Toxic Admixture Content of Industrial Polychlorophenolic Preparations

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Abstract

The problem of contamination of chlorophenolic biocides with polychlorinated dibenzo-*n*-dioxines and dibenzofurans formed as admixtures in the process of prepartion synthesis is considered. Results of assay of chloroorganic admixtures in the sodium pentachlorophenolate synthesized in this country are presented. A high toxicity of the preparation determined by the content of less chlorinated congenerics of polychlorinated dibenzo-*n*-dioxines is demonstrated.

INTRODUCTION

Detection and estimation of sources of biosphere contamination by stable organic pollutants (SOP), especially those formed in technological processes as by-products, is an important task nowadays for real measures for their elimination from the environment for sustainable development [1].

Among the sources of environment pollution by stable chloroorganic compounds, the leading place in the world was occupied by the synthesis and use of polychlorinated phenols [2]. The imperfection of technological processes of obtaining polychlorophenols led to formation of polychlorinated dibenzo-*n*-dioxines and dibenzofurans (PCDD/PCDP). With respect to the degree of danger of production and of the use for the life activity of the biosphere, polychlorophenolic preparations were situated in the following order [3]: 2,4,5-trichlorophenoxyacetic acid> pentachlorophenol> tetrachlorophenol > 2,4,5-trichlorophenol.

One of the most widespread trends in the use of dioxine-containing polychlorophenols was their application for the protection of forests from pests and of fresh-sawed wood from biological damage both in the form of monopreparations and in compositions with other compounds. Thus, according to WHO data, in 1987 in the USA 95–98 % of pentachlorophenol (PCP) and its derivatives was used directly or indirectly for impregnation of wood, in Canada so were used 95 %, and in Germany 61 % [4]. After having detected in the mentioned preparations polychlorinated dioxines and furans, their production and use in the majority of countries in early 1980ies was completely stopped. At present, in the countries of the European Union, these preparations are not produced, but imported mostly from the USA [5]. In Russia, sodium pentachlorophenolate (PCPNa) was manufactured whose use was prohibited in 1987 [6]. The use of preparations during a long time contributed to a local contamination of environmental objects with polychlorophenols and PCDD/PCDF. Ecological consequences and the degree of environment component pollution are determined first of all by the composition of the preparation, behavior of its components in the environment and by geographical and climatic peculiarities of the territory.

Biocide preparations represented a mixture of chlorophenols of various chlorination degrees. So, in Finland, the preparation KY-5 was produced which consisted mainly of 2,3,4,6-tetrachlorophenol (80 %) and pentachlorophenol (6–10 %) [7]. Canadian preparations represented mixtures of sodium salts of 2,3,4,6-tetrachlorophenol and pentachlorophenol in various ratios [8]. In the preparation Dowicide-G, 80 % was made up of 2,3,4,6-tetrachlorophenol [9].

Especially widespread in the world were pentachlorophenol and its sodium salt – sodium pentachlorophenolate. PCP production began in the USA in the 1930ies by the technology of direct catalyticphenol chlorination. Annual use of PCP in the whole world in late 1900ies amounted to 100–150 thousand tons [10].

Production of pentachlorophenol was considered as one of the main sources of polychlorinated dibenzo-*n*-dioxines and dibenzofurans supply to the environment [11]. The amount and composition of PCDD/PCDP in technical preparations of polychlorophenols depend on the technology of their production [8]. So, the use of direct catalytic chlorination of phenol contributed to obtaining pentachlorophenol preparations with preferential PCDP content. In alkaline hydrolysis of hexachlorobenzene (HCB), the conditions are the most favorable for PCDD formation. In American preparations of pentachlorophenol, the content of PCDD and PCDF for each of the prevalent groups of congenerics embraces a wide interval of values – from 1 to 1500 mg/kg [3, 8]. The maximal amount of PCDD, according to [12], is equal to 1900–2650 mg/kg, and that of PCDP to 7700 mg/kg. In foreign preparations, prevalent in the composition of dioxine admixtures are highly chlorinated congenerics: hexa-, hepta- and octa chlorine-substituted dibenzo-*n*-dioxines and dibenzofurans [3, 8, 11, 13].

In Russia, the production of sodium pentachlorophenolate was organized at the plant of mineral fertilizers in the city of Chapaevsk (Samara region) by a technology worked out in Germany [2]. The volume of PCPNa production amounted to 2.4 thousand tons per year [14]. Used as the initial raw material for the synthesis were wastes of Lindane production representing a mixture of non-toxic hexachlorocyclohexane stereoisomers. PCP/PCPNa synthesis is a multistage process in which, together with the target product of completed chlorination step (hexachlorobenzene), a complicated mixture of chlorobenzene isomers of various chlorination degrees are formed as intermediate products. Alkaline hydrolysis of the mixture of these isomers/homologs, apart from the main product (PCP/PCPNa) leads to the formation of less chlorinated phenols and of polychlorinated dioxines and furans. In this way, one could expect that in PCPNa a wide spectrum of organochloric compounds dangerous in various degrees for the environment would be present.

In the present work, results of analysis of a preparation sodium pentachlorophenolate, which was produced and used in the territory of the USSR are presented, an estimation of its composition and ecological hazard for the environment as compared to foreign biocide analogs is made.

EXPERIMENTAL

The preparation of PCPNa made in this country was produced according to TU 6-04–80 as two brands differing in the content of the main substance (92–97 %) with the free alkali content of 1.0 %.*

The assay of the preparatioin for PCDD/PCDF content was carried out at a laboratory of the Research Center for Emergency Situations (Moscow) within the framework of works in the Federal programme "Protection of Environment and Population from Dioxines and Dioxine-Like Toxicants" for 1996–1997.

Analysis of a sample of sodium pentachlorophenolate for PCDD/PCDF was carried out by means of chromatomass spectrometry using isotope-labeled internal standard simulator.

The preparation was treated with a mixture of hexane with methylene chloride; the extract was purified on "multilayer" columns with modified silicagel on a column with activated carbon and aluminium oxide. Identifica-

*The preparation was given by scientists of the Central Research Institute of Mechanical Wood Treatment (Archangel'sk, Russia).

tion and quantitative analysis were performed on a chromatospectrometric system including a gas chromatograph Varian 3400, a mass spectrometer Finnigan MAT 8200. A standard solution of mixture of 17 2,3,7,8-chlorine-substituted PCDD/PCDF produced by the company SIL (EDF-799) was used.

Assay of other chlororganic admixtures was carried out at the Laboratory of Analytical Ecotoxicology of the Severtsov Institute of Ecology and Evolution, RAS (Moscow, Russia).

A sodium pentachlorophenolate specimen was extracted with *n*-hexane, used as inner standard was 4,4-difluorobiphenyl in acetone. For estimation of chlorophenolic compounds, the specimen was preliminarily treated with 0.01 M $H_2SO_4$and extracted with benzene.

The extracts were analyzed in a chromatomass spectrometric system including a gas chromatograph "Varian 3400" and a spectrometric detector "Ion trap" MAGNUM (FINNIGAN MAT). Separation was carried out on a quartz capillary column (25 m × 0.2 mm) with a fixed phase ULTRA-2 in temperature programming regime. Identification of the detected components was carried out by the retention times and mass-spectra of chromatographic peaks, quantitative measurement by the areas of chromatographic peaks using the internal standard technique.

The contamination level of the PCDD and PCDF was expressed in toxic equivalents (I-TEQ) using the value of the international toxic equivalent factor (I-TEF) (Table 1).

TABLE 1

Toxic equivalent factors (I-TEQ) of PCDD

No.	Compound	I-TEF
	PCDD	
1	2,3,7,8-TCDD	1.0
2	1,2,3,7,8-PeCDD	0.5
3	1,2,3,4,7,8-HxCDD	0.1
4	1,2,3,6,7,8-HxCDD	0.1
5	1,2,3,7,8,9-HxCDD	0.1
6	1,2,3,4,6,7,8-HpCDD	0.01
7	OCDD	0.001
	PCDF	
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PeCDF	0.05
10	1,2,3,7,8-PeCDF	0.05
11	1,2,3,4,7,8-HxCDF	0.1
12	1,2,3,6,7,8-HxCDF	0.1
13	2,3,4,6,7,8-HxCDF	0.1
14	1,2,3,7,8,9-HxCDF	0.1
15	1,2,3,4,6,7,8-HnCDF	0.01
16	1,2,3,4,7,8,9-HnCDF	0.01
17	OCDF	0.001

RESULTS AND DISCUSSION

In the sodium pentachlorophenolate preparation, 93.0 % of chlorophenolic compounds with prevalent pentachlorophenol content (83.3 %) was detected. The most significant contribution to the composition were the following chlorophenols, %: 2,3,4,5-tetrachlorophenol 3.43, 2,3,4,6-tetrachlorophenol 2.18, 2,4,6-trichlorophenol 2.00. Found in insignificant amounts were 2,4,5-, 2,3,4- and 2,3,5-trichlorophenols and also 2,4-and 2,6-dichlorophenols.

The content of neutral chloroorganic admixtures in PCPNa amounted to 3.6 %. Among them, hexachlorobenzene prevails – 72.5 %. Found in insignificant amounts were trichlorobenzene, 1,2,4,5- and 1,2,3,4-tetrachlorobenzenes, pentachlorobenzene, tetra- and pentachlorodiphenylic esters, decachlorobiphenyl.

The total absolute concentration of 2,3,7,8-substituted congenerics of PCDD and PCDF in the preparation manufactured in this country amounted to 32.2 mg/kg. In the composition of PCDD/PCDF polychlorinated dioxines prevailed (83.4 %). As it is shown in Fig. 1, the basic components are 1,2,3,4,6,7,8-heptachlorodibenzo-*n*-dioxine (HpCDD) and 1,2,3,4,7,8-hexachlorodibenzo-*n*-dioxine (HxCDD) whose fractions make up 33.7 and 21.75 %, respectively. Unlike in foreign specimens, in the preparation of this country the contribution of 2,3,7,8-tetrachlorodibenzo-*n*-dioxine (TCDD) (11.33 %) and 1,2.3,7,8-pentachlorodibenzo-*n*-dioxine (PeCDD) (7.7 %) is considerable. The octachlorodibenzo-*n*-dioxine (OCDD) and octachlorodibenzofuran (OCDF) here is not high – 5.6 and 12.0 %, respectively.

By estimates in toxic equivalent, the contamination of this country preparation was extraordinarily high and amounted to

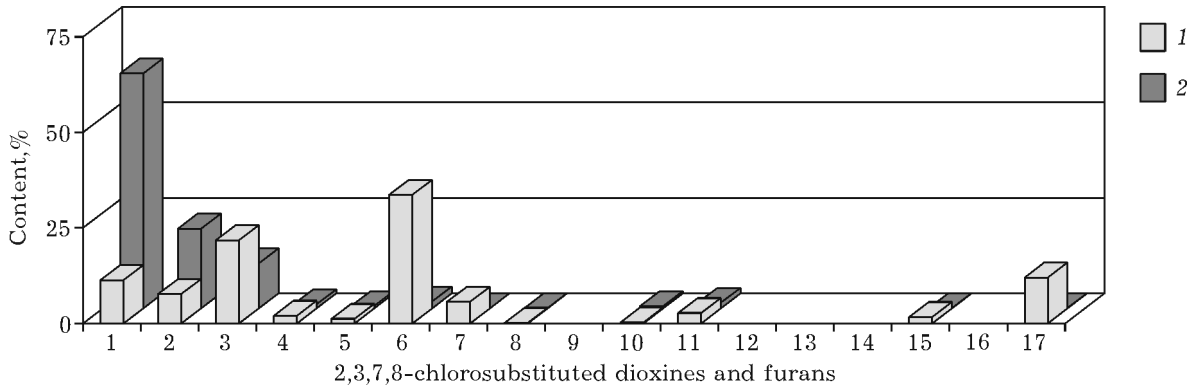

Fig. 1. Composition of PCDD and PCDF in the Russian preparation of sodium pentachlorophenolate in normalized values: *1* – absolute concentrations, *2* – I-TEQ (for designations see Table 1).

5938.9 μg/kg as compared to the contamination range in foreign preparations - 45 to 2701.86 μg/kg, by the data of various authors [11, 13, 15]. As one can see in Fig. 1, the main contribution to the total toxicity is made by polychlorinated dibenzo-*n*-dioxines (97.7 %), and among these, by the three most toxic components – 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD which make up 61.55, 20.85 and 11.8 %, respectively. The contribution of highly chlorinated dioxines and furans is not high: OCDD 0.03 %, OCDF 0.07 %.

The contribution of 2,3,7,8-TCDD is estimated at 62.9 % of the sum of PCDD in I-TEQ, which is in a good accordance with the data of the Tayfun concern obtained in the late 1980ies, according to which the 2,3,7,8-TCDD in the preparation amounted to 80 % of the PCDD sum in the toxic equivalent [16].

In Table 2, where characteristics of some foreign PCP/PCPNa preparations are presented, one can see well an increased polychlorinated dioxine content as compared to that of furans. All the preparations are close in their composition to PCDD/PCDP and represented mainly by highly chlorinated less toxic OCDD and 1,2,3,4,6,7,8-HpCDD and also by 1,2,3,6,7,8-HxCDD.

As shown in Fig. 2 where homologous profiles of PCDD/PCDF of this country and USA preparations are presented [15], a characteristic feature of the latter is also a high content of highly chlorinated hepta- and octachlorosubstituted dibenzo-*n*-dioxines and dibenzofurans.

The content of the most toxic congeneric 2,3,7,8-TCDD in the preparations was below the detection threshold and did not exceed 0.51 μg/kg. Its maximal contribution to the total toxicity was as high as 12% in the most contaminated Chinese pentachlorophenol preparation obtained by the hexachlorobenzene alkaline hydrolysis technology [13].

The Finnish preparation KY-5 differed from the other preparations by the absence of poly-

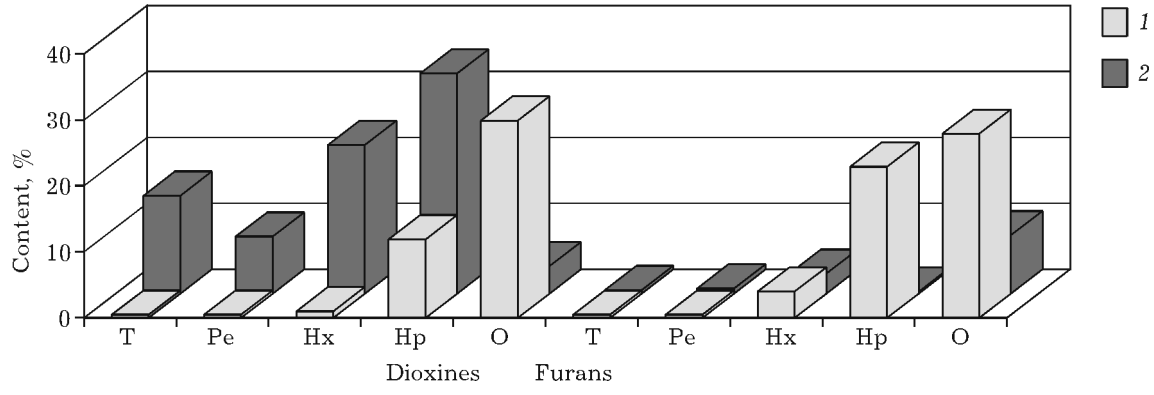

Fig. 2. Normalized homologous profiles of PCDD/PCDF in sodium pentachlorophenolate preparations: *1* – averaged, USA; *2* – Russian.

TABLE 2

Comparative characteristic of polychlorophenolic preparations

Preparation	PCDD/PCDF concentration		Contribution of PCDD, %		Contribution of prevalent PCDD/PCDF congeners, %			Reference
	μg/kg	I-TEQ, μg/kg	Absolute concentration	I-TEQ	Congener	Absolute concentration	I-TEQ	
				Pentachlorophenol				
Witophen (Germany)	975188.0	2118.3	86.7	88.0	OCDD	75.2	34.6	[18]
					1,2,3,4,6,7,8-HpCDD	11.5	52.8	
Rhone Ponlene (Germany)	1087765.0	2701.8	85.5	86.0	OCDD	72.6	25.2	[18]
					1,2,3,4,6,7,8-HpCDD	12.6	51.0	
Chinese	30 210.0	142.0	86.0	82.6	OCDD	76.12	18.7	[20]
					1,2,3,4,7,8-HxCDD	1.2	29.8	
					1,2,3,4,6,7,8-HpCDD	8.5	20.5	
				Sodium pentachlorophenolate				
Preventol PN (Germany)	40 267.0	84.3	88.8	89.9	OCDD	80.4	38.4	[18]
					1,2,3,4,6,7,8-HpCDD	8.1	0.6	
Dowicide G	97 557.0	509.5	60.2	85.2	OCDD	42.6	8.2	[18]
					1,2,3,4,7,8-HxCDD	2.0	40.0	
					1,2,3,4,6,7,8-HpCDD	15.7	23.1	
Chinese	18 020.0	92.0	88.2	79.7	OCDD	76.2	16.5	[20]
					1,2,3,4,7,8-HxCDD	1.5	32.1	
					1,2,3,4,6,7,8-HpCDD	10.4	22.4	
KY-5 (Finland)	63 000	612	0.0	0.0	OCDF	3.2	0.3	[12]
					1,2,3,4,6,7,8-HpCDF	98.6	99.7	
Russian	32 228	5938.9	83.2	97.7	2,3,7,8-TCDD	11.3	61.4	
					1,2,3,7,8-PeCDD	7.6	20.8	
					1,2,3,4,7,8-HxCDD	21.7	11.8	

chlorinated dibenzo-*n*-dioxines [7]. The equivalent contamination of the preparation – 612 μg I-TEQ/kg – is represented by 1,2,3,4,6,7,8-HpCDF (99.7 %) and OCDF (0.3 %).

The Russian PCPNa also seems to be very contaminated with PCDD/PCDF with respect to other widely known chlorine-containing industrial preparations. Thus, a comparative analysis of results of studies carried out in 1970–1980 with respect to dioxine admixtures in technical chlorophenolic preparations has demonstrated that the 2,3,7,8-TCDD content in our preparation is by 1.8 times higher than the average content of this congener in Agent Orange (mixture of *n*-butylic esters 2,4-D and 2,4,5-T) [15] and by 60 times higher than in one of other Agent Orange preparations [17]. The use of this preparation in the territory of Viet Nam as a defoliant during the war in 1972 was the cause of dioxine pollution of the environment of that country [18].

When estimating the ecological hazard of dioxine-containing products, important is the isomer-specific composition of PCDD and PCDP, since with an equal I-TEQ value the most ecologically dangerous are the preparations with a prevalent contribution of less chlorinated PCDD – 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD [19]. Indeed, as it was shown hereinabove, at high total concentrations of polychlorinated dioxines and furans in technical polychlorophenolic preparations the toxic equivalent may be also very high due to considerable amounts of less toxic hexa-, hepta- and octachlorosubstituted dioxines and furans. On this background the Russian sodium pentachlorophenolate preparation differed strongly not only by a higher toxic equivalent, but also by the presence of the most toxic PCDD congeners.

It is noteworthy that from the modern viewpoint of the value of toxic equivalent factor for PCDD and PCDF when estimating their danger to man, fishes and other representatives of the animal kingdom, the ecological hazard of Russian PCPNa increases still more, because, according to the proposals of WHO, the value of I-TEQ for 1,2,3,7,8-PeCDD increases to 1.0 as compared to 0.5 by the current international system [20]. Therein, it is proposed to increase the I-TEQ for 1,2,3,4,7,8-HxCDD when estimating the risk for fishes, from 0.1 to 0.5. This is very important for estimation of ecological hazard of preparations whose use has been carried out as a rule on open grounds of woodworking enterprises near water bodies.

The ecological danger of a preparation is increased also by the presence of hexachlorobenzene in the composition of admixtures since it belongs to the category of stable organic pollutants [1] and possesses dioxine-like effects [21].

CONCLUSION

On the basis of a comparative analysis of the composition of PCP/PCPNa it is demonstrated that the main difference of PCPNa produced in this country from foreign analogs is determined by congener profiles of PCDD/PCDF with prevalent content of polychlorinated dioxines in absolute concentrations and in toxic equivalent and with an insignificant contributions of octachlorine-substituted dioxine and furan.

The Russian preparation of sodium pentachlorophenolate possessed a relatively higher toxicity due to the presence of less chlorinated congeners of PCDD/PCDF – 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD.

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