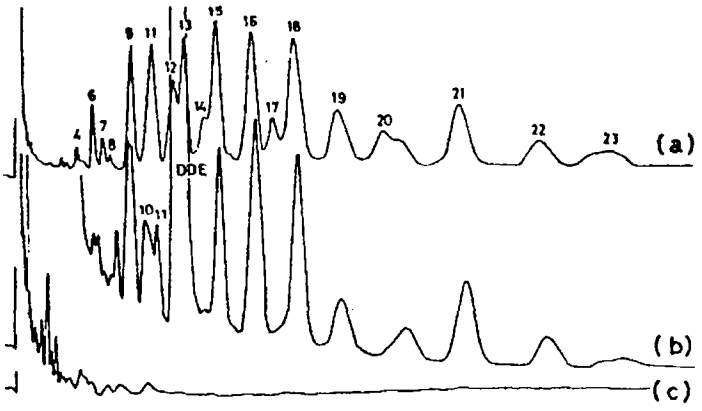


Figure 2. Gas chromatogram of PCB residues in human blood.
(a) : PCB standard (KC500 : KC600 = 2 : 1).
(b) : Human blood. (c) : Reagent blank.

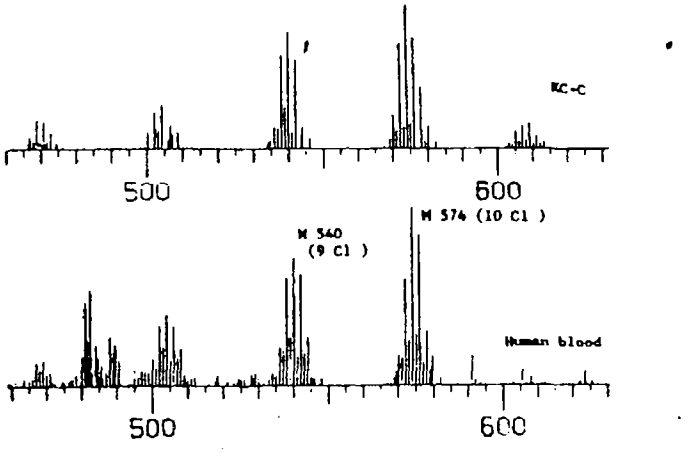


Figure 3. Mass spectrum of PCT residues in human blood at ionization energy of 70 eV.

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As far as the levels of these substances are concerned, DDT compounds were most abundant in the blood.

Available data (9) indicate that about 70% of the DDT in human fat and milk is present in the form of DDE and no p,p'-DDD is detectable. As DDT and its metabolites are not individually analysable, we are unable to demonstrate the absence of DDD in human blood. However, if we assume that the constitution of DDT compounds in human blood is not significantly different from those in human fat and milk, we may consider that the levels obtained in this study represent approximate levels of DDT in the sample blood.

The Ministry of Health and Welfare reported that the average level of PCB residues was 7.8 ppb in human blood collected from 128 subjects in the 7 prefectures where PCB pollution is regarded high, and the average level of PCBs was about 3 ppb(n=16) in Simane prefecture where the pollution is supposedly low (11). A study on the 37 Yusho patients and equal number of control subjects showed that the average PCB concentration in the blood of the former was twice as high as of the latter (6 ppb compaired with 3 ppb) (12). The level of PCBs in Osaka prefecture was 3 ppb, much the same as obtained in this study (13).

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