"SOVTOL" (COMMERCIAL PCBs) NEUTRALISATION: TOXICOLOGICAL ASSESSMENT OF TECHNOLOGY

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Introduction

PCBs in Russia were produced up to the 90s. Most widely applied were trichlorbiphenyl and different commercial brands of mixtures of tetra- and pentachlorobiphenyls ("Sovol"): a blend of Sovol (75-90%) and trichlorobenzene ("Sovtol"), an Arctic variant – a mixture of 92.5% Sovol and α-nitronaphthalene ("Nitrosovol"), a mixture of Sovol (25%) and hexachlorbutadiene ("Geksol").

Sanitary standards for PCBs content in the Russian Federation are as follows:

- in the air of working area– 1.0 mg/m^3, in drinking and municipal water – 0.001 mg/l;
- in soil – 0.06 mg/kg;
- in water for fishery – PCBs are not allowed.

There are no sanitary standards for the air of inhabited areas and for permissible content in foodstuff. This does not allow to make risk assessment of living in polluted areas. All normalized values are given for the standard mixture of PCBs-Arochlor 1254.

Industrial production of these substances resulted in considerable pollution of enterprises and cities in Russia [1,2,3]. These are first of all the cities where either PCBs production or capacitors filling were organized: Serpukhov, Dzerzhinsk, Novomoskovsk, Ufa. There are places of strong pollution in the former Soviet Union in Kazakhstan, Armenia, Uzbekistan and Ukraine [1].

Of no less importance and complexity are the problems connected with disposal of used transformer oils containing PCB additives. In Sverdlovskaya region that is a large industrial area of Russia great amounts of PCB-containing transformer fillers were accumulated, primarily Sovtol-10 (a mixture consisting of 10% of trichlorobenzene and 90% of Cl_2, -Cl_4, PCBs). High levels of PCDD/Fs content were registered in blood and breast milk of people living in large cities of this region [4].

To remove PCBs from used transformer oils a neutralizing technology was introduced at the Verkhne-Isetsky chemical plant. This is a process of neutralizing by sulphurization with oleum at 210^{0}C with consequent transformation of sulfonic acids into a neutral salt by triethanolamine (60^{0}C). The product of reaction is a complex mixture of organic compounds where residual PCBs makes up to 1.8 % w.

The product of Sovtol utilization was supposed to be used for treatment of wood (sleepers) what finally could result in environmental pollution and probable impact on human organism. It should be pointed out that there is no information on toxicity of the mixture and its components. Due to complexity of preparative separation it was decided to study toxic properties of the mixture as a whole and to obtain an integrated toxicological assessment of the introduced technology.

A process based on their sulphurization with abundant quantity of H_2SO_4 and neutralization of its excess with triethanolamine patented by a Russian firm gives water-soluble products that should not be accumulated in fat tissues and so should be far less bio-persistent as compared with PCBs. One could not exclude, however, a possibility of some metabolic desulphurization of neutralized PCBs (PCB-N).

Methods and Materials

A sample of these products (P) containing ca. 40% PCB-N, ca. 60% triethanolamine sulfate (TEA-S), ca. 1% water-soluble sulfones and 0.01% residual PCBs was tested on white rats, mice and rabbits in parallel with a sample of TEA-S.

Gastric intoxication of rats with these products was carried out and DLPCBs in their fat tissue was determined as compared with control group of animals.

Table 1 Characteristics of studied groups

Group	Number of animals	Intoxicating product	Dose, g/kg	Time
1	18	P	11.61	8 weeks
2	14	TEA-S	10.06	8 weeks
3	7 (control)	No	No	8 weeks

Pool samples of fat from the animals were taken, frozen at minus 20^0C and kept till the moment of analyzing. For analysis 5 grams of fat were taken. Labeled standards of all analyzed compounds were introduced into the fat (500 pg/sample of each isomer).

After drying the fat samples by 40g of Na_2SO_4 lipids were extracted with 300 ml of mixture containing methylene chloride/hexane = 1/1. The content of lipids in fat tissue was determined, it made about 90%. After treatment of lipids with SiO_2/H_2SO_4 a standard pattern of purification was used including application of columns with SiO_2, Al_2O_3 and Florisil.

Determination of DLPCBs was performed by the method of HRGC/HRMS in compliance with EPA 1668 rev. A method. Measurements were carried out with a system of a chromatograph Carlo Erba and mass-spectrometer Autospec-Ultima, 10000, a column DB-5MS, 60 m was used.

Detection limit was 5-10 pg/g lipids of the sample depending on the isomer. TEQ of the sample was calculated according to the scale of toxicity factors TEF-WHO (1998).

Results and Discussion

1. All macroscopic fat was excised from rats that had been given water solutions of P or TEA-S by gavage for 8 weeks, 5 times a week in total doses of 11 610 mg/kg and 10 060 mg/kg respectively together with fat of control rats frozen and then analyzed by HRGC/HRMS.

In all samples dioxin-like PCBs were determined. The total content of 4 non-orto- and 8 mono-ortho-substituted PCBs was 0.04 μg/g lipids for control sample, 0.03 μg/g lipids for sample (II) after intoxication by TEC and 1.7 μg/g lipids for sample (I) after intoxication with PCDC-T.

2. In control sample (C) and in the sample treated with TEC (II) the change in the content of PCB isomers is not significant and it lies within experimental error. The total dioxin equivalent of toxicity in both samples was about 9 pg/g lipids TEQ-WHO.

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3. In the sample treated with the products of reaction PCBs content was sharply increased: Nos. 105, 114, 118, 156, 157, 167 and 189. The sample toxicity equivalent to 2,3,7,8-TCDD grew approximately by 100 times and made over 600 pg/g lipids TEQ-WHO.

The results of studying isomer-specific analysis of DLPCBs are given in Table 2.

Table 2 DLPCBs in rat fat, pg/g of lipids

PCBs	# IUPAC	Group 1	Group 2	Control
33'44'-TCB	77	58.0	40.12	63.6
344'5-TCB	81	ND(12)	ND(3)	ND(4)
233'44'-PnCB	105	15349	2247	6327
2344'5-PnCB	114	3356.5	149.7	395
23'44'5-PnCB	118	49877	11373	18444
2'344'5-PnCB	123	ND(21)	ND(7)	ND(4)
33'44'5-PnCB	126	126.9	41.3	46.9
233'44'5-HxCB	156	56088	1361.7	2062
233'44'5'-HxCB	157	810713	2060.7	1612
23'44'55'-HxCB	167	368338	8183	10252
33'44'55'-HxCB	169	12924	47.8	29.3
233'44'55'-HpCB	189	365817	2521	1624
TEQ-WHO, pg/g fat		**632**	**8.1**	**9.7**

ND = ½ MDL.

In toxicological experiments it was shown that P is moderately toxic, non-mutagenic, moderately irritating for skin and notably irritating for eyes.

PCBs dose received together with product P is 1.2 mg/kg or 20 μg/kg/day. This dose by more than an order exceeds the value of 0.1 μg/kg/day which has no detrimental effect on the organisms of experimental animals.

LD50 for rats was determined being 4 668 mg/kg for P and 1 251 mg/kg for TEA-S and biological accumulation of residual PCBs in concentration up to 1.7 mg/g of fat was confirmed.

Conclusions in relation to the possibility of using the product of desulphurization are rather reserved because toxicological characteristics of the product testify to the presence of residual PCBs that are sufficiently toxic. When getting to the environment they will be consequently accumulated in living organisms.

The standard of the WHO (the admitted daily PCB intake) for man is only by 50 times higher than that for rats (5 μg/kg of weight).

References

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